An Apparatus for Refined Thermal Analysis Exemplified by a Study of the System *p*-Dichlorobenzene–*p*-Dibromobenzene–*p*-Chlorobromobenzene

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Introduction

The relative merits of the various types of cooling curve have been discussed by Burgess[1] and by Rosenhain.[2] Although it is easy, in systems showing solid solution formation, to locate the freezing point, *i. e.*, the liquidus, it is not easy to determine the temperature of complete solidification, *i. e.*, the corresponding point on the solidus curve. Theoretically it should be possible to do this, but in practice the change of slope is too ill-defined to admit of certainty. The present paper describes a successful attempt to overcome this difficulty. Our method consists in the application of Plato's method,[3] whereby a straight-line cooling curve is obtained, and the use of an environment of rigidly controlled temperature, together with minor refinements.

During the liquid–solid transformation of a system which forms solid solutions, the temperature does not remain constant but decreases as the solid solution deposits. The gradient remains essentially constant from the freezing point to the melting point, where a break in the cooling curve marks the disappearance of the liquid phase. The solid solution then cools rapidly from this point until the cooling rate of the furnace is re-established.

As a test of the apparatus we chose the ternary system *p*-dichlorobenzene–*p*-chlorobromobenzene–*p*-dibromobenzene, which has been investigated for freezing points only by Bruni and Gorni.[4]

These authors find that all three binary systems form a continuous series of solid solutions, the two systems containing dichlorobenzene as one component each exhibiting a minimum freezing point. Adding chlorobromobenzene to dichlorobenzene produces a depression in the freezing point of the mixture up to a concentration of 3.5%, after which the freezing point of the mixture rises continuously to the freezing point of pure chlorobromobenzene. Similarly, the system dichlorobenzene–dibromobenzene exhibits a minimum freezing point at 2.5% dibromobenzene. 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 chlorobromobenzene–dibromobenzene approaches very closely to a straight line. Küster[5] examined the freezing curve of the system dichlorobenzene–dibromobenzene but overlooked the minimum freezing point discovered by Bruni and Gorni, who also determined the freezing surface of the ternary system. The liquidus isotherms in triangular projection are all convex toward the lowest temperature (the freezing point of pure *p*-dichlorobenzene, 52.7°), indicating that the freezing surface of the isobaric model is concave downward. Moreover, 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 dichlorobenzene corner.

The shape of their isotherms clearly characterizes the system as an example of Schreinemakers' type 1.3.3. (c), that is, there should exist a ternary freezing point, at which the compositions of liquid and solid solutions are the same, but which is neither a maximum nor a minimum temperature. Nevertheless, Bruni in the first edition of his book, "Über die feste Lösungen,"[6] states that a minimum freezing temperature exists in the ternary system. This statement is absent from a later edition of the book. Our own results show that in the ternary system, there is neither a minimum freezing temperature nor a point of identity of composition of liquid and solid solutions.

Data for the solidus curves of the binary systems and the solidus surface of the ternary system appear to be almost completely lacking. Kruyt[7] has determined the approximate position of the melting curve for the system dichlorobenzene–dibromobenzene. His results indicate a maximum freezing interval of approximately 14°, but with this our results are in serious disagreement.

Experimental

Construction of the Apparatus

The Environment.—In order to obtain regulated cooling entirely independent of external conditions, an arrangement had to be constructed whereby the loss of heat by radiation from the furnace is constant. The apparatus designed for this purpose is shown in Fig. 1.

A circular tank, 45 cm. in diameter, was constructed from #24 gage copper sheet (1). In the center of this tank a cylinder 15 cm. in diameter was soldered. The central opening was lined with asbestos paper and the annular space was filled with water, the total capacity being about 20 liters. The tank was set on a 0.5 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 placed at the top and bottom, respectively, the latter pipe being provided with a stopcock 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. A hole 4 cm. in diameter cut in the center 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. The leads were brought out to terminals (9) (Fig. 1).

The desired working range of the apparatus was from 20 to 100°; to obtain linear cooling at a reasonably rapid

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(1) G. K. Burgess, *Bull. Bur. Standards*, **5**, 199 (1908).

(2) W. Rosenhain, *Proc. Phys. Soc.*, **21**, 180 (1908).

(3) W. Plato, *Z. physik. Chem.*, **55**, 46 (1906); **58**, 350 (1907).

(4) G. Bruni and F. Gorni, *Atti R. Accad. Lincei*, **8**, 212 (1899).

(5) F. Küster, *Z. physik. Chem.*, **50**, 65 (1905).

(6) Bruni, 27 (1901 edit.).

(7) H. R. Kruyt, *Z. physik. Chem.*, **79**, 657 (1912).

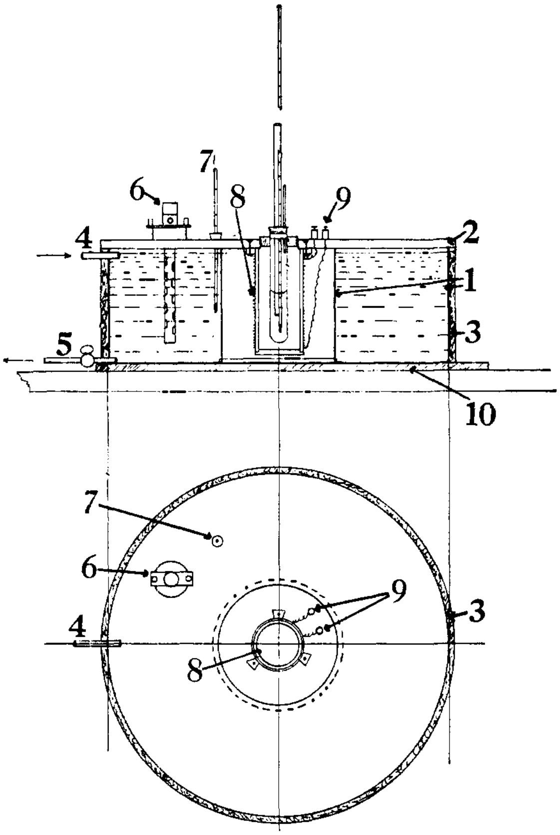

Fig. 1.—Apparatus: scale: $^1/_4''$ = 6 cm.

rate necessitated an environment temperature 10–20° below the lower working limit. An environment temperature of 10° was found by experiment to be adequate, though a lower temperature was preferable. To maintain the temperature of the environment constant a thermostated circulation system was introduced. The temperature of the environment was read on the thermometer (7). A mercury thermoregulator (6), sensitive to 0.02, mounted on the cover, served to control the temperature of the circulating system.

The Cooling Circuit.—The cooling system is shown diagrammatically in Fig. 2. 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, tightly fitting wooden cover and was insulated with felt. The cooling coil (14) was made from $^3/_8$ inch copper tubing and was actually the freezing coil of a methyl chloride refrigerator unit. The outlet pipe (5) from the tank A directed the water through a copper coil (15), which was immersed in the kerosene, to water pump (12). The outlet pipe from the pump was connected to the inlet (4) of tank A. A rubber tube, not shown in the diagram, was connected to the inner end of the inlet pipe (4); its purpose was to conduct the violent 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.

Operation.—The temperature of the kerosene tank (B) was maintained constant at 1 ± 0.5° by means of a bimetallic thermoregulator (16) connected in series with the a. c. line and the refrigerator motor. The kerosene tank was stirred with a vigorous current of air.

The temperature of bath A was kept constant at 10 ± 0.02° by means of regulator (6). Closing of the relay circuit caused the circulating pump to operate. The temperature of bath B, which could not be lower than 0°, 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° 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 so the pump operated almost continuously when the furnace was at 90°.

Furnace Construction.—A 14.5 cm. length of 5 cm. diameter hard glass tubing, wall thickness 2 mm., was wrapped with two thicknesses of asbestos paper soaked in sodium silicate solution. Fifty turns of #22 gage B and S nichrome wire were wound on this form. To obtain uniform heating of the melt a flat heating coil was provided

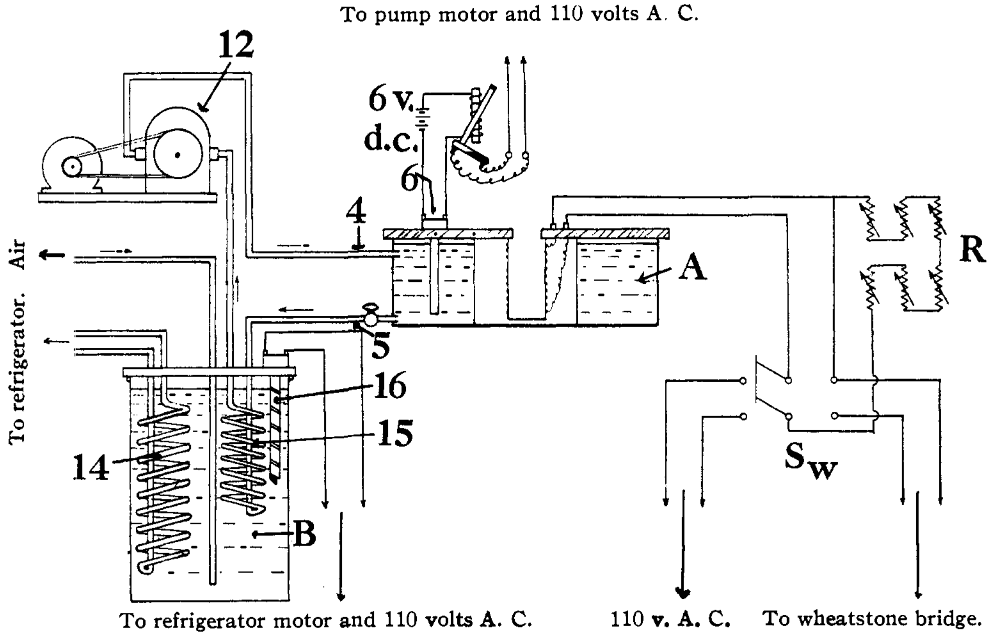

Fig. 2.—Wiring.

at the lower end of the furnace tube; it was wired in series with the main coil. The completed furnace was lined with two layers of asbestos paper and the whole fastened to the water-bath cover as shown in Fig. 1. The total resistance of the furnace was 49 ohms.

The Electrical Circuit.—The control circuit is shown in Fig. 2. Accurate temperature control was obtained by adjustment 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 capacity of 3 amperes. The source of current was the 110-volt a. c. line, but the fluctuations in line voltage made this a not entirely satisfactory source of power; a battery of storage cells, such as was used by Plato,[3] would have been better. A double-pole double-throw switch (Sw) was wired into the circuit in such a way that in one position the 110-volt line was connected to the furnace and resistance R in series, and in the other position the external resistance alone was connected to a Wheatstone bridge circuit.

Temperature Measurement.—All temperatures were measured on a mercury in glass thermometer, having a scale of 0–110° in 0.1°. The thermometer was calibrated against an identical type of thermometer certified by the National Bureau of Standards. By means of a reading lens temperatures were read to ±0.01°. The exposed stem correction was applied to all readings.

Calibration of the Apparatus.—A Pyrex test-tube, 2.5 cm. in diameter and 13 cm. long, formed the containing vessel for the melt. This tube was fixed in the furnace with a rubber stopper. It was fitted with a rubber stopper on which were mounted the stirrer and the thermometer.

From the results of a large number of trials using paraffin oil and the organic melts in the furnace, a cooling rate of 1.5° in five minutes was decided on. With paraffin oil as the calibrating fluid, the circuit resistance was adjusted so that the thermometer registered 95° with the stirrer running. Then, largely by trial and error, resistance was slowly inserted in the furnace circuit in steps; each increment of resistance was measured by throwing the d. p. d. t. switch to the Wheatstone bridge circuit. Readings were taken every minute to assure a constant cooling rate of 0.3° per minute. It was often 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 to 20° 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 the exact resistance to be inserted in the circuit every 2.5 minutes to produce a linear cooling rate of 0.3° per minute could be read. Plotting temperature against time a straight line resulted deviating from perfect linearity by no more than 0.2°.

Stirring.—The greatest practical difficulty was encountered in the attempt to devise a flawless stirring mechanism. Mechanical stirrers are useless for this work.

Efficient stirring in a closed system was finally obtained by employing a fluctuating air pressure. The complete stirring assembly is shown diagrammatically in Fig. 3. 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 0.25 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, formed by the two parts of the apparatus, and the reciprocating mechanism were clamped to a suitable stand, the U was filled with mercury. The top end of tube (6) was connected by means of rubber tubing to the stirring tube (8), placed close to the thermometer (11) which was centered in the main container (9). The stirring tube was merely a piece of $^3/_8$ inch bore glass tubing, whose immersed orifice was slightly constricted. 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. This U-tube contained concentrated sulfuric acid, partly as a trap to keep moisture out of the apparatus, but chiefly because sulfuric acid offered less resistance than mercury to the oscillating air pressure within the closed system.

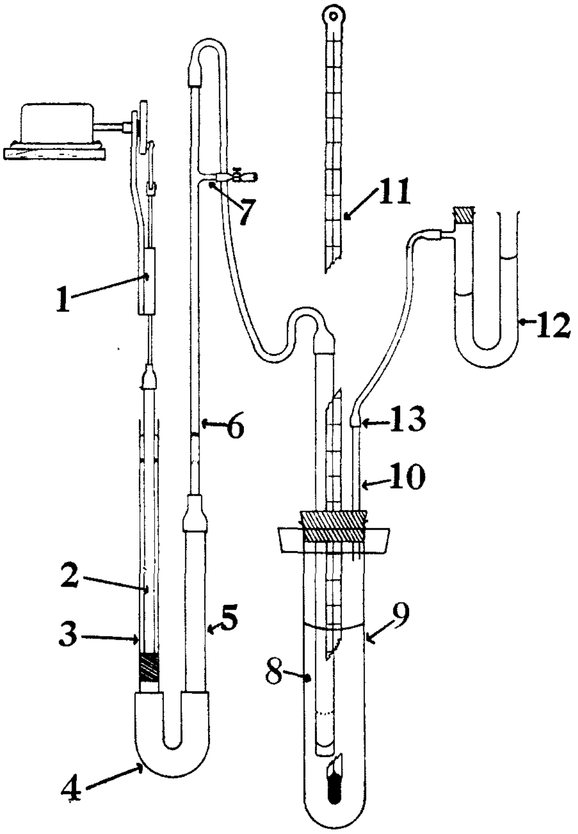

Fig. 3.

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 adjusted so that the fused melt oscillated a distance of 1.5 inches in the stirring tube. The position of the liquid level in tube (8) could be adjusted quickly by altering the air pressure within the system through tube (7). This apparatus, when properly adjusted, produced a vigorous and efficient agitation of the melt and depositing crystals. The position of the orifice of the stirring tube was critical. For best results it was immersed two-thirds of the total depth of the melt. In contrast 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.

Performance of the Apparatus.—In order to show the accuracy with which the temperature of complete solidification (solidus line) can be obtained, Fig. 4 is a plot of the cooling data of a binary mixture containing 30.03 mole per cent. dibromobenzene and 69.97 mole per cent. dichlorobenzene. This mixture showed one of the largest cooling intervals. When the results are plotted, as was always done, on millimeter paper so that 1 mm. equals 0.04° of temperature or two minutes of time, the freezing and melting points are clearly defined as 59.49° and 55.20°, respectively. All curves were repeated on the same mixture, and mixtures of approximately the same composition were frequently made up for double checking.

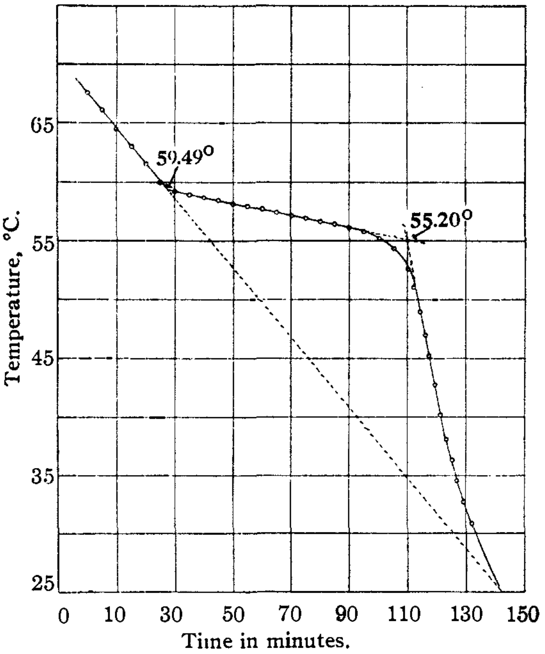

Fig. 4.—A typical cooling curve: freezing point, 59.49°; melting point, 55.20°; internal 4.29°.

Purification of Materials.—Each of the materials, *viz.*, *p*-dichlorobenzene, *p*-dibromobenzene, and *p*-chlorobromobenzene, was steam distilled once from dilute sulfuric acid, once from dilute sodium hydroxide and finally distilled using a short column. The dichlorobenzene thus obtained melted at 52.5°, but a cooling curve showed a freezing interval of 0.8°, indicating impurity. The ortho-isomer (b. p. 179°) was separated from the desired para-isomer (b. p. 173°) by crystallization from ethyl alcohol. After six crystallizations, the material froze at 53.08° with no detectable freezing interval.

The dibromobenzene was treated in a similar manner. Distillation as a means of purification was useless since the *meta*-isomer boils at exactly the same temperature as the *para*-isomer, *viz.*, 219°. Six crystallizations from ethyl alcohol yielded a product freezing at 87.30°.

Distillation is again useless as a method of separating *p*-chlorobromobenzene from its isomers, but purification by crystallization from ethyl alcohol was again effective. Eight crystallizations were necessary to obtain a product which froze at 64.58° with a freezing interval of 0.07°.

All these substances were stored over concentrated sulfuric acid for two months before use.

Results

Freezing Points of the Pure Components.—

The freezing point of *p*-dichlorobenzene is variously reported as 52.7° (Bruni)[8]; 52.7° (Küster, *loc. cit.*); 52.8° (Nagornow[9]); 52.9° (Narbutt[10]); 53.1° (Speranski[11]); 53.0° (Kruyt, *loc. cit.*); 53.13° ± 0.02 (Cooper[12]). Our value is 53.08 ± 0.02°.

The freezing point of *p*-chlorobromobenzene is given as 67° by Auwers[13] and by Bruni,[8] as 64.7° by Speranski[11] and as 64.6° by Narbutt.[10] Our freezing point of 64.58° agrees with that of Narbutt.

The dibromobenzene used by Bruni[8] froze at 85.9°. Küster[5] and Narbutt[10] report 86.4° and 86.9°, respectively, while reports by Kruyt[7] and Narbutt[10] give 87.2° and 87.1°, respectively. The value obtained from our cooling curves is 87.30 ± 0.02°, a higher value than any previously reported. There was no crystallization interval, so our preparation was undoubtedly pure.

Transition Temperature of *p*-Dichlorobenzene.—When examining the cooling curves of *p*-dichlorobenzene closely, a break in the line of cooling was discovered. In four experiments, the break resulted at 39.8, 39.7, 39.6 and 39.4°, respectively. The change in slope at 39° was not abrupt and it was thought at first that the effect was due to an error in the calibration of the apparatus. A search of the literature revealed, however, that a transition point had been reported by Beck and Ebbinghaus[14] at 39.5°. Conflicting data have been reported by Wallerant,[15] who concluded from the results of microscopic studies that *p*-dichlorobenzene is trimorphic, the reversible transitions occurring at 29 and 25°. That *p*-dichlorobenzene does exist in at least two forms under atmospheric pressure appears to be an

TABLE I

THE SYSTEM: *p*-DIBROMOBENZENE–*p*-CHLOROBROMOBENZENE

Mole % dibromobenzene	F. p. in °C.	M. p. in °C.	Mole % dibromobenzene	F. p. in °C.	M. p. in °C.
2.85	65.10	64.60	54.70	77.06	74.32
2.89	65.01	64.46	62.00	78.67	77.14
2.92	65.11	64.89	65.08	79.55	77.00
7.09	65.97	65.34	69.25	80.70	77.96
8.84	66.32	65.60	69.25	80.68	77.91
16.06	67.90	66.61	75.00	81.75	80.54
16.21	67.88	66.98	80.01	83.16	80.85
24.89	70.00	68.40	83.21	84.07	81.59
25.01	69.89	68.43	88.00	84.76	83.96
26.21	70.11	68.55	89.76	85.24	83.60
34.89	72.42	70.80	94.08	86.26	84.95
38.00	72.97	71.37	95.11	86.33	85.37
39.18	73.44	71.08	95.98	86.50	86.14
47.83	75.39	72.42	97.59	86.95	86.40
51.92	76.25	74.53	98.30	87.12	86.55
52.52	76.47	73.52			

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(8) G. Bruni, *Gazz. chim. ital.*, **30**, II, 127 (1900).

(9) Nagornow, *Z. physik. Chem.*, **75**, 578 (1911).

(10) J. Narbutt, *Ber.*, **52**, 1028 (1919).

(11) Speranski, *Z. physik. Chem.*, **51**, 45 (1905).

(12) N. C. Cooper, *Can. Chem. Met.*, **9**, 59 (1925).

(13) V. Auwers, *Z. physik. Chem.*, **30**, 312 (1899).

(14) Beck and Ebbinghaus, *Ber.*, **39**, 3870 (1906).

(15) F. Wallerant, *Compt. rend.*, **158**, 385 (1911).

undisputed fact. From the results of thermal analysis we conclude that a transformation in the solid state occurs at 39.6°.

The Binary System *p*-Dibromobenzene–*p*-Chlorobromobenzene.—The complete data for the system dibromobenzene–chlorobromobenzene are given in Table I.

The equilibrium diagram for this system is given in Fig. 5. The liquidus curve appears to be almost a straight line but it is actually S-shaped, the high temperature portion lying above and the low temperature portion below, the straight line joining the freezing points of the pure components. The system is an example of Roozeboom's Type I.

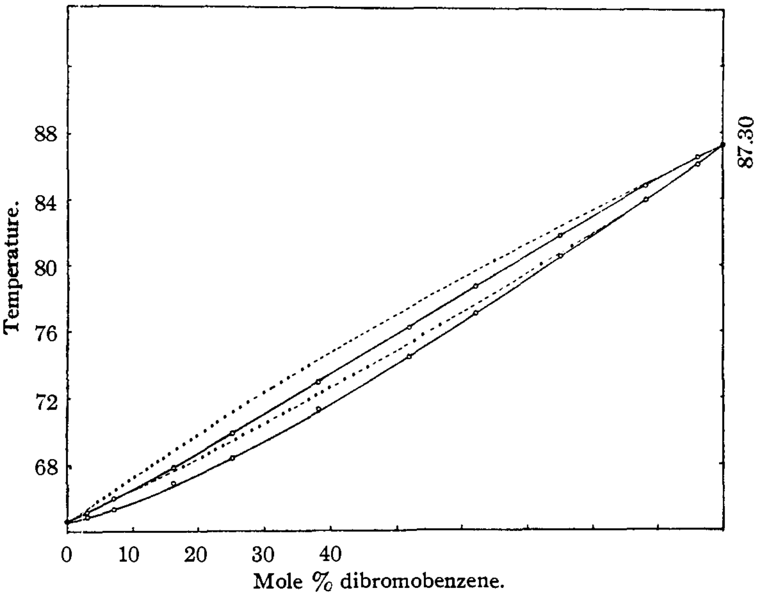

Fig. 5.—The binary system: *p*-dibromobenzene–*p*-chlorobromobenzene: —O—, exptl.; - - - - calculated.

Perhaps the most reliable equations for the calculation of solidus and liquidus curves are those of Seltz,[16] in the derivation of which he uses the concepts of activity and fugacity introduced by G. N. Lewis for ideal liquid solutions.

Using these equations and the following heats of fusion, the liquidus and solidus curves were calculated. Heats of fusion[17]: p-$C_6H_4Cl_2$ = 29.50 ± 0.11 cal. per gram = 4340 cal./mole; p-C_6H_4ClBr = 23.42 ± 0.09 cal./gram = 4484 cal./mole; p-$C_6H_4Br_2$ = 20.80 cal./gram = 4908 cal./mole. The solidus and liquidus curves thus calculated are expressed as dotted lines in Fig. 5.

The Binary System *p*-Dichlorobenzene–*p*-Dibromobenzene.—The system *p*-dichlorobenzene–*p*-dibromobenzene falls under Type III of Roozeboom. Data relevant to this system are given in Table II and the results are expressed graphically in Fig. 6. A distinct minimum freezing temperature of 52.90° was detected at a concentration of 1.22 mole per cent. 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. In Fig. 6 the region of the minimum is presented in a separate diagram, greatly enlarged.

TABLE II

THE SYSTEM *p*-DICHLOROBENZENE–*p*-DIBROMOBENZENE

Mole % dibromobenzene	F. p. in °C.	M. p. in °C.	Mole % dibromobenzene	F. p. in °C.	M. p. in °C.
0.30	53.06	53.01	20.13	55.95	54.37
0.62	53.02	52.95	30.03	59.49	55.20
1.01	52.93	52.91	40.08	63.81	59.14
1.20	52.90	52.90	47.96	67.05	62.93
1.60	52.94	52.90	57.06	71.13	67.09
1.98	52.96	52.91	64.89	74.18	70.66
2.56	53.00	52.94	74.93	78.26	75.62
3.03	53.03	52.95	85.01	82.11	80.09
4.91	53.15	53.01	95.03	85.70	84.59
9.90	53.68	53.37			

The experimentally determined liquidus and solidus curves are both straight lines over a restricted concentration range of approximately 40 to 80% dibromobenzene. As in the system chlorobromobenzene–dibromobenzene, the liquidus curve of this system is S-shaped. At no point does the liquidus curve lie above the straight line joining the freezing points of the pure components.

The Binary System *p*-Dichlorobenzene–*p*-Chlorobromobenzene.—Examination of the data in Table III and the plot of these data in Fig. 7 shows that the experimental curves for both liquidus and solids lie far below the straight line joining the freezing points of the pure com-

TABLE III

THE SYSTEM *p*-DICHLOROBENZENE–*p*-CHLOROBROMOBENZENE

Mole % chlorobromobenzene	F. p. in °C.	M. p. in °C.	Mole % chlorobromobenzene	F. p. in °C.	M. p. in °C.
0.41	53.08	53.03	5.04	53.11	53.03
0.98	53.05	53.01	5.96	53.16	53.10
1.54	53.03	52.99	10.00	53.48	53.26
2.16	52.99	52.96	25.04	54.55	54.26
2.57	52.96	52.96	38.00	55.83	55.37
2.96	53.00	52.97	50.03	57.36	56.61
2.97	53.00	52.96	60.03	58.50	57.78
3.91	53.05	53.00	74.99	60.67	60.15
4.03	53.05	52.99	90.73	62.91	62.61
4.53	53.09	53.00	97.00	64.06	63.85

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[16] H. Seltz, THIS JOURNAL, **56**, 307 (1934); Marsh, "Principles of Phase Diagrams," McGraw-Hill, New York, 1935, p. 43.

[17] J. Narbutt, *Z. Elektrochem.*, **24**, 339 (1918).

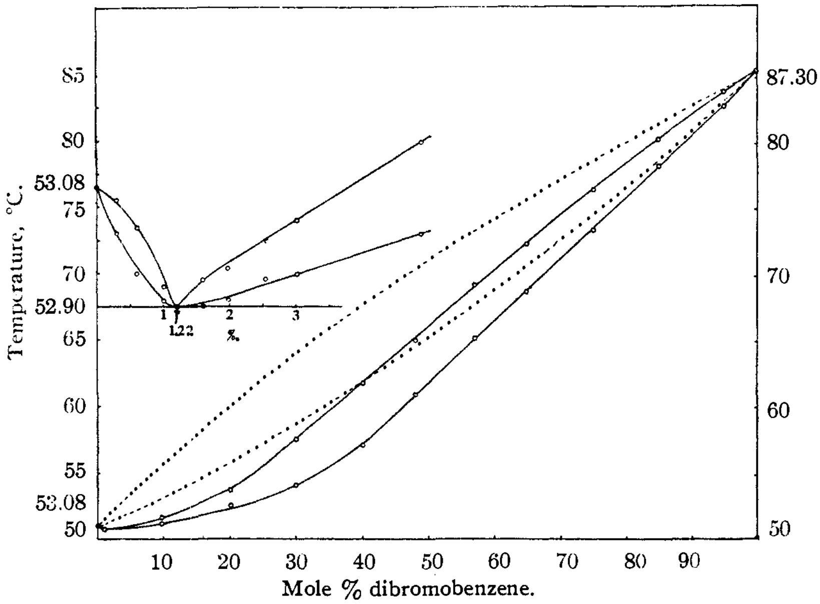

Fig. 6.—The binary system: *p*-dichlorobenzene–*p*-dibromobenzene: —O—, experimental; - - - - calculated.

ponents, and that the experimental curves lie considerably below the calculated curves which straddle the straight line. Calculated and experimental curves agree only in so far as the freezing intervals are approximately the same. As with the system dichlorobenzene–dibromobenzene this binary system possesses a minimum freezing point, lying at 52.96° and 2.57 mole per cent. chlorobromobenzene.

The Ternary System *p*-Dichlorobenzene–*p*-Chlorobromobenzene–*p*-Dibromobenzene.—Table IV contains all data relevant to the freezing and melting points of the ternary mixtures examined. The data have been classified into five sections, corresponding to five quasi-binary[18] systems investigated.

Construction of some of the isotherms of the ternary system by graphical interpolation from the quasi-binary sections gave the diagram of Fig. 8. The isotherms shown are those lying on the solidus surface at the temperatures indicated.

A very similar diagram for the liquidus isotherms was obtained. In the body of the diagram the isotherms were substantially straight lines. This can be seen from Fig. 9, which illustrates the relations between the solidus and liquidus isotherms. Each liquidus isotherm (full curve) with its corresponding solidus isotherm (broken line) constitutes the boundary of a heterogeneous liquid–solid region. Tie-lines have been inserted qualitatively to illustrate the direction of crystallization and composition changes 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.

The liquidus and solidus isotherms in the dichlorobenzene corner are represented on a larger scale in Figs. 10, 11 and 12. The position and the shape of the isotherms preclude any possibility of the existence of a ternary minimum freezing point as was suggested by Bruni.[19] Plotting selected liquidus and corresponding solidus isotherms, the unusual diagram of Fig. 12 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.

It is apparent that at no point do solidus and liquidus curves coincide and this is convincing evidence that there is no minimum of temperature in the ternary system. Evidence resting purely on temperature measurement might be open to doubt since the extreme temperature range in this region is not more than 0.1°, although we believe that the sensitivity of our apparatus is such that a minimum of temperature would have been detected directly had it existed.

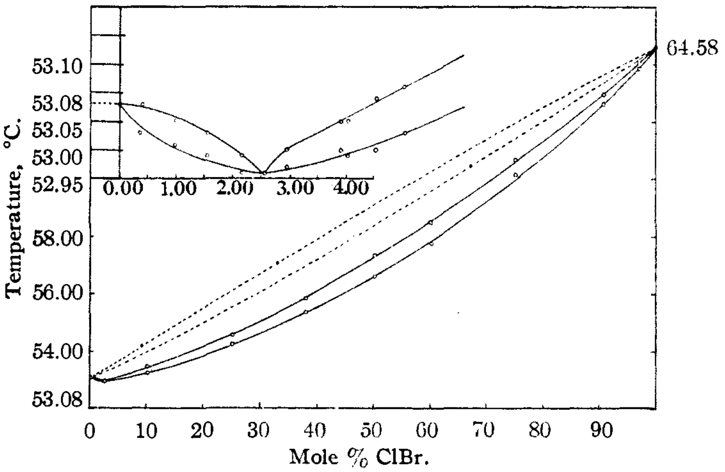

Fig. 7.—The binary system: *p*-dichlorobenzene–*p*-chlorobromobenzene; —O—, experimental; - - - - calculated.

Discussion

The great delicacy of the technique described

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(18) *Cf.* Marsh, ref. 16, p. 151, for the use of this expression.

(19) G. Bruni, "Über die feste Lösungen," 1901, p. 27.

is proved by the fact that the temperatures of complete solidification and hence the form and direction of the solidus line are clearly discernible on the cooling curves.

The experimental results indicate a temperature of reversible transition for *p*-dichlorobenzene of 39.6°. Cooling curves of those binary mixtures which contained this substance as one of the components were examined for a break. In mixtures containing from 95 to 100% *p*-dichlorobenzene a change in slope of the cooling curve was detected. The effect of the addition of *p*-dibromobenzene or *p*-chlorobromobenzene to the pure *p*-dichlorobenzene was to depress the transition temperature of the latter. Beck and Ebbinghaus[14] have determined the transition curve for the system *p*-dichlorobenzene—*p*-dibromobenzene and find it to be a straight line running from 39.5°, the transition temperature of pure *p*-dichlorobenzene, to −8°, the transition temperature of pure *p*-dibromobenzene. Our apparatus was unable to detect the transformation of *p*-dibromobenzene and, since the break in the cooling curve of pure dichlorobenzene was barely detectable, it is not

TABLE IV

THE SYSTEM *p*-DICHLOROBENZENE—*p*-CHLOROBROMOBENZENE-*p*-DIBROMOBENZENE

Mole % dichlorobenzene	Mole % chlorobromobenzene	F. p. in °C.	M. p. in °C.
Section 1			
0.00	48.08	76.25	74.53
7.87	44.31	74.22	72.15
10.65	42.84	73.54	70.86
21.59	37.72	70.35	67.14
25.10	35.90	69.33	66.47
37.33	30.13	65.67	62.73
38.47	29.50	65.32	62.42
47.61	25.11	62.57	59.69
62.74	17.92	58.72	56.38
72.41	13.27	56.42	55.20
81.35	8.96	54.67	54.19
92.38	3.65	53.34	53.22
96.39	1.74	53.05	52.98
97.18	1.35	53.01	52.95
98.24	0.85	52.97	52.94
98.80	0.63	52.95	52.92
99.32	0.33	53.02	52.98
Section 2			
0.00	62.00	72.97	71.37
10.00	55.80	70.47	68.29
25.00	46.50	66.30	63.01
40.00	37.20	62.82	60.76
50.00	31.00	60.37	58.29
65.00	21.70	57.10	55.60
80.00	12.40	54.55	54.06
90.00	6.20	53.46	53.30
95.00	3.10	53.10	53.03
97.36	1.63	52.99	52.93
98.22	1.09	52.94	52.90
99.09	0.56	53.03	52.97
99.55	0.25	53.08	53.00
Section 3			
0.00	74.99	69.89	68.43
10.24	67.34	67.58	66.24
25.28	56.05	64.39	63.09
39.99	45.02	61.12	59.42
41.00	44.24	60.99	59.32
50.22	37.34	59.10	57.72
65.74	25.44	56.44	55.46
71.77	21.15	55.49	54.92
81.64	13.77	54.20	53.89
91.28	6.54	53.35	53.27
94.94	3.80	53.11	53.03
96.51	2.63	52.99	52.94
97.44	1.94	52.97	52.93
98.37	1.22	53.00	52.95
99.19	0.61	53.06	53.01
Section 4			
0.00	25.00	81.75	80.54
10.00	22.50	78.96	78.04
25.00	18.75	73.87	71.47
40.00	15.00	68.49	65.39
50.00	12.50	64.82	60.86
65.00	8.75	59.49	57.35
80.00	5.00	55.28	54.39
91.00	2.25	53.51	53.30
95.00	1.25	53.15	53.08
97.50	0.63	52.99	52.93
98.80	0.30	52.96	52.92
99.50	0.13	53.05	52.98
Section 5			
90.93	7.97	53.35	53.21
95.15	3.99	53.11	52.99
97.82	2.00	52.95	52.92
98.18	0.63	52.94	52.91
98.40	0.41	52.93	52.91
98.80	0.00	52.90	52.90

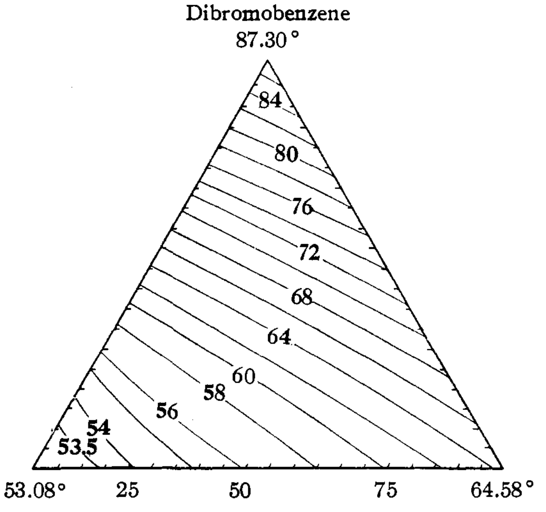

Fig. 8.—Solidus isotherms in the system: p-$C_6H_4Cl_2$:p-C_6H_4ClBr:p-$C_6H_4Br_2$.

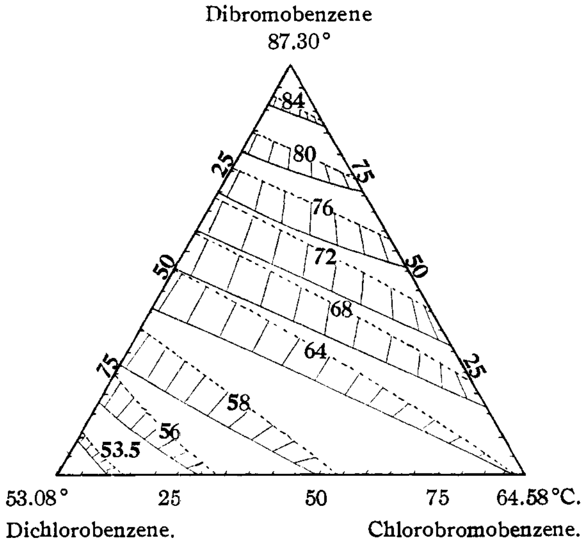

Fig. 9.—Selected heterogeneous bands in the system $p\text{-}C_6H_4Cl_2$:$p\text{-}C_6H_4ClBr$:$p\text{-}C_6H_4Br_2$: —, liquidus; - - - -, solidus.

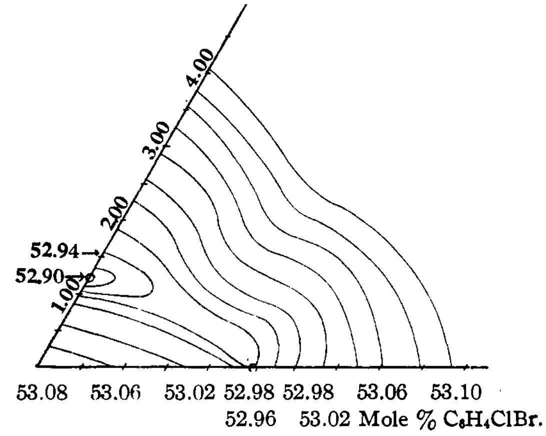

Fig. 10.—Liquidus isotherms in the $p\text{-}C_6H_4Cl_2$ corner.

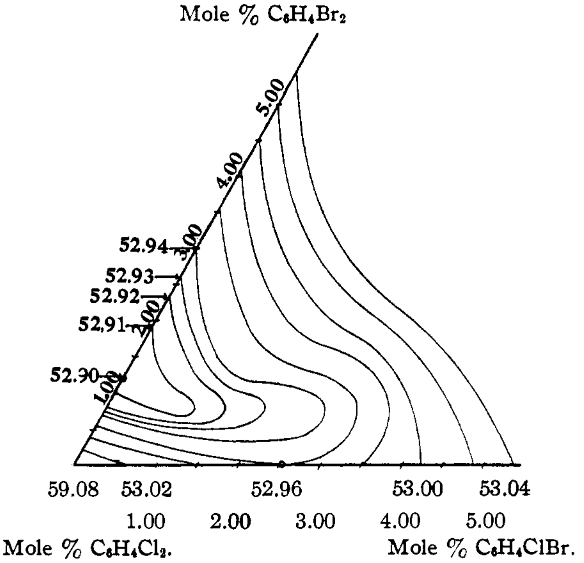

Fig. 11.—Solidus isotherms in the $p\text{-}C_6H_4Cl_2$ corner.

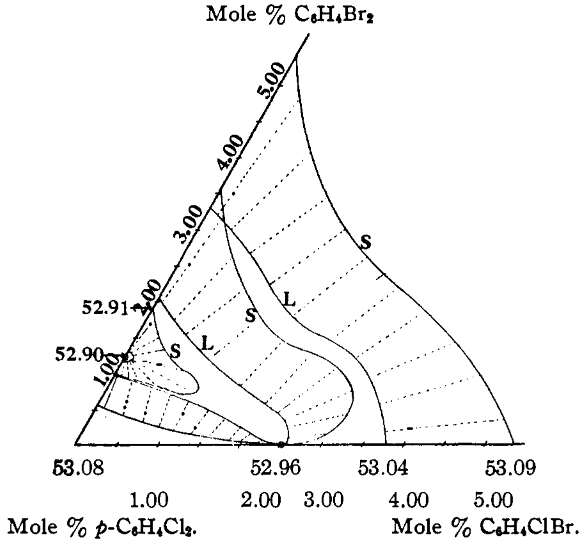

Fig. 12.—Selected isotherms in the $p\text{-}C_6H_4Cl_2$ corner: L, liquidus; S, solidus.

surprising that it disappeared completely in mixtures containing more than 5% of either of the other two components.

In view of the great similarity in molecular and crystallographic structure it is not surprising that these dihalogen benzenes should be miscible in all proportions in both liquid and solid states. All three binary systems, however, exhibit a decided tendency toward positive deviation from Raoult's law; at some lower temperature a miscibility gap may come into being.

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 chlorobromobenzene molecule or even with the symmetrical dibromobenzene molecule. Addition of a higher melting foreign material of similar structure such as *p*-chlorobromobenzene or *p*-dibromobenzene produces a depression in the freezing point of the pure dichlorobenzene. The heavier, higher melting dibromobenzene produces the greater and more rapid depression. More of the lighter chlorobromobenzene molecule, relative to the quantity of dibromobenzene, is required to produce a given freezing point depression.

Summary

An apparatus is described by means of which it is possible, by means of thermal analysis, to determine not merely the liquidus but also the solidus curve, and therefore the extent of solid solution.

As a test of technique, the system *p*-dichlorobenzene—*p*-dibromobenzene – *p* - chlorobromoben-

zene has been investigated. The results of this investigation are as follows:

The freezing points of pure *p*-dichlorobenzene, *p*-chlorobromobenzene and *p*-dibromobenzene were redetermined as 53.08, 64.58 and 87.30°, respectively. It was confirmed that pure *p*-dichlorobenzene exists in at least two forms under atmospheric pressure, the reversible transformation occurring at 39.6°.

p-Dibromobenzene and *p*-chlorobromobenzene are miscible in all proportions in both liquid and solid states; the freezing points of all solutions lie between the freezing points of the pure components. The binary system *p*-dichlorobenzene–*p*-dibromobenzene exhibits a minimum freezing temperature of 52.90° at a concentration of 1.22 mole per cent. dibromobenzene. The components are miscible in all proportions in both liquid and solid states. The binary system *p*-dichlorobenzene–*p*-chlorobromobenzene exhibits a minimum freezing temperature of 52.96° at a concentration of 2.57 mole per cent. chlorobromobenzene. The components are miscible in all proportions in both liquid and solid states.

The ternary system *p*-dichlorobenzene–*p*-chlorobromobenzene–*p*-dibromobenzene exhibits miscibility in all proportions in both liquid and solid states. No ternary solution of minimum freezing point exists; neither is there any temperature at which the compositions of liquid and solid solutions coincide.

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[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE UNIVERSITY OF AKRON, GOVERNMENT LABORATORIES]

Potentiometric Determination of Oxygen Using the Dropping Mercury Electrode[1]

BY H. A. LAITINEN,[1a] T. HIGUCHI[1b] AND MICHAEL CZUHA[1b]

A dropping mercury electrode in a solution free of capillary-active substances or electro-reducible or oxidizable substances assumes a potential corresponding to the electrocapillary zero potential of mercury. Under these conditions, the electrokinetic potential of mercury, with respect to the solution, is zero. To maintain the dropping electrode at any other potential, it is necessary to supply electrons or to remove electrons from the reservoir of mercury connected to the capillary from which the mercury is dropping. Thus, it is necessary to maintain a continuous flow of electrons to charge electrically the double layer existing between the mercury and the solution because the double layer is continually being formed. The polarographic charging or condenser current is a familiar manifestation of this phenomenon. The charging current as shown in Fig. 1 is negative in sign (corresponding to an anodic process at the dropping electrode) at potentials more positive than the electrocapillary maximum, at which point the charging current changes sign and increases in positive value as the potential is made more negative.

Any substance, such as oxygen, which is reducible on the positive side of the electrocapillary maximum, will yield a polarographic diffusion current which is positive in sign and hence opposed in direction to the charging current. For very small concentrations of oxygen, it is evident that at some value of the potential the diffusion and charging currents will be equal in magnitude but opposite in direction and hence will cancel. Since the instantaneous value of the diffusion current varies with the one-sixth power of the time and is independent of the potential while the charging current at a constant potential varies with the two-thirds power of the time,[2] it is evident that the null potential must vary with time in such a way that the instantaneous current will be zero at all times.

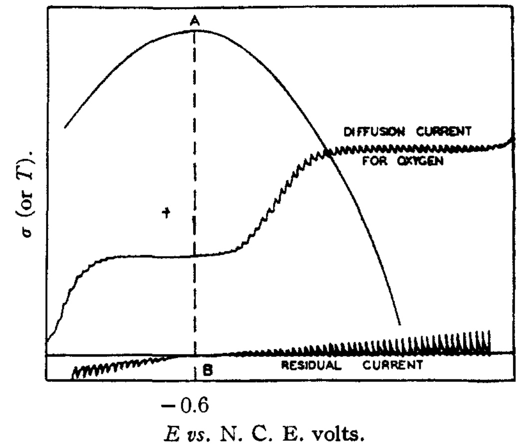

Fig. 1.—Electrocapillary curve.

To calculate the magnitude of the effect, it is convenient to equate the total charge, $(q_c)_t$, held by the drop at any time, t, with the number of coulombs, $(q_d)_t$, lost by the drop through the electro-reduction of oxygen molecules from the beginning of the drop formation to time, t, or

$$(q_c)_t = (q_d)_t \quad (1)$$

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[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.