


THE VAPOR PRESSURES OF SOLID SOLUTIONS OF  
p-DICHLOROBENZENE IN p-BROMOCHLOROBENZENE

by

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INTRODUCTI ON

One of the chief criteria for the ideality of a solution is its adherence to Raoult's law. In the literature can be found many papers concerning the theoretical and experimental deviations of liquid solutions from this criterion. The same source, however, shows not only that very little has been published on the deviations from ideality of solid solutions but that even less experimental work has been done to verify any theories or predictions made. Moreover H. Seltz (36), who has done most of the theoretical work in this field, makes the unsupported statement that positive deviations probably do not occur in the solid state. A desire to investigate Seltz's statement and deviations from ideality of solid solutions in general, by means of measurement of their vapor pressures, formed the basis and purpose of this research problem. The measurement of the total vapor pressure of the solid solution was chosen as the method of approach to this problem, for from the total vapor pressure curves the partial vapor pressure curves of the components may be calculated. The activities and thus the deviations from Raoult's law can be readily obtained from the partial vapor pressure curves.

THEORETICAL BASIS

OF

THE PROBLEM

### Ideal and Non-Ideal Liquid Solutions

A solution may be defined as any homogeneous phase whose composition may be varied within limits (18). 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 homogeneous 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 to which very few solutions met with in practice compare closely. When two liquids form an ideal solution  $V_i = \bar{V}_i$  and  $H_i = \bar{H}_i$ , where  $V_i$  and  $H_i$  are the molar volume and molar heat content, respectively, of the pure  $i$ 'th component and the  $\bar{V}_i$  and  $\bar{H}_i$  are the corresponding partial molar volume and heat content of the same component in solution. Further, 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. These are the laws of van't Hoff, the modified form of this law proposed by Morse and Frazer, the law of Raoult or the law of Henry. They are all essentially for the infinitely dilute solution. For a solution of finite concentration, however, one, but not all, of these laws can be chosen to define the ideal solution. G.N. Lewis (19) originally stated that the law which holds for the greatest number of substances over the widest limits of concentration and which is therefore the most fundamental, is the law of Raoult. That is, at constant pressure and temperature, the partial pressure of any component in an ideal solution is proportional to its mole fraction. This is expressed by

$$p_i = p_i^{\circ} N_i$$

where  $p_i$  is the partial pressure of the  $i$ 'th component in solution,  $p_i^0$  the vapor pressure of the pure  $i$ 'th component and  $N_i$  the mole fraction of the  $i$ 'th component in the solution. If any solution can be shown to obey this law, that is<sup>a</sup> sufficient criterion to establish it as an ideal one.

Deviations from the laws of ideal solutions must be attributed to interaction of the molecules of the components in the solution. In the non-ideal solution the force between two kinds of molecules is either one of excess attraction or excess repulsion. To make possible the application of the exact thermodynamic relations of ideal solutions to non-ideal solutions, G.N. Lewis (21) invented the concepts of fugacity and activity. The fugacity is a measure of the escaping tendency of a component in solution while the activity is the ratio between the fugacity of a component in some given state to its fugacity in some arbitrarily chosen standard state, at the same temperature. These functions serve only to bring experimental results into agreement with the laws of ideal solutions.

#### Ideal and Non-Ideal Solid Solutions

A solid solution may be considered as analogous to a liquid solution, its distinguishing feature being the possession of 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 (2).



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. Guggenheim (12) has recently stated that much of the treatment and equations derived for liquid solutions is directly applicable to solid solutions. Thus for example, the Gibbs-Duhem and Duhem-Margules equations would be expected to hold for solid solutions. Guggenheim further states that a solid solution is precisely analogous to a liquid solution, only the emphasis should be placed on the activity rather than on the partial vapor pressure because of the relative involatility of most solid solutions. Therefore, the criterion of ideality in a solid solution is analogous to the criterion in the liquid solution. Thus, the criterion for a solid solution is adherence to Raoult's law written in the form of

$$a_i = a_i^{\circ} N_i$$

where  $a_i$  is the activity of the  $i$ 'th component in the given solution,  $a_i^{\circ}$  is the activity of the pure solid  $i$ 'th component and  $N_i$  is the mole fraction of the  $i$ 'th component in solution.

#### Thermodynamics of Ideal and Non-Ideal Solid Solutions.

For the phase transformation of liquid solution to solid solution it should be possible to derive a relation between the composition of the coexisting liquid and solid and the heat content of the system. Such a relation would permit the calculation of the relative positions of the liquidus and solidus curves for the well known temperature - composition phase diagram.

Van't Hoff's law of freezing point depression 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 (32) has derived an expression relating composition of liquid and solid phases with temperature, on the assumption that the solid solution obeys Raoult's law and that the heat of fusion of the solid is constant over the temperature range considered. In a discussion of the lens-shaped figure common in temperature-composition diagrams, van Laar (16) introduced equations for the liquidus and solidus curves of ideal and non-ideal solid solutions which are applicable for all concentrations in the liquid and solid solutions. Other equations for the solidus and liquidus curves, based on somewhat similar assumptions, are those derived more recently by Seltz (35), using the concepts of activity and fugacity introduced by G.N. Lewis (21) for ideal liquid solutions. The latter equations were derived for coexisting solid and liquid solutions both of which obey Raoult's law, and do not take into account the change of heats of fusion with temperature.

In another and later publication (36), Seltz extends his equations to non-ideal solutions. This extension was confined to binary systems which show complete solid miscibility and so only derives the conditions under which Roozeboom's types I, II and III of solid solutions arise. In doing this the pure solid phase is taken as the reference state (unit activity at every temperature) and three cases are considered. In each case the A component melts at a lower temperature than does the B component.

(1) Positive Deviations in the Liquid - Negative in the Solid:

When the component in the liquid solutions shows positive and in the solid solutions negative deviation from Raoult's law the phase diagram for the system will have a maximum, with the liquidus and solidus curves coincident at this point.

(2) Negative Deviations in Both Phases - More Marked in the Solid than in the Liquid:

(a) The phase diagram has a maximum as in case (1), if, in the plot of activity versus mole fraction, the curve representing the activity of the A component in the liquid solution does not fall completely below the curve of the activity of the A component in the solid solution when the melting point of the B component is reached.

(b) Should, however, the curve representing the activity of the A component in the liquid solution fall below that for the A component in the solid solution before  $T_B$ , the melting point of pure component B, has been reached, no maximum will appear. All the points on the liquidus and solidus curves will lie between  $T_B$  and  $T_A$ , the melting point of pure component A. The resulting phase diagram, however, will have both curves displaced above the curves calculated on the basis of perfect solution behavior.

(3) Negative Deviations in both Phases - More Marked in the Liquid than in the Solid:

(a) If at  $T_A$  (the melting point of the lower melting component) the activity curve for the B component in the liquid solution does not fall completely above the activity curve for

B component in the solid solution, then the phase diagram will show a minimum.

(b) The other possibility for deviations of this type is that the activity curve for B component in liquid solution falls completely above the activity curve for the B component in the solid solution at the melting point  $T_A$ . This condition gives rise to liquidus and solidus curves lying entirely between  $T_A$  and  $T_B$ , but displaced below the curves for perfect solution behavior.

As the basis of the preceding treatment, however, Seltz makes the unqualified statement that "In a continuous series of solid solutions it is doubtful that positive deviations from Raoult's law will ever occur; the general nature and properties of such solutions would probably give rise to negative deviations . . . . ." We doubt, however, the validity of this statement, in view of the well-established existence of partial miscibility in the solid state, find it difficult to believe that positive deviations cannot exist in solid solutions. This belief is further supported by the direct experimental work of F.W. Küster (15).

It is thus seen that, as stated earlier, Seltz's treatment accounts for Roozeboom's types I, II and III. His discussion, however, does not include the special case of type I described by Ruer (33), namely that in binary systems where the components form a continuous series of solid solutions, liquidus and solidus curves show a point of inflection.

#### The Calculation of Partial Vapor Pressures from the Total Vapor Pressure.

When this problem was first undertaken we thought there would not be sufficient time available to permit analysis of the vapor phase and thus determination of the partial pressure curves. These curves, however, could be obtained by calculation from the total pressures corresponding to

a given mole fraction, a calculation which would indeed be simple if the Margules equation could only be integrated . . . viz.

$$\left( \frac{\partial \ln p_1}{\partial N_1} \right)_{P,T} / \left( \frac{\partial \ln p_2}{\partial N_2} \right)_{P,T} = \frac{N_a}{N_b} \quad (1)$$

where  $p_1, p_2$  = the partial pressures of the two constituents in the vapor in equilibrium with the liquid containing the mole fractions  $N_a$  and  $N_b$ , respectively, of these constituents.

This is a differential equation containing two dependent variables  $p_1$  and  $p_2$  and is therefore indeterminate. The literature contains various solutions of it, all involving the use of constants or approximations.

Lewis and Murphee (20) have devised a method of computing the vapor compositions of binary mixtures from total pressure determinations alone. This is accomplished through a step-wise integration of the Duhem-Margules equation, when the latter is written:

$$\frac{d \ln p_1}{d \ln p_2} = - \left( \frac{1-x}{x} \right) = \frac{d \ln x}{d \ln (1-x)} \quad (2)$$

where  $x$  = the composition of a component in the liquid phase.

Integrating this equation and expressing it in terms of the vapor composition  $y$  of the same component yields:

$$(1-a-b) \log \frac{1-y_1}{1-y_2} - a \log \frac{y_2}{y_1} = \log P_2 - \log P_1 \quad (3)$$

$$\text{where } b = \frac{x_2 - x_1}{y_2 - y_1}, \quad a = x_1 - \frac{x_2 - x_1}{y_2 - y_1} y_1$$

and  $P_1, P_2$  = the total pressures for two successive trials, 1 and 2.

This method does not assume Raoult's law for any concentration and gives an accuracy of plus or minus two percent over a ten percent range on the calculated curves. The constants a and b are determined by two methods, the first being by direct measurement of values of total pressures. Although the second is based upon the initial slope of the total pressure-composition curve, the constants are determined to correspond quantitatively with the chosen experimental point on the total pressure curve. In consequence, inaccuracy in determination of the initial slope has little influence on the computed result.

Porter (28) integrated the Duhem-Margules equation, dealing only with the first powers, to obtain the expression for the partial pressures

$$p_1 = p_1^{\circ} N_1 e^{\beta (1 - N_1)^2} \quad (4)$$

$$p_2 = p_2^{\circ} N_2 e^{\beta (1 - N_2)^2} \quad (5)$$

where  $p_1^{\circ}$ ,  $p_2^{\circ}$  = the partial pressures of the pure components.

e = the naperian base

$\beta$  = a constant

Equations (4) and (5) may be extended to ternary solutions.

Beatty and Calingaert (3) showed that a good preliminary indication of the reliability of partial pressure data can be gained directly by inspection, using a few simple corollaries of the Duhem-Margules equation.

Zawidzki (42) integrated the Duhem-Margules equation to give a power series with three or more arbitrary constants, namely

$$\frac{\log p_1 (1-x)}{p_2^x} = A + Bx + Cx^2 + Dx^3 + \dots \quad (6)$$

and with it partial pressure curves were drawn and compared with experimental data.

An empirical equation:

$$\frac{dP}{dx} = \left( \frac{p_1^0 - p_2^0}{\log p_1^0 - \log p_2^0} \right) \left( \log \frac{p_1 (1-x)}{p_2^x} \right) \quad (7)$$

has been used by Rosanoff, Bacon and Schulze (30). This requires an equation of P in terms of x which is obtained empirically from the data using arbitrary constants. The partial pressures have also been obtained from the P curve by Marshall (24) using a trial and error graphical method founded on the Duhem-Margules equation and  $P = p_1 + p_2 + \dots + p_n$

Margules (23) has recommended the following functions of x for representing the partial pressures of binary mixtures determined isothermally:

$$p_1 = p_1^0 x e^{\frac{\alpha_2}{2} (1-x)^2 + \frac{\alpha_3}{3} (1-x)^3 + \frac{\alpha_4}{4} (1-x)^4} \quad (8)$$

$$p_2 = p_2^0 (1-x) e^{\frac{\beta_2}{2} x^2 + \frac{\beta_3}{3} x^3 + \frac{\beta_4}{4} x^4} \quad (9)$$

where  $\alpha$  and  $\beta$  are constants

Margules himself, and later Zawidzki, carried the exponents only to the third power of x and 1-x. The results of Rosanoff and Easley (31) indicate that it is necessary and sufficient to add the fourth power and the corresponding constants  $\alpha_4$  and  $\beta_4$ . Wohl (41) has proposed a special four and five suffix Margules-type equation which appears promising.

A semi-empirical expression has been found by Levy (22) which closely approximates observed experimental results for a variety of mixtures. Levy's treatment is based on the thermodynamic definition of the activity coefficients  $\gamma_1$  and  $\gamma_2$  of the components of a binary liquid solution which are defined as follows:

$$\gamma_1 = \frac{f_1}{f_1^\circ x} \quad \gamma_2 = \frac{f_2}{f_2^\circ(1-x)} \quad (10)$$

where  $f_1, f_2$  = the fugacities of components whose mole fractions are  $x$  and  $1-x$ .

$f_1^\circ, f_2^\circ$  = the fugacities in the arbitrarily chosen standard state.

Then, assuming that the vapors behave as perfect gases, which is usually the case at ordinary temperatures and pressures,  $p_1 = f_1$  and  $p_1^\circ = f_1^\circ$  so that:

$$\gamma_1 = \frac{p_1}{p_1^\circ x} \quad \gamma_2 = \frac{p_2}{p_2^\circ(1-x)} \quad (11)$$

where  $p_1, p_2$  = the partial pressures of components in the mixture

$p_1^\circ, p_2^\circ$  = the vapor pressures of the pure components.

Equation (8) and (9) may be rewritten as:

$$\ln \gamma_1 = \frac{\alpha_2}{2} (1-x)^2 + \frac{\alpha_3}{3} (1-x)^3 + \dots \quad (12)$$

$$\ln \gamma_2 = \frac{\beta_2}{2} x^2 + \frac{\beta_3}{3} x^3 + \dots \quad (13)$$

These equations apply to a wide range of mixtures as shown by Zawidzki, and their application is based on the assumption that the two-term



Margules expansion is an adequate solution for the Duhem equation.

Margules gives the relation between the constants as follows:

$$\beta_2 = \alpha_2 + \alpha_3 ; \quad \beta_3 = -\alpha_3 \quad (14)$$

To evaluate the constants one determines the tangents to the total pressure curve at each end. The Margules relationship then is:

$$\frac{\alpha_2}{2} + \frac{\alpha_3}{3} = \ln (T_0 + p_2^0) - \ln p_1^0 \quad (15)$$

$$\frac{\alpha_2}{2} + \frac{\alpha_3}{6} = \ln (p_1^0 + T_1) - \ln p_2^0 \quad (16)$$

$$\text{where } T_0 = \left( \frac{dP}{dx} \right)_{x=0} \quad T_1 = \left( \frac{dP}{dx} \right)_{x=1}$$

To obviate the error in measuring the slope, Levy derives the following expressions for  $T_0$  and  $T_1$ :

$$T_0 = \frac{P - p_2^0}{x} \quad \text{at } x \Rightarrow 0 \quad (17)$$

$$T_1 = \frac{p_1^0 - P}{1 - x} \quad \text{at } x \Rightarrow 1 \quad (18)$$

Then to calculate the partial pressure curves, one measures two values of  $P$  at very small values of  $x$  and  $1-x$ . Thus from (17) and (18)  $T_0$  and  $T_1$  are obtained. With these latter values  $\alpha$  and  $\beta$  are then obtained from (14), (15) and (16). Solving for  $V_1$  and  $V_2$  in (12) and (13) and using (11) one calculates the partial pressures.

Redlich and Kister (29) gave a set of equations, assuming small deviations from ideality, which may be applied to calculation of partial pressures. Ebert, Tschamler and Wächter (11) have proposed a new equation to replace the Margules solution of the Duhem-Margules equation. This equation reportedly represents more adequately the experimental data and extends the relation to all phases of a two-component system.

A graphical method by which the Duhem-Margules equation can be integrated exactly is proposed by Orlicek (27). It permits determination of the activity coefficients from measurements of the total vapor pressure. No assumption was made on the functional relation between concentration and activity coefficient. Further, the method is primarily suited for non-ideal solutions that show a very great deviation from ideal properties.

An excellent paper by Carlson and Colburn (8) summarizes and compares the work of van Laar (17), Margules (23) and Scatchard and Hammer (34). The comparison was made by revising the equations of the latter four men such that the constants in their equations became identical. Thus the van Laar equations were written:

$$\log V_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \quad \log V_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \quad (19)$$

the Margules:

$$\begin{aligned} \log V_1 &= (2B - A) x_2^2 + 2(A - B) x_2^3 \\ \log V_2 &= (2A - B) x_1^2 + 2(B - A) x_1^3 \end{aligned} \quad (20)$$

and the Scatchard-Hammer equations:

$$\begin{aligned} \log V_1 &= A \left( \frac{2BV_1}{AV_2} - 1 \right) Z_2^2 - 2A \left( \frac{BV_1}{AV_2} - 1 \right) Z_2^3 \\ \log V_2 &= B \left( \frac{2AV_2}{BV_1} - 1 \right) Z_1^2 - 2B \left( \frac{AV_2}{BV_1} - 1 \right) Z_1^3 \end{aligned} \quad (21)$$

where  $V_1, V_2$  = the molar volumes

$Z$  = volume fraction of the components, i.e.:

for component one -

$$Z_1 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2}$$

For convenience in calculation, the constants in equations (19) and (20) have been solved simultaneously to give, for the van Laar equations:

$$\begin{aligned} A &= \log V_1 \left( 1 + \frac{x_2 \log V_2}{x_1 \log V_1} \right)^2 \\ B &= \log V_2 \left( 1 + \frac{x_1 \log V_1}{x_2 \log V_2} \right)^2 \end{aligned} \quad (22)$$

and for the Margules equations:

$$\begin{aligned} A &= \frac{(x_2 - x_1) \log V_1}{x_2^2} + \frac{2 \log V_2}{x_1} \\ B &= \frac{(x_1 - x_2) \log V_2}{x_1^2} + \frac{2 \log V_1}{x_2} \end{aligned} \quad (23)$$

Carlson and Colburn stated that when the A/B ratio departs considerably from unity that the van Laar and Margules equations differ the most. When the ratio A/B is less than one we use the Margules equations and when it is greater, the van Laar equations. The clue as to which set of equations to use apparently follows from the values of the molar volumes. If the ratio for the two components in the system is approximately equal to, or greater than two to one, we use the van Laar equations.

Further, on the assumption that activity does not change with temperature, Carlson and Colburn gave a method for the calculation, from total pressure, of the activity coefficient and thus the partial pressure. Their equations are:

$$V_1 = \frac{P - V_2 p_2^\circ x_2}{p_1^\circ x_1} \quad V_2 = \frac{P - V_1 p_1^\circ x_1}{p_2^\circ x_2} \quad (24)$$

Subscripts: 1 = the component of the binary mixture  
with the lowest boiling point.

2, 3... = the components with progressively  
higher boiling points.

The use of equation (24) is based on the fact that as  $x_2$  approaches one,  
 $\gamma_2$  approaches one, and therefore an approximate activity coefficient may  
be calculated for component one, assuming  $\gamma_2 = 1$ . The apparent activity  
coefficients are then plotted on semi-log paper and extrapolated to find  
the terminal values of the activity coefficient, whose logarithms are  
the constants in the van Laar or Margules equations.

PREVIOUS INVESTIGATIONS

OF VAPOR PRESSURES OF SOLID SOLUTIONS

Hollman (13) measured the vapor pressures of solid solutions of alums and salt hydrates by an indirect method in which the solid solutions were allowed to stand over sulphuric acid until equilibrium was established. Kruyt (14) measured the course of the three-phase line in the system p-dibromobenzene-p-dichlorobenzene. The partial pressures of p-dibromobenzene and p-dichlorobenzene over solid solutions of both were obtained by Küster (15) using the air-saturation method and analysis of the vapor phase for each component. Our work, and that of Küster was done at 49.1°C. in anticipation that further work done on this problem would include measurements of the total pressure of all three binary systems composed of p-dibromobenzene, p-dichlorobenzene, p-bromochlorobenzene. Küster's investigations showed slight positive deviations along the p-dibromobenzene partial pressure curve. Speranski (37) measured the vapor pressure of solid solutions of B-naphthol in naphthalene, only one component, the naphthalene, being volatile. This same author, using a tensimeter, measured the total pressures, at various temperatures, for the binary systems p-bromchlorobenzene - p-dibromobenzene and p-dibromobenzene - p-dichlorobenzene. The result of this latter investigation also showed positive deviations in the system p-dibromobenzene - p-dichlorobenzene.

CHOICE OF THE PROBLEM

From the preceding section of this thesis, the theoretical reasons behind the choice of the research problem are obvious. What substances could<sup>be</sup> and were used in the problem, however, have not, as yet, been considered. It is clear that the substances constituting the solid solutions should have a relatively high vapor pressure, that is, several millimeters at the temperature of experimentation. Further, it is desirable that the components form a complete series of solid solutions over the required temperature range.

On first consideration it was felt that certain halides or naphthalene derivatives would be suitable. The latter class was rejected, for, if further work done on this problem included analysis of the vapor phase, an accurate quantitative determination of the components would prove difficult. Professor J.H. Hildebrand of the University of California had, in the meantime, indicated by private communication that, because of their molecular symmetry, he would be pleased to see work done on the tetrahalides of the group IV elements. This class of compounds was also rejected as they had very low vapor pressures.

It was found (as has been discussed) that previous work in our field of investigation had been done using the dihalogenated benzenes, p-dichlorobenzene, p-dibromobenzene and p-bromochlorobenzene. These substances had been found to have vapor pressures of between two and six millimetres and formed complete series of solid solutions. Further, the ternary temperature-composition model for these three components had been investigated by Campbell and Prodan (7) at the University of Manitoba. Thus for the reasons stated, and, as accurate potentiometric methods of analysis for the halogens bromine and chlorine were known, the dihalogenated benzenes were chosen as the components of the solid solutions.



THERMAL ANALYSIS

Types and Interpretations of Cooling Curves.

The transformation of any liquid to a solid is accompanied by a change in the energy content of the system, the change manifesting itself by an evolution of heat. The method of thermal analysis is any thermometric method by which this temperature of transformation may be measured.

Suppose that a single substance is heated to thirty degrees above its melting point and then allowed to cool under room conditions. According to Newton's law of cooling the rate at which the liquid cools will be proportional to the difference between the room temperature and the temperature of the liquid. Should the temperature of the liquid be measured at fixed time intervals, the plot of the temperature versus time will have the appearance of Fig. 1a. Such a plot is called a cooling curve. Were a transformation to take place a corresponding break in the cooling curve would be observed. For the liquid-solid transformation of a pure substance the first appearance of solid, barring supercooling, marks the freezing point and here the temperature must remain constant until all the liquid has changed to solid. At this temperature the system becomes invariant, for, according to the phase rule,  $F = C - P + 2$ , the system is isobarically invariant as there is one component in two phases at constant pressure. This invariance is depicted on the cooling curve by a "halt", represented by the horizontal portion  $f m$  in Fig. 1b. When the transformation is complete the system is no longer invariant, the solid begins cooling rapidly along  $m p$  and then more slowly in accordance with Newton's law.

When "ideal" or "linear" rather than "free" or "Newtonian" cooling

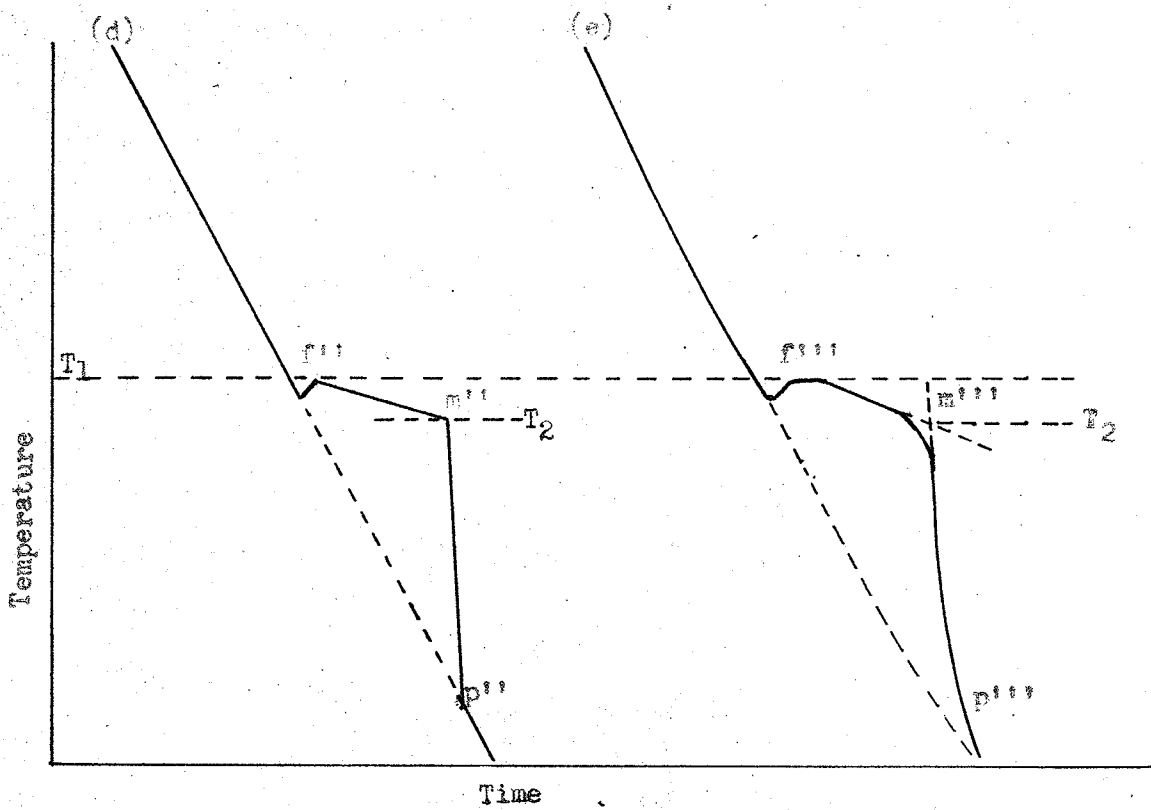
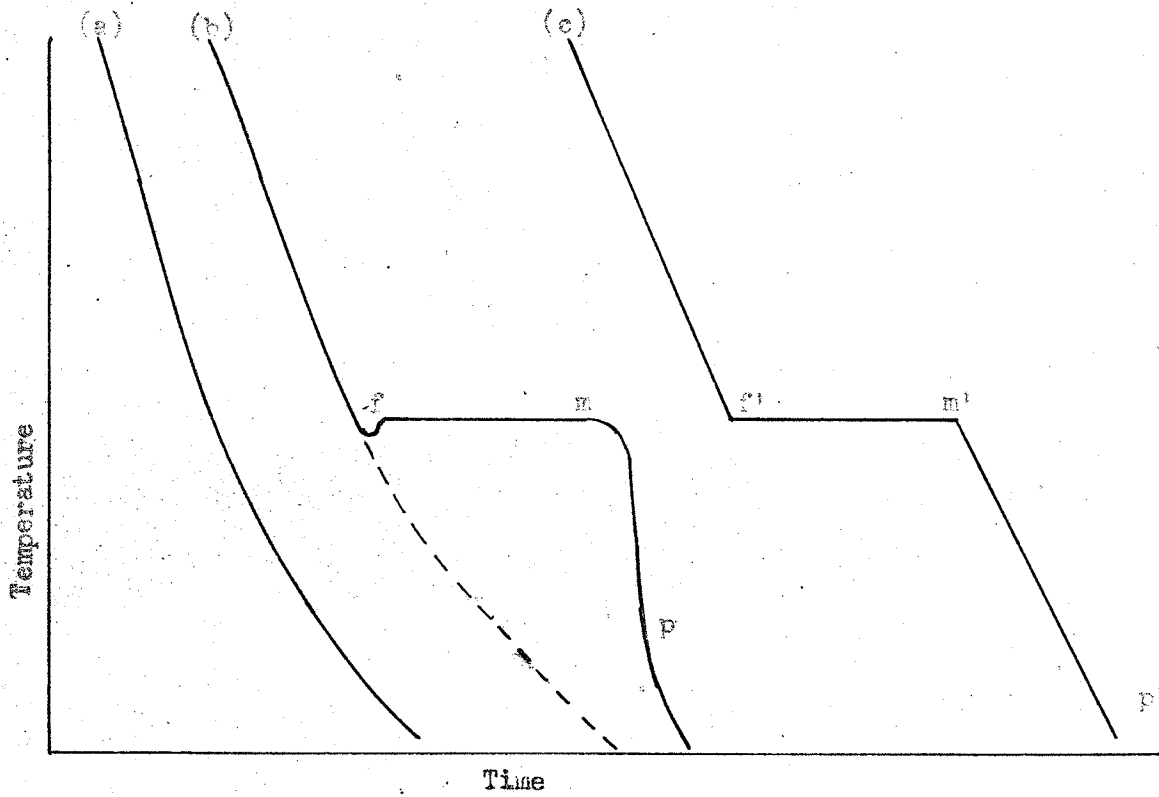


Figure 1.

is utilized, that is, when the rate of loss of heat by radiation from the environment is made constant (thus permitting a cooling rate independent of the nature of the material examined) the cooling curve representing a single substance has the form of Fig. 1c. For a liquid solution 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. The linear cooling curve for such a system is shown in Fig. 1d and the slope of the portion  $f''m''$  thereof is constant from the freezing point  $T_1$  to the melting point  $T_2$ , where a sharp break in the curve marks the disappearance of the liquid phase. The solid solution cools rapidly from  $m''$  to  $p''$  finally assuming a cooling rate equal to that of the environment at  $p''$ . The analogous free cooling curve, Fig. 1e, like that of a pure component, has a pronounced curvature as the freezing nears completion. A sharp break in Fig. 1e is not observed because the amount of heat liberated by the last small portion of solidifying liquid is insufficient to compensate for the heat lost to the surroundings by radiation. Furthermore, the thermometer bulb at this time is surrounded by a solid which cools faster than the liquid by virtue of its lower specific heat.

The phenomenon of supercooling is observed in almost all the instances cited, this effect being represented by the small depressions at  $f$ ,  $f''$ ,  $f'''$  on curves 1b, 1d, 1e. The precision of a freezing point measurement is greatly affected by the extent of supercooling, particularly viscous melts and those possessing poor thermal conductivity. Severe supercooling can be avoided by inoculation of the melt.

with a fragment of the crystallizing substance just before solidification of the melt commences.

Criteria of Purity.

Experimental work done by Le Chatelier (18) shows that the "halt" on the temperature-time graph will accurately determine the freezing point of either a pure constituent or a fused mixture. Tammann (38) has shown that the extensions of portions of the curves  $f''' m'''$  and  $p''' m'''$  intersect at the true melting point, Fig. 1e. Most authorities conclude, therefore, that as long as  $f''' m'''$  and  $p''' m'''$  have a reasonably linear portion, it is possible to arrive at melting points which may be duplicated. It is obvious that for a pure substance the freezing and melting points should be identical. When, however, they are not identical, a freezing point interval exists. For the highest degree of purity of a substance it can be seen that not just a "reasonably linear portion" is desirable, but that the melting point range should be negligibly small or at least within the error of the determination. With these views in mind the freezing range was chosen as the criterion of purity for the dihalogenated benzenes.

EXPERIMENTAL TECHNIQUES

### Melting Point Apparatus

It was hoped that the melting point range might also be used as a criterion of purity. Samples of dihalogenated benzene were placed in a melting point capillary in a Thiele tube filled with mineral oil and melting points determined. Inability to hold the temperature steady with an open flame at the melting point as well as to maintain uniform temperature rise resulted in this method being discarded. Electric heating was tried using a Fisher melting point apparatus, but this, too, was discarded because the thermometer was read only in tenths of a degree, and the heating could not be controlled accurately. A trial was then made using an electric furnace into which was inserted a thermometer, attached to a melting point tube containing some of the sample. Through a small opening in the side of the furnace the crystals could be observed by means of reflected light and a magnifying lens. The current in the furnace was controlled by two rheostats, one fine and one coarse in setting. The entire apparatus was enclosed in a metal cabinet with glass windows thus eliminating fluctuations in temperature resulting from air drafts. This method of obtaining melting points also had to be discarded as the sample commenced to "sweat" obscuring the true melting point. Further, both "sweating" and melting always proceeded from the top to the bottom of the sample despite several attempts to obviate this trouble. Having met with nothing but failure the method of melting point range as a criterion of purity was rejected and that of the freezing point range investigated thoroughly and successfully.

Method of Stirring Melts.

It was realized at the outset of this research problem that, in the determination of a cooling curve, a method of stirring the cooling system would have to be used which employed the principle of a closed system. This is necessary as the components are very volatile and would easily sublime, so changing the composition of the remaining mixture. For the pure substances, however, it was thought that hand stirring would suffice. This was done by means of a brass stirrer bent around a thermometer which was centrally located in the test tube containing the melt. The method was rejected for the following reasons. First, the thermometer bulb and stem soon became encrusted with a thin layer of the crystallizing substance which prohibited good thermal conductance. Second, as solidification progressed beyond the half-way stage the crystals interfered with the smooth movement of the stirrer and the resulting vibration made readings very inaccurate. Third, the results obtained by this method of stirring were often not reproducible.

It was then decided to use the apparatus described by Campbell and Prodan (7) in which efficient stirring is obtained by employing a fluctuating current of dry air. Several weeks were spent in modifying and adjusting this apparatus to the desired efficiency of stirring because the diameter of the glass tubing, the volume of the enclosed system, the mercury levels and the type of piston used were all found to be rather critical. The complete stirring assembly is shown in Fig. 2 and in Plate 1.

The reciprocating mechanism consisted of a motor, a set of pulleys and a vertical action reciprocator. Attached to the one-quarter horse power motor (1) was a one and a half inch pulley (2), which ran to a set



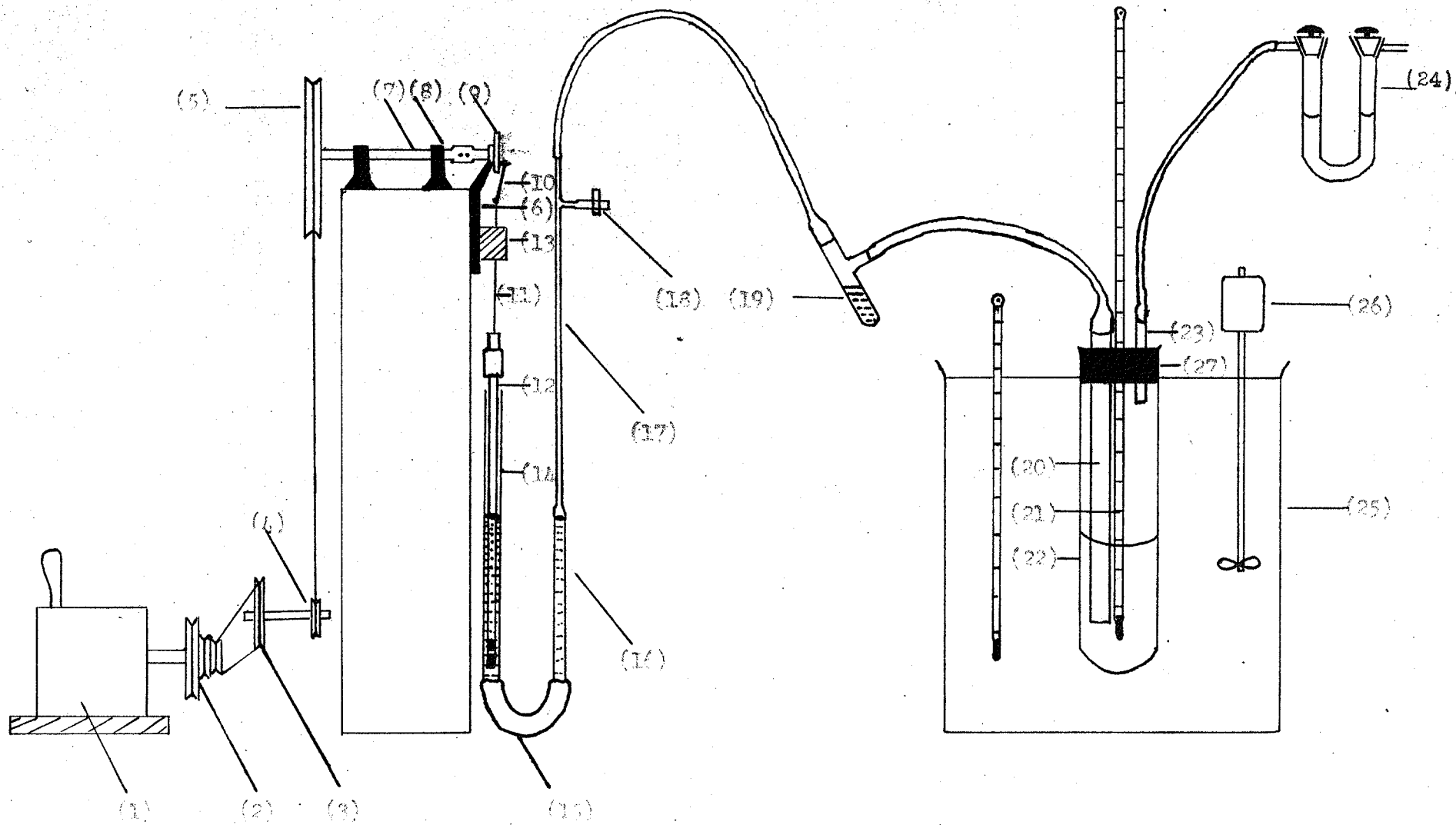


Figure 2.

x

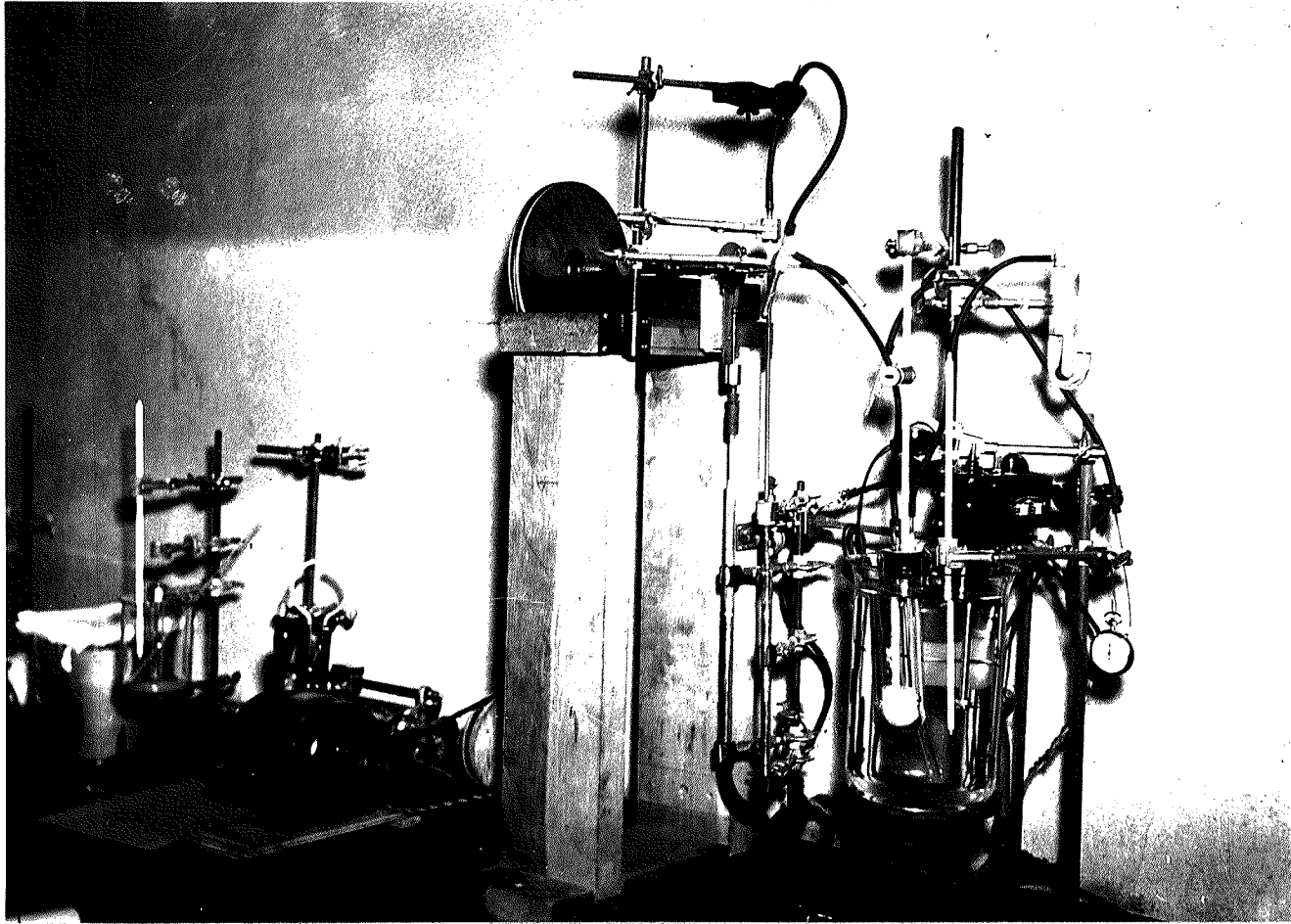


Plate (1).

of pulleys of diameters five inches (3) and two and one half inches (4) which in turn ran an eight-inch pulley (5). The body of the reciprocator (6), was made of brass bent to shape. The steel drive shaft (7) ran in a bronze bearing (8) and was joined to a brass fly wheel (9). The latter was two and three-eighths inches in diameter and had holes drilled in it one-half, five-eighths, one, and one and three quarters inches from the centre to which the connecting rod (10) could be fastened and thus its amplitude varied. The four-inch connecting rod, pivoted on the fly wheel and on the four and one-half inch vertical steel shaft (11), transmitted the power from the fly wheel to the glass stirrer shaft (12). The stirrer bearing (13) was made from a solid brass rod through which a hole had been carefully drilled so as to obtain a close fitting but smoothly operating bearing.

A three-eighths inch internal diameter glass cylinder (14) of twelve and three quarter inches in length contained the one-quarter inch glass piston. Over the lower end of this piston were two smooth rubber washers three-quarter inches and one and one-eighth inches and which were one-eighth of an inch apart. A piece of rubber pressure tubing (15) connected the cylinder to a second piece of glass tubing (16) which, in turn, was joined to a long tube of smaller bore (17), having as one outlet a T-joint closed by a clamp on an attached length of rubber tubing (18). When the U-tube and reciprocating mechanism were clamped to a suitable stand the U-tube was filled with clean, dry mercury to a height of eight and one-half inches above the pressure tubing in the right hand arm. The top end of the tube (17) was connected by means of rubber tubing to a mercury trap (19) and thence to the stirring tube (20), located adjacent to the thermo-

meter (21) which was centred in the main container (22). A three hole number nine rubber stopper (27), previously boiled in sodium hydroxide, was inserted into the top of this latter container. The stirring tube consisted simply of a glass-tube of three-eighths inch internal diameter, the immersed orifice of which was constricted slightly. An outlet tube (23) consisting of a four-inch length of one-eighth inch-bore glass tubing, was connected to a U-tube (24) by a short length of rubber tubing. Sulphuric acid was used to fill the U-tube (24) because of its hygroscopic nature and because it offered less resistance to the oscillating air current within the closed system than did mercury. The environment of the stirring tube consisted of a four-litre beaker (25) filled with water and stirred by an electric stirrer (26).

As the piston oscillated in the cylinder at a rate of approximately four revolutions per second, the mercury in the U-tube was forced to oscillate in resonance with it. The oscillation of the mercury column in tube (16) produced a sympathetic oscillation of the air in the system which was transferred to the liquid in the stirring tube (20). The throw of the reciprocating mechanism was fixed so that the fused melt oscillated a distance of one and one-half to two inches in the stirring tube. The position of the liquid level in tube (20) could be easily adjusted by altering the air pressure within the system through tube (18). Usually, when the piston reached bottom dead centre, the liquid level was at the orifice of the stirring tube.

The positioning of the orifice of the stirring tube was critical. For best results it was immersed two-thirds of the total depth of the melt. The thermometer bulb was then placed one-quarter inch below the orifice.

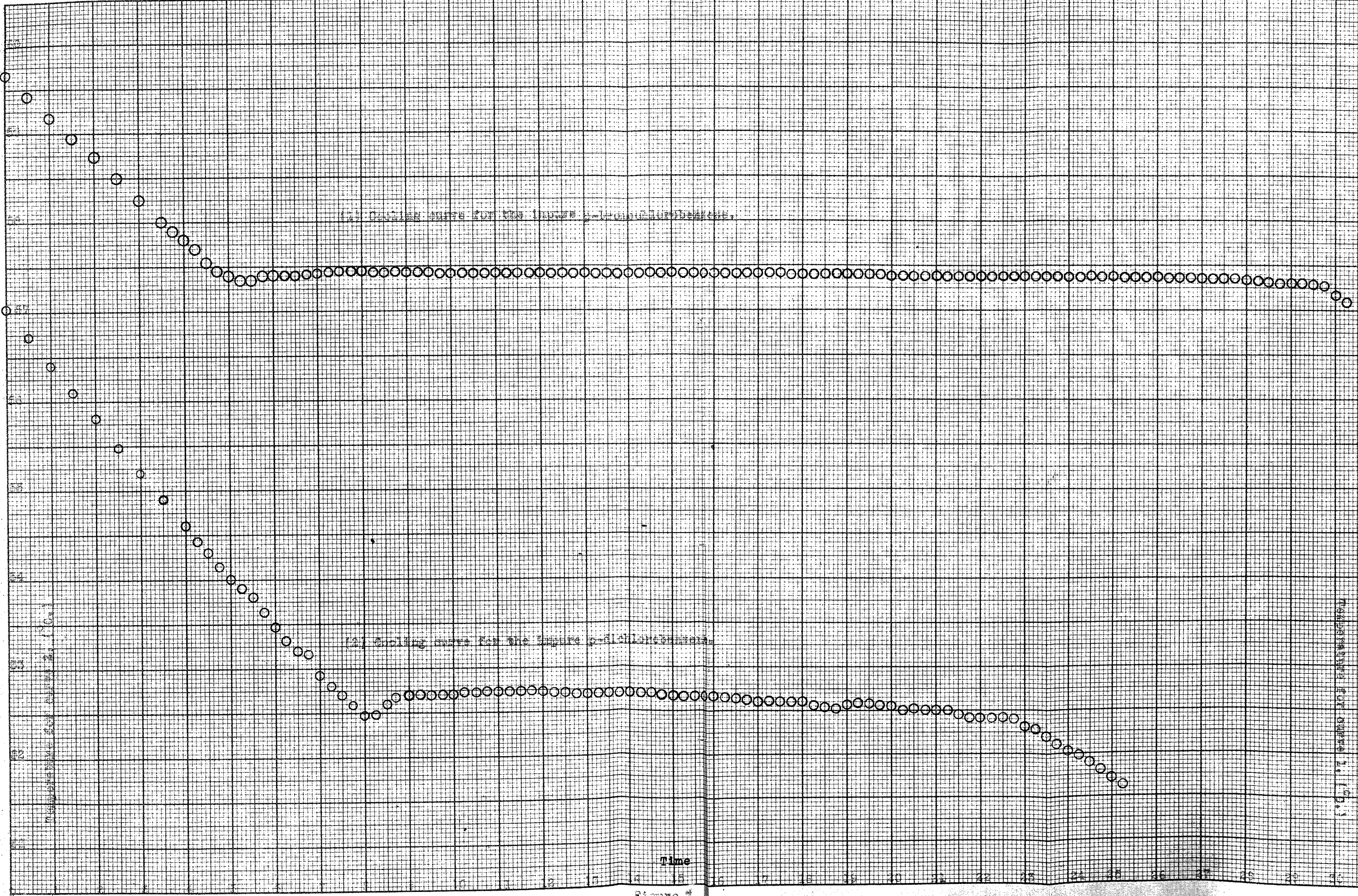
As the freezing process approached completion the liquid in the stirring tube slowly solidified and finally sealed the orifice or some higher point in the tube. The cessation of stirring action was detected by the gradually diminishing amplitude of the oscillations in tube (20) or (24) and their ultimate disappearance.

Loss through the stirring tube was very slight. The outlet tube (23), however, always collected a sublimate which could be returned to the body of the melt if necessary by removing the connecting rubber tubing and scraping the deposit down with a glass rod or heavy copper wire. Collection of sublimate in the tube (23) was actually an advantage, since by tapping the outside of the tube at the proper instant the melt in the container could be seeded and therefore supercooling avoided.

#### Purification of Substances.

The materials used, namely p-dichlorobenzene and p-bromochlorobenzene, were obtained both from the British Drug House and Eastman Kodak Company. Though the latter firm supplied approximately two-thirds of the dihalogenated benzenes, materials from both firms were mixed together before purification commenced. In order to ascertain their degree of purity cooling curves were obtained for the impure p-dichlorobenzene and p-bromochlorobenzene. These are given in Fig. 3.

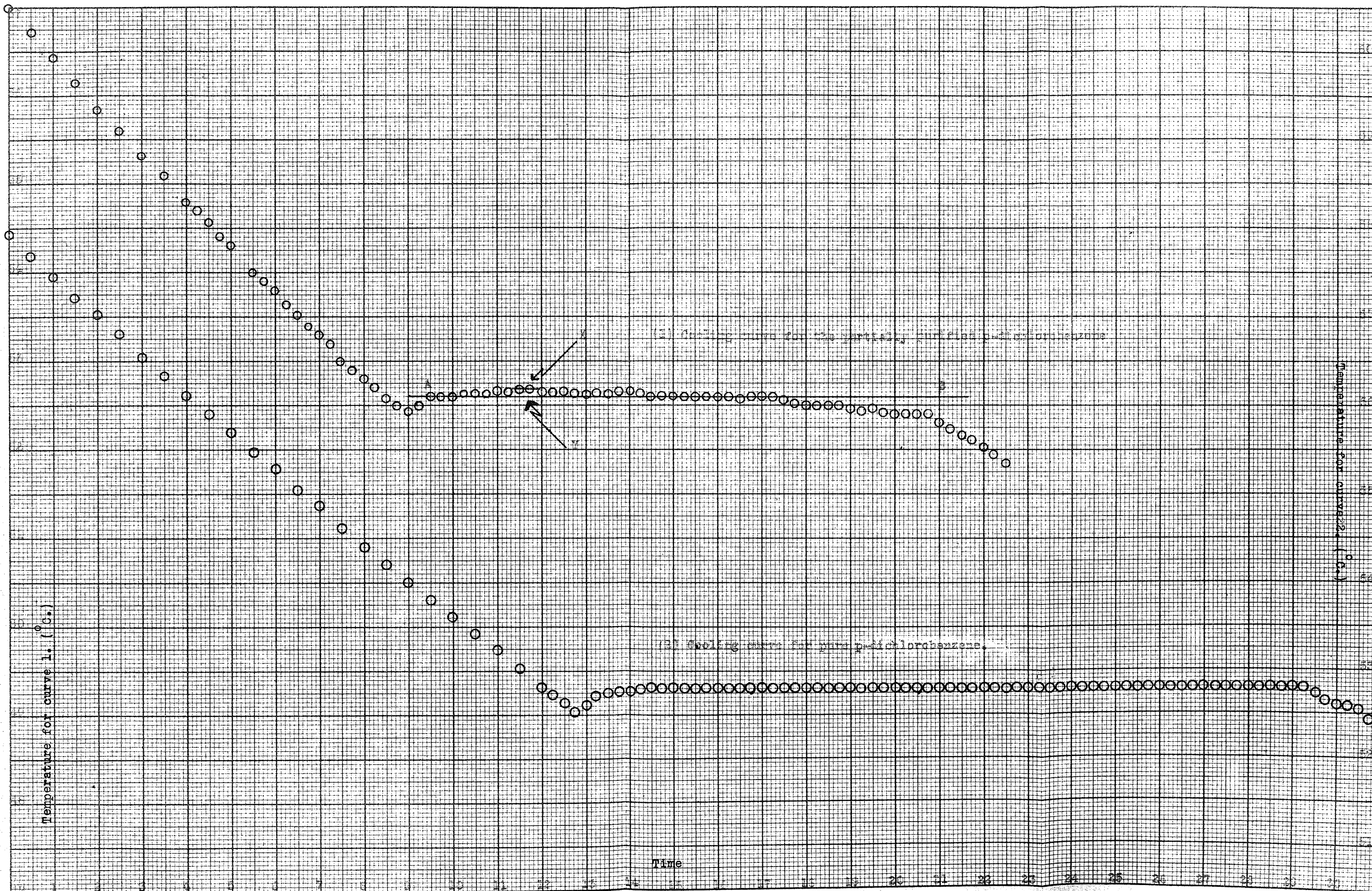
As an initial step in their purification each of the materials was distilled once from dilute sodium hydroxide to remove acidic organic impurities and once from dilute sulphuric acid to remove basic organic impurities. Cooling curves determined on portions of the resulting materials indicated that they were as yet in an impure state. Several difficulties were encountered in these steam distillations as a result of the



low melting point of the components and their high volatility. The high volatility made it advisable to use an all glass apparatus employing dry ground-glass joints. Further, the receiving flask not only had to be immersed in a cooling bath but had to be fitted with two condensers to trap the vapors that failed to condense. Plugging of condensers was a common source of trouble and therefore all were fitted with connections for hot as well as for cold water. At the first signs of plugging, hot water was run through the condensers and the adhering solid melted.

Separation of ortho and meta-isomers from the desired para isomers was effected in both cases by successive recrystallizations from ethyl alcohol. The cooling curves for samples of the p-dichlorobenzene and p-bromochlorobenzene after three such recrystallizations are shown in Figs. 4 and 5. It can be observed that even at this stage a state of purity had not been reached. The impurity was thought to be traces of unremoved alcohol. To remove these traces, the recrystallized product was placed in a vacuum desiccator, and allowed to stand under reduced pressure for a period varying from twelve to twenty-four hours. A cooling curve for the resulting substance indicated no increase in the purity. Attempts to remove the adhering alcohol were then made by centrifuging ten-gram samples, four at a time, and for thirty minutes. The centrifuged product also showed no signs of increasing purity as determined by a cooling curve.

It was then decided to try fractionation. A partial take-off fractionating column, twenty-two inches in length, was constructed. The central column was filled with glass helices and enclosed in a concentric glass jacket. Between the jacket and the column was strung a heating element,





the voltage across which was controlled by a Variac. A thermometer was cemented to the outside of the fractionating column so as to ascertain the temperature inside the jacket and thus the approximate temperature of the column. In order to prevent the cooled products from freezing and therefore plugging the take-off arm of the distillation head, it too was electrically heated. As a result of this heating, the dihalogenated benzene was in the molten state when it entered the receiving flask. There it had to be rapidly cooled, or, because of its high volatility, loss through vaporization would have been nearly twenty per cent. As it was desirable to have a constant temperature of distillation, the latter was operated by a Variac-controlled "Glass Col" heating jacket. The column was found to fractionate efficiently when operating on a four to one ratio.

This column was first used to reflux and then distil several litres of ethyl alcohol from potassium hydroxide in order to remove any aldehydic or ketonic impurities. The dihalogenated benzenes which had been recrystallized from ninety-five per cent ethyl alcohol were now recrystallized from the purified alcohol and then fractionated, the fraction retained being that which came off over a  $.60^{\circ}$  C. range. Cooling curves were determined on samples of the resulting products. They showed that though the p-dichlorobenzene was pure, the p-bromochlorobenzene as yet did not freeze at a constant temperature and thus was impure. Two successive recrystallizations and distillations were necessary before the cooling curve for the p-bromochlorobenzene, Fig. 5, showed the desired purity.

Further experimentation showed that a steam distillation from acid and alkali followed by a fractionation, then fractional recrystallization from alcohol and finally another fractionation were sufficient treatment for the

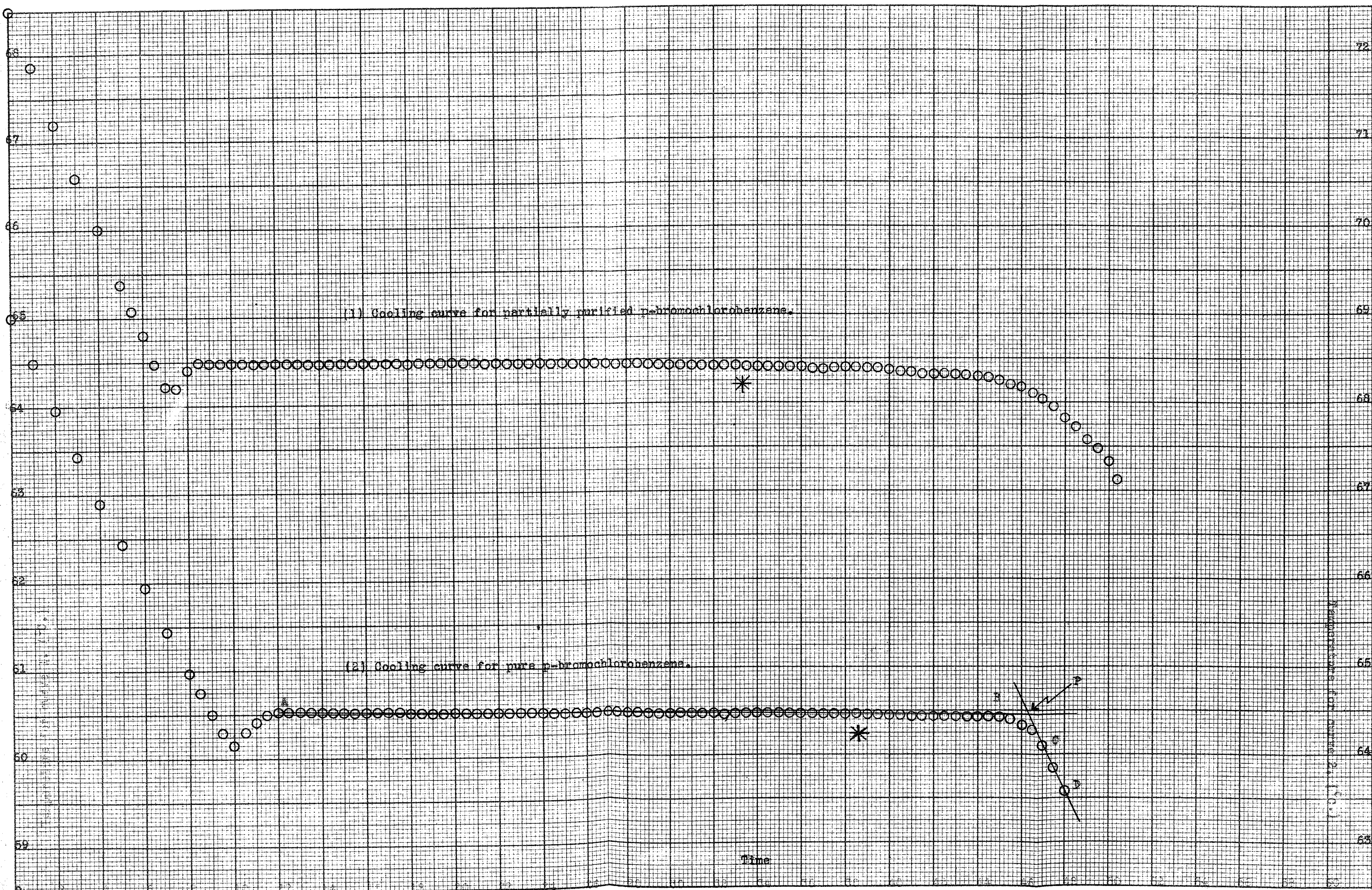


Figure 5.

p-dichlorobenzene to give the desired purity, Fig. 4. It is to be noted that three alcoholic recrystallizations for this substance before the final fractionation seemed to increase the purity. However, the loss of products through the recrystallizations hardly offset the slight increase in purity (if any). Once having the cooling curves for each stage of purification the question immediately arose as to what was the freezing range and by what amount had it decreased. The accepted method of determining the freezing interval would have been to draw lines joining A to B and C to D, Fig. 5, and producing these lines to meet at P. The difference between the ordinates of A and P would be the freezing point interval. It can be seen that for some of the p-dichlorobenzene curves this method is not applicable, for, once supercooling is broken, the curve goes up in a stepwise fashion to a maximum and down in the same manner. For these curves, drawing an average line A-B was considered, Fig. 4, where the freezing point range is taken as plus or minus the difference between the highest group of identical readings and the average deviation line, that is the distance X-Y. This method had to be rejected however, for as the dihalogenated benzenes froze, they not only did so inwards from the walls but, because of the oscillation of the compressed air column and the imparted wave motion of the liquid surface, they built upwards with a concave surface. Thus the thermometer bulb, regardless of the initial amount of substance present became partially exposed after two-thirds of the solution had frozen. It is clear that once part of the bulb is exposed further readings cannot be used in determining the freezing point interval. The asterisks below each curve in Fig. 5 show at what point in the freezing process the bulb of the thermometer first became exposed. Not only did

the thermometer become exposed during the last stage of freezing, but often the stirrer became plugged with crystals freezing out of solution. A description of the phenomenon as taken from my notebook reads as follows:

"The first heavy crystals appear one-third down from the top of the stirring tube. They are deposited as a result of the splash in this tube and they continue to extend in area until two inches from the bottom of the stirring tube. Fine crystals appear in the remainder of the stirring tube. The crystal layer thickens in the central one-third portion of the tube. Amplitude of stirring decreases, thermometer bulb just commencing to be exposed. Container still holds one-third to one-quarter of its original liquid content".

Upon closer inspection of all the cooling curves, it was observed that though neither of the methods of estimating purity could be applied to both substances in going from one purification step to another, the first and accepted method could be applied to the curves for the final purified products. For p-dichlorobenzene the freezing point was found to be  $52.99^{\circ}$  C., after stem correction and calibration with a standard thermometer. The freezing point range was .00 of a degree C., while the accuracy in the thermometer readings was plus or minus  $.02^{\circ}$  C. For the p-bromochlorobenzene the melting point, after correction, was  $64.82^{\circ}$  C., with a freezing point range of  $.06^{\circ}$  C. and again an accuracy in the thermometer readings of plus or minus  $.02^{\circ}$  C.

For the remaining curves only the method of visual inspection could be used to ascertain by what degree the purity had increased at each step of purification. That is, one could only observe when disregarding small or

irregular temperature fluctuations that the curves approach more and more the ideal curve for a pure substance.

#### The Apparatus for Pressure Measurement.

##### (a) The Construction

A static method of measuring the total vapor pressures was used in this investigation. As difficulty was anticipated in finding a suitable stop-cock lubricant, it was decided not to take measurements by any method which involved a tensimeter. An apparatus was therefore constructed as shown in Fig. 6 and Plate 2.

The flask (1) contained the substance whose vapor pressure was going to be measured. A steel bracket (2), which was hinged at the top, thus permitting it to be swung back and therefore free from the flask, supported the latter at the ground-glass joint (3) (standard taper 20/40). Above this joint was a sharp reverse bend in the glass tubing. This constituted a trap for solid which splattered during the degassing process (to be described later). The vacuum line then continued to the mercury manometer (4). Silicone oil had been considered, but rejected as the manometric liquid, for tests had shown that it absorbed the dihalogenated benzene vapors. The mercury in the manometer was raised and lowered from its reservoir (5) (assuming a vacuum in the system) by means of the three-way stop-cock (6), which was open to the air through one connection (7) and led to an efficient water aspirator through the other (8). On the "low pressure" side of the manometer was a vapor-trap (9) fitted with a ground-glass joint (standard taper 20/40) so as to permit removal and therefore cleaning. From the vapor trap the high vacuum line led to a McLeod gauge (10). The stop-cock (11) was incorporated in the system in order that air and water vapor need not be

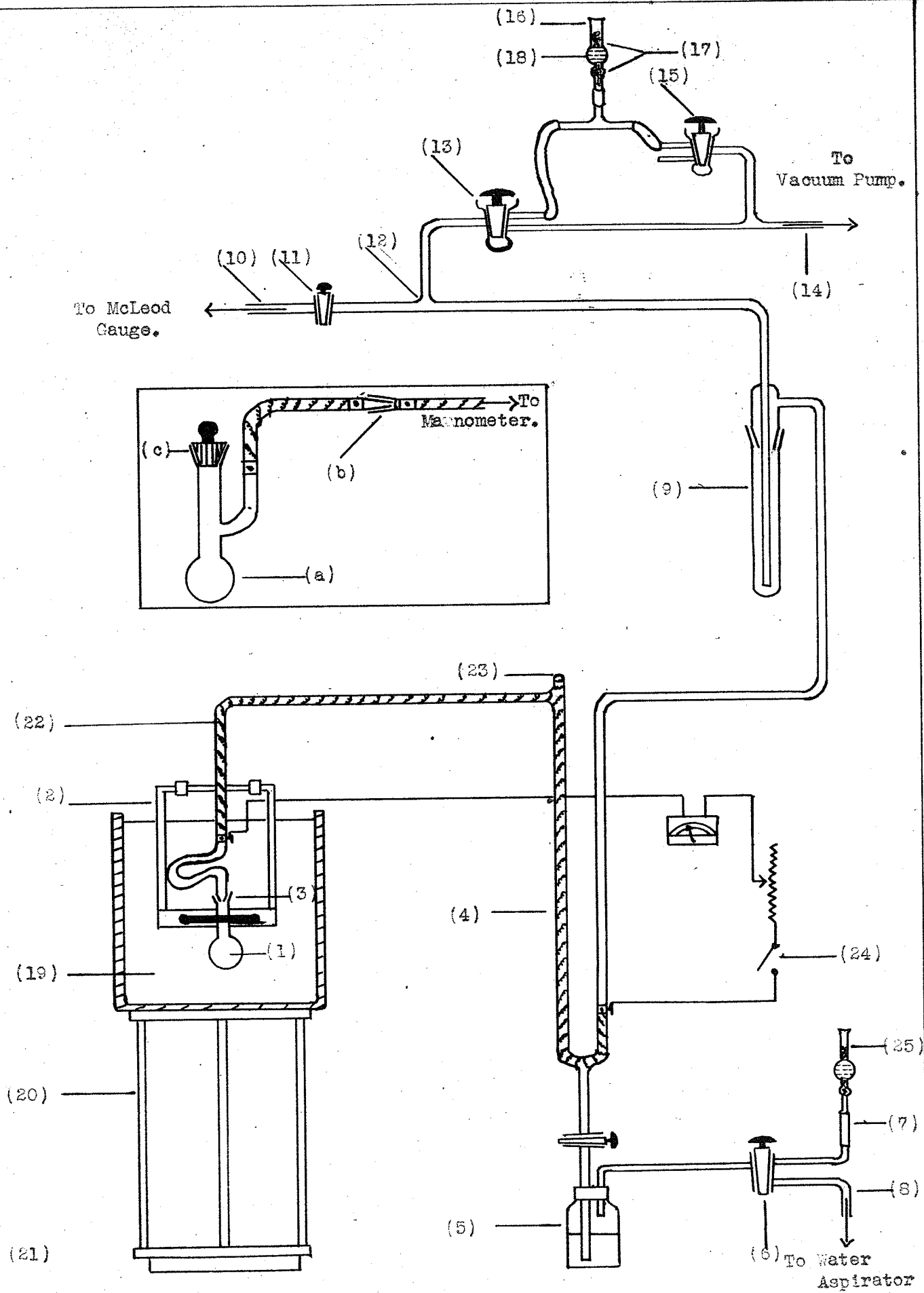


Figure 6.

admitted into the gauge every time the remainder of the vacuum system was opened to the atmosphere. From the T-joint (12), the vacuum line ran to a three-way stop-cock (13) with mercury seal. One arm of this was open to the atmosphere; the other led to a Cenco high vacuum pump (14). A mercury seal stop-cock (15) was joined to this latter arm in order that, while the stop-cock closed the evacuated system from the atmosphere, air could be let into the pump before turning it off. The drying tube (16) contained a glass wool plug (17) and a layer of anhydrous calcium chloride (18) above it as did also tube (25). This helped to reduce, to a small extent, the amount of moisture drawn into the system whenever it was opened to atmospheric pressure.

The apparatus and electrical circuit necessary to maintain a constant temperature bath around the flask (1) is not shown in Fig. 6. This, however, consisted of a sealed mercury thermoregulator and relay sensitive to  $\pm .02^{\circ}$  C., a three hundred-watt water immersion heater, an electric stirrer, a low-lag heater (nine-inch carbon filament light bulb) and a thermometer. These pieces of equipment, excluding the relay switch, were clamped inside the felt insulated glass water bath (19), of .786 cubic feet capacity.

The constant temperature bath was supported by a three-legged wooden stand sixteen inches in height, which stood on another circular stand three inches in height. The purpose of these two stands may be explained as follows: During the degassing process it was necessary to remove the constant temperature bath. Removal of the stand (20) permitted the lowering of the bath below the level of the apparatus contained within it. The lowered bath rested on the circular stand (21), the purpose of which was to permit the removal of your fingers from between it, the table and the surrounding stands

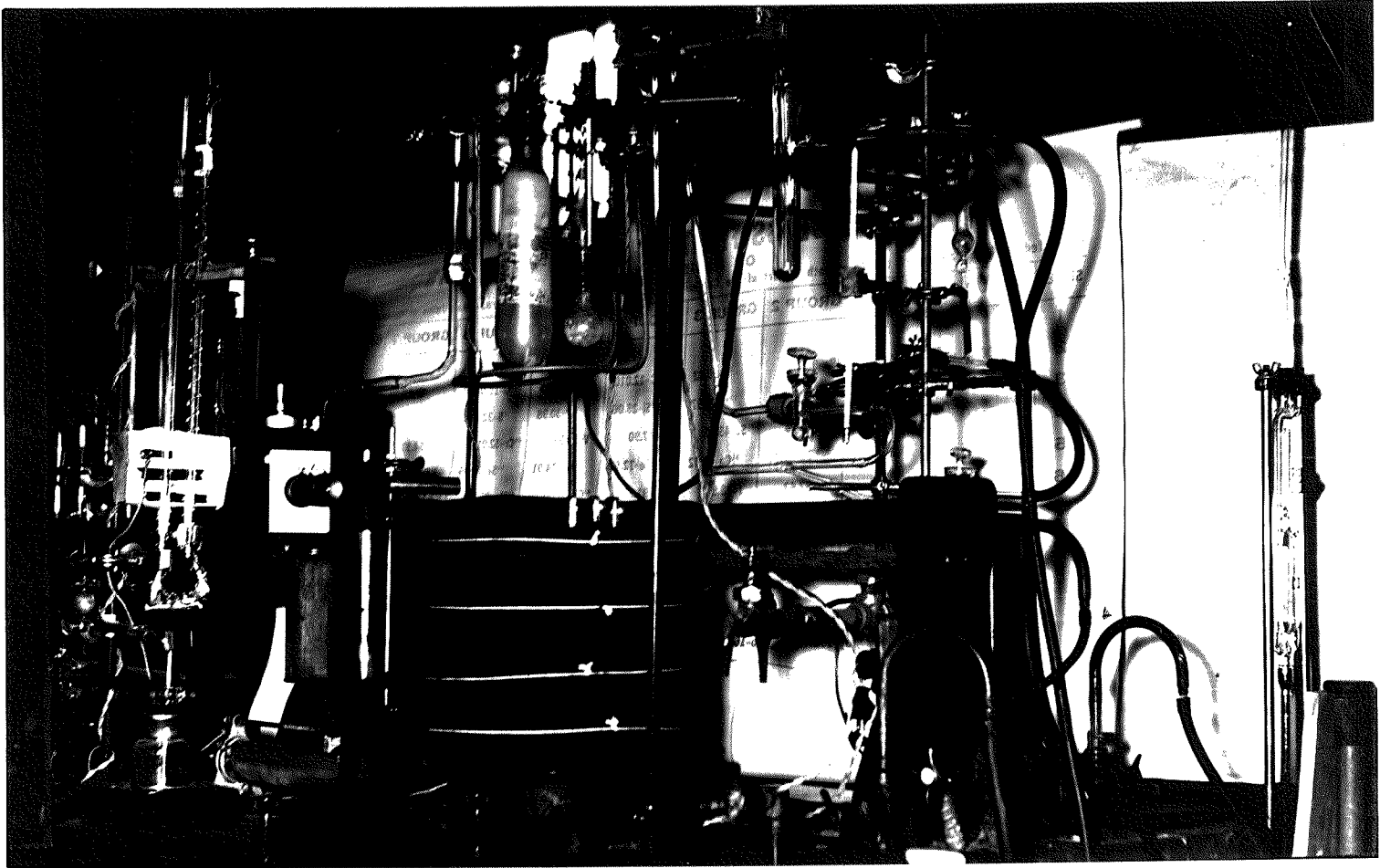


Plate (2),



which supported the apparatus above.

(b) The External Heating Circuit.

As a result of the high volatility of the substances whose vapor pressures were being measured, the temperature gradient between the water bath and the room caused them to sublime from the flask onto the walls of the manometer and connecting tubing. Thus this latter section of the apparatus had to be wrapped with a nichrome wire spiral heating coil (22) and kept at a temperature of approximately sixty-five degrees centigrade. Because of this heating, the mercury when raised in the manometer expanded and therefore necessitated a volume correction. To do this the density and thus the temperature of the mercury column had to be known accurately for a given current passing through the heating coil. A thermometer, therefore, was lowered into the mercury column through the tube (23) (which was later sealed) and the temperature measured for various current strengths.

The heating coil had to be extended down to, and a little below, the surface of the water bath in order to prevent sublimation. The water, being a conductor, therefore carried a potential of one hundred and twenty volts. Thus, when handling apparatus in the bath, care was taken that the knifeswitch (24) was open. To reduce this stray voltage, the wires near and below the surface of the water were painted with Glyptal.

(c) Stop-Cock Lubricants.

When the apparatus was originally constructed, the flask (1) was designed as shown in the inset, (a), Fig. 6. Furthermore, all ground-glass surfaces were lubricated with a good grade of Cenco High Vacuum grease, this being the best grease produced by the company for temperatures of 10-20° C. above room temperature. It was

found that when the temperature of the external circuit was raised to above fifty degrees centigrade part of the lubricant on the ground-glass joint (b) (see inset, Fig. 6), bubbled or distilled away and, if the joint was kept below fifty degrees centigrade, that the material in the flask sublimed onto the inside walls. Further, during the degassing of the sample, the lubricant on the stopper (c) was leached by the hot dihalogenated benzene vapors and spattering liquid. Thus, the apparatus was modified to that shown in Fig. 6.

For this new design a lubricant was needed that would not distil at temperatures up to fifty degrees centigrade, that was not water-soluble and that would not be leached by the hot dihalogenated benzene vapors. Though the second qualification was not complied with, lubricants prepared from glycerol were tried. Dextrin, mannitol and what was hoped to be anhydrous glycerol, were mixed together in varying proportions to form a series of lubricants. When used on the ground-glass surfaces (3), Fig. 6, a thin coating of Plicene vacuum wax was spread on the top of the joint in order that the lubricant would be protected from the water. All lubricants prepared from these three substances had to be rejected because of what appeared to be a distillation of the glycerol out of the joint. As glycerol has a very low vapor pressure at fifty degrees centigrade, it was considered that that which had been prepared had not been anhydrous. Any pressure readings obtained using this lubricant, therefore, would be too high by an undetermined amount. A secondary effect resulting from this distillation of the lubricant was the difficulty of separating the ground-glass surfaces which had a tendency to "freeze" together.

Dr. Puddington, of the National Research Council was now consulted and he forwarded two samples of lubricants that had been found effective in resisting attack by dihalogenated benzenes. One of these samples consisted of a mixture of seventy-two percent anhydrous glycerol and twenty-eight percent silica. This was tested and found as unsatisfactory as the previous lubricants. The second sample, called Perfluorolube and prepared by Du Pont also had to be discarded as the lubricant flowed downward at the temperature of fifty degrees centigrade and the joint invariably froze.

Even though the silicone oils were known to absorb the vapors of the dihalogenated benzenes, it was decided to try a silicone stop-cock grease, namely that manufactured by the Dow Corning Corporation. It was not water-soluble and had a negligible vapor pressure up to a temperature of two hundred degrees centigrade. Trials using only a three-eighths inch band on the upper end of the ground-glass joint proved satisfactory. As the bottom half of the joint was dry and as such a thin film of lubricant was present, it was assumed that the amount of vapor absorbed by the grease would be negligible.

#### Degassing of the Sample.

Once a sample was introduced into the flask (1), Fig.6, removal of air from the system and of occluded air from within the solid was accomplished as follows: One Dewar flask containing a mixture of dry ice and acetone was raised around the flask (1) while another was placed around the vapor trap (9). After the sample had been thoroughly frozen the entire system was evacuated, the mercury raised in the manometer, and the current in the external heating circuit turned on. With the Dewar now removed from

around the flask the substances were gently heated until completely molten. This melting was accompanied by very violent bumping of the solid and liquid. When all the solid had been melted the liquid was again frozen, care being taken that air bubbles were not trapped in the cooling melt. The freezing mixture was kept around the flask until all the material that had spattered in heating sublimed back onto the bulk of the material. The mercury in the manometer was then lowered and any air liberated during the liquefaction pumped off. This operation was repeated two or three times.

Several determinations were made in order to ascertain whether or not there was a detectable change in the composition of the solid solution as a result of the degassing process. Within the error of the measurements, the composition of the sample before and after degassing was found in all instances to be the same.

#### Measurements of Pressure

In order to exclude any gaseous contaminants that might exert an appreciable vapor pressure, the flask (1) Fig. 6, was filled with the pure substances (for example p-dichlorobenzene) as follows: The flask which had been thoroughly cleaned and dried, was immersed up to the neck and thus clamped in a freezing mixture. For a fifteen minute period clean and dry nitrogen gas was passed through the cold flask. Then, as the nitrogen continued to pass through the flask, liquid p-dichlorobenzene was poured from its glass container, where it had been melted while the container was as yet stoppered, through a funnel and into the bottom of the flask. There, without vaporization or sublimation, it rapidly froze while the p-dichlorobenzene remained at a temperature below

approximately  $-30^{\circ}$  C., the flask was removed from the freezing mixture and fitted on to the ground-glass joint (3). The sample and system were then degassed as described in the preceding section.

Before taking a vapor pressure reading, the leveling device on the cathetometer was checked for reliability. With the "leveling bubble" accurately centred, the cathetometer was focused first on one and then the other arm of a mercury manometer open to the atmosphere. As the cathetometer reading for both arms of the manometer did not agree, shims were placed under the "oil level" and adjusted until the bubble was centred for successive readings of the two mercury levels. The cathetometer for an undetermined reason, however, did not keep this adjustment. Thus before taking a vapor pressure reading the cathetometer was leveled by placing the "open" manometer directly in front of the manometer (4) Fig. 6, and adjusting the cathetometer until identical readings were obtained for both arms of the "open" manometer. Then the latter manometer was removed leaving the cathetometer leveled and in position for the vapor pressure readings.

With a degassed sample of p-dichlorobenzene in the flask and with the cathetometer leveled, a series of pressure readings were made and an average taken. The sample was then left overnight at  $49.10^{\circ}$  C. and a pressure measurement taken the following morning. All values obtained were found to be approximately four hundred and fifty percent higher than the value given in the International Critical Tables.

P-dichlorobenzene exists in at least two forms, (4), (40), the reversible transformation occurring at a temperature below  $40^{\circ}$  C. It was considered, as the sample had been frozen during degassing, that the metastable form might as yet be present. To eliminate this possibility, the constant

temperature bath was filled with water heated to sixty-five to seventy degrees centigrade. The p-dichlorobenzene melted at this temperature and then froze as the temperature fell to the value where the constant temperature controls were again connected. Pressure readings, extending over a two day period, were then taken.

The values obtained varied from one another by approximately two millimeters. The variance was found to be the result of sublimation of the p-dichlorobenzene onto the upper walls of the reverse bend above the ground-glass joint (3), Fig. 6. This sublimation occurred during the night, when as a result of evaporation of water, the liquid level in the constant temperature bath fell below the last spiral of the external heating coil (22). It was hoped that by adding two gallons of glycerine to the water in the bath that the rate of evaporation would be reduced. The rate was reduced, but not sufficiently to prevent small amounts of sublimation overnight. A constant level water bath was then constructed and connected to the constant temperature bath by means of a siphon. This kept at all times the water level in the constant temperature bath at the required height.

With the difficulty of water evaporation obviated, vapor pressure readings were taken over a two day period for the p-dichlorobenzene. The sample was then twice degassed and pressure readings again taken several times a day for three successive days.

No further vapor pressure readings were taken as the time allotted for this research project had by now elapsed.

EXPERIMENTAL RESULTS

### Freezing Points

The freezing point of p-dichlorobenzene has been reported by various authors: Bruni (5) gives the freezing point as  $52.7^{\circ}$  C.; Küster (15),  $52.7^{\circ}$  C.; Nagornow (25),  $52.8^{\circ}$  C.; Narbutt (26),  $52.9^{\circ}$  C.; Kruyt (14),  $53.0^{\circ}$  C.; Speranski (37),  $53.1^{\circ}$  C. An accurate freezing point determination was reported by Cooper (9) who used a large mass of the dihalogenated benzene contained in a tall cylinder with a totally immersed National Bureau of Standards certified thermometer. His value was  $53.13 \pm .02^{\circ}$  C. Campbell and Prodan (7) found the freezing point to be  $53.08 \pm .02^{\circ}$  C. The value of the freezing point as determined in this investigation was  $52.99 \pm .02^{\circ}$  C. This is in fairly good agreement with Prodan's, Narbutt's and Kruyt's results.

With regard to the freezing point of p-bromochlorobenzene the literature does not show good agreement. Narbutt (26) prepared a quantity of p-bromochlorobenzene which he claimed froze sharply at  $64.6^{\circ}$  C. without visible evidence of a freezing range. Campbell and Prodan (7) found the freezing point to be  $64.58 \pm .07^{\circ}$  C. By bromination of chlorobenzene, Auwers (1) and Bruni (5) obtained products melting at  $67^{\circ}$  C. Speranski (37), however, employing the same method, obtained for his material a freezing point of  $64.7^{\circ}$  C. Analysis by the Carius method indicated a purity of 99.68%. This same author also prepared a quantity of p-bromochlorobenzene by diazotization of p-bromaniline; the product froze at  $64.7^{\circ}$  C. The value of  $64.82 \pm .05^{\circ}$  C was found in this investigation for the freezing point. The difference in the freezing points quoted was probably the result of small differences in the purity of the substances, for the precision of the recent work would seem to be about the same.



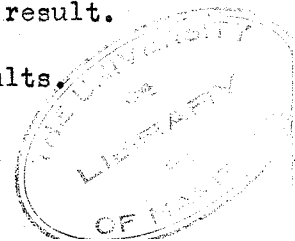
Vapor Pressure of the Pure Components.

Kuster (15), from an average of seven trials found the vapor pressure of p-dichlorobenzene to be 5.23 mm. at 49.1° C. Speranski's data (37) were interpolated to 49.1° C. to give a value of 6.12 mm. Our value for the vapor pressure at 49.10° C. varied considerably, as discussed, until the experimental procedure for determining the vapor pressure was refined. The following table gives the value of the vapor pressure for corresponding vapor pressure determinations.

<u>Trial</u>	<u>Experimental Conditions</u>	<u>Vapor Pressure</u> <u>(mm.)</u>
1	The sample after being degassed twice.	24.02 ± .06
2	Repeat of trial 1, after 24 hours had elapsed.	23.34 ± .08
3	The same sample after a further degassing, freezing at the temperature of the water bath and standing in the system for 3 hours so as to obtain equilibrium.	23.71 ± .02
4	Repeat of trial 3, after 24 hours had elapsed.	21.94 ± .01
5	A new sample, degassed twice, allowed to freeze at the temperature of the water bath and stand in the system for 3 hours so as to obtain equilibrium.	21.57 ± .04
6	The same sample after a further degassing, freezing at the temperature of the water bath and standing in the system for 3 hours so as to obtain equilibrium.	22.03 ± .06
7	The same sample after a further degassing, freezing at the temperature of the water bath and standing in the system for 3 hours so as to obtain equilibrium.	19.98 ± .02
8	Repeat of trial 7 after 24 hours had elapsed.	19.51 ± .03
9	Repeat of trial 7 after 36 hours had elapsed.	19.58 ± .02
10	Repeat of trial 7 after 48 hours had elapsed.	19.07 ± .06

<u>Trial</u>	<u>Experimental Conditions</u>	<u>Vapor Pressure</u> <u>(mm.)</u>
11	Repeat of trial 7 after 54 hours had elapsed.	19.24 ± .07
12	Repeat of trial 7 after 57 hours had elapsed.	19.44 ± .06
13	The same sample after a further degassing, freezing at the temperature of the water bath and standing in the system for 3 hours so as to obtain equilibrium.	19.42 ± .13
14	The same sample after 24 hours had elapsed.	19.20
15	The same sample after 27 hours had elapsed.	19.05
16	The same sample after 28 hours had elapsed.	19.05
17	The same sample after 29 hours had elapsed.	19.04
18	The same sample after 30 hours had elapsed.	19.04
19	The same sample after 31 hours had elapsed.	18.94
20	The same sample after 32 hours had elapsed.	18.94
21	The same sample after 51 hours had elapsed.	19.23
22	The same sample after 54 hours had elapsed.	19.41
23	The same sample after 57 hours had elapsed.	19.07

It can be seen that it is impossible to state definitely what is the vapor pressure of the p-dichlorobenzene. In our opinion, however, the most probable value is the average of the low values, that is  $19.02 \pm .06$  mm. or  $18.79 \pm .06$  mm. when corrected for the temperature of the mercury column. At equilibrium, variations in room temperature should have no effect on the vapor pressure of the substance in the system. Warming up of the room, however, would require some of the vapor in the system to condense into solid in order to maintain constant pressure. Were there a lag in this condensation process, temporary high values would result. Further, it is hard to see how our method could give low results.



As the value of 18.79 mm. for the vapor pressure varied widely from that of Küster and that of Speranski a more thorough search of the literature was made. We found a paper referring to measurements made on p-dichlorobenzene by the Dow Chemical Company (10) in 1938. It partially substantiated the work of Küster and Speranski in that it gave the vapor pressure of molten p-dichlorobenzene as 10 mm. at 54.8° C. This value, however, is very unreliable, for it was obtained by determining vapor pressures from between 126 mm. and one atmosphere and extrapolating these values by means of a "Cox Chart" down to 10 mm. Until the time of cessation of this research project, no reason could be found to cast doubt either on our method of measuring the vapor pressures or the results obtained.

Though time was not available to check the result, Speranski's data (37) were extrapolated to give a value of 2.10 mm. for the vapor pressure of pure p-bromochlorobenzene at 49.1° C.

GENERAL DISCUSSION

Though not based on data resulting from this research problem, the fact that positive deviations do exist in solid solutions has been indicated. Should further work definitely confirm their existence it should be possible to write a theoretical paper paralleling that of Seltz's (36). This would include the three further cases that would arise as a result of the existence of positive deviations in solid solutions and should, if Seltz's theories are sound, again give a theoretical basis for the five types of solid solutions as classified by Roozeboom.

It should be clear, were further work to be done on this problem using the approach as given in this thesis, that the apparatus should be modified. A means of withdrawing a vapor sample from the system for analysis should be incorporated. Further, the constant temperature bath should be enlarged in order to include the sample flask, a shortened manometer, a mercury reservoir and connecting glass tubing.

In conclusion, it should be observed that this is a relatively new field of physical chemistry. The fact that in this project substances are used which have a relatively high vapor pressure does not restrict studies in this field to solids of this nature. The literature contains several methods for the accurate determination of the vapor pressures of relatively involatile solids. Several of these methods permit an analysis of the vapor above the solid - a desirable feature for the elucidation of the problems of the solid state.

BIBLIOGRAPHY

1. Auwers, V., - Z. physik. Chem., 30, 312, (1899).
2. Bain, E.C., - Chem. Met. Eng., 28, 21, (1923).
3. Beatty, H.A. and Calingaert, G.,  
- Ind. Eng. Chem., 26, 504, (1934).
4. Beck, and Ebbinghaus,  
- Ber., 39, 3870, (1906).
5. Bruni, G., - Gazz. chem. ital., 30, II, 127, (1900).
6. Bruni, G. and Gorni, F.,  
- Atti. reale. accad. Lincei, 8, 212, (1899).
7. Campbell, A.N. and Prodan, L.A.,  
- J. Am. Chem. Soc., 70, 553, (1948).
8. Carlson, H.C. and Colburn, A.P.,  
- Ind. Eng. Chem., 34, 581, (1942).
9. Cooper, N.C., - Can. Chem. Met., 9, 59, (1925).
10. Dow Chemical Company Files.
11. Ebert, L., Tschamler, H. and Wächter, H.,  
- Monatschrifte, 80, 731, (1949).
12. Guggenheim, E.A.,  
- "Thermodynamics", North Holland Publishing Co.,  
Amsterdam.
13. Hollmann, R., - Z. physik. Chem., 37, 202, (1901).
14. Kruyt, H.R., - Z. physik. Chem., 79, 657, (1912).
15. Küster, F.W., - Z. physik. Chem., 51, 222, (1905).
16. Laar, J.J. van,- Z. physik. Chem., 55, 435, (1906).
17. Laar, J.J. van,- Z. physik. Chem., 72, 723, (1910), 83, 599, (1913).
18. Le Chatelier, - Bull. soc. chëm., 47, 1.

19. Lewis, G.N., - Z. physik. Chem., 61, 129, (1907).  
- Proc. Am. Acad., 43, 259, (1907).
20. Lewis, W.K. and Murphree, E.V.,  
- J. Am. Chem. Soc., 46, 1, (1924).
21. Lewis, G.N. and Randall, M.,  
- "Thermodynamics and the Free Energy of  
Chemical Substances". McGraw Hill Book  
Co., Inc., New York.
22. Levy, R., - Ind. Eng. Chem., 33, 928, (1941).
23. Margules, M., - Sitzber. Akad. Wiss. Wien. Math. naturw.  
Klasse, II, 104, 1243, (1895).
24. Marshall, A., - J. Am. Chem. Soc., 89, 1350, (1906).
25. Nagornow. - Z. physik. Chem., 75, 578, (1911).
26. Narbutt, J., - Ber., 52, 1028, (1919).
27. Orlicek, A.F., - Österr. Chem.-Ztg., 50, 86, (1949).
28. Porter, N.P., - Trans. Faraday Soc., 16, 336, (1920).
29. Redlich, O. and Kister, A.T.,  
- J. Am. Chem. Soc., 71, 505, (1949).
30. Rosanoff, M., Bacon, G.W. and Schulze, J.F.W.,  
- J. Am. Chem. Soc., 36, 1933, (1914).
31. Rosanoff, M. and Easley, G.,  
- J. Am. Chem. Soc., 31, 448, (1909).
32. Rothmund, V., - Z. physik. Chem., 24, 705, (1897).
33. Ruer, K., - Metallographie, 153, (1922).
34. Scatchard, G. and Hamer, W.J.,  
- J. Am. Chem. Soc., 57, 1805, (1935).
35. Seltz, H., - J. Am. Chem. Soc., 56, 307, (1934).
36. Seltz, H., - J. Am. Chem. Soc., 57, 391, (1935).

37. Speranski, A., - Z. physik. Chem., 51, 45, (1905), 46, 70, (1903).
38. Tammann, G., - Z. anorg. Chem., 43, 218, 47, 290.
39. van't Hoff, J.H.,  
- Z. physik. Chem., 5, 322, (1890).
40. Wallerant, F., - Compt. rend., 158, 385, (1911).
41. Whol, K., - Unpublished notes, University of Delaware, (1948).
42. Zawidzki, J.V., - Z. physik. Chem., 35, 165, (1900).