A STUDY OF SOME OF THE FAMILIAR PRECIPITATION

REACTIONS OF COPPER BY MEANS OF ELECTRICAL CONDUCTIVITY

MEASUREMENTS.

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by

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A STUDY OF SOME OF THE FAMILIAR PRECIPITATION REACTIONS OF COPPER BY MEANS OF ELECTRICAL CONDUCTIVITY MEASUREMENTS.

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Nature of Problem.

This paper contains a record of the measurements of the electrical conductivity following the precipitation reactions of copper which are most commonly used for its detection and estimation in ordinary qualitative and quantitative analysis. The investigation was carried out with the object of a possible application of one or more of these reactions to the volumetric determination of copper using the property of electrical conductivity as a means of indicating the end point by which the reaction could be measured.

Since volumetric methods are of especial value in practical and applied chemistry, the accuracy usually attained in commercial work, the simplicity which could be attained in the necessary apparatus, and the speed with which the manipulation could be conducted, were kept constantly in mind.

The Method.

This method of studying chemical change admits of many possibilities in its practical application. The fact that conductivity is a measurement easily and rapidly made, coupled with the great accuracy with which small quantities of materials may be detected, renders the method one which may be applied both to quantitative estimation and qualitative examination of chemical changes in commercial work as well as in purely theoretical study.

Most volumetric analysis depends on the detection of a more or less well defined color change. Accuracy in this method of analysis is, therefore, dependent on the capability of the manipulator to detect delicate color change. The method itself is limited to such reactions as do not involve color changes or in which the substances undergoing change do not exhibit a color which will interfere with the indicator.

Accordingly, it can be seen that if another physical property can be readily utilized in the determination of end points in reactions,

a large number of them can be adapted to rapid
analytical work which have been hitherto exclu-
ded.

The theory upon which this method is based
is too well known to need repetition. Any recent
text in physical chemistry will give complete
information concerning theory, method of setting
up apparatus, etc..

Previous Work of Other Investigators.

M. Boll (1) has showed that an electrometer
used as a zero instrument, may be useful in follow-
ing chemical changes. By calculation he indicated
that changes in amounts of certain materials, of
the order or .0000001 mg, can be detected.

P. Dutoit (2) investigated the changes in
electrical conductivity which accompany certain
chemical reactions, at some length. In addition
to details of manipulation he studied a number
of precipitation reactions by means of measure-
ments of conductivity. As bases his work was
with the alkaline earths, lead, silver, zinc,
chromium and cadmium. The acids studied were:

Hydrochloric, hydrobromic, hydriodic, hydrocyanic, sulphuric, carbonic, oxalic, benzoic, chromic, phosphoric, and fluosilicic.   He deduced seven rules for guides as to the most favorable circumstances under which to conduct the method.

P. Dutoit and P. Mojoiu (3) applied the precipitation curves to the determination of barium, strontium and calcium, in the presence of each other.

P. Dutoit and Duboux (4) used conductivity measurements in determining the degree of acidity of wines. In this article they adopt a nomenclature to designate more specifically the particular type of reaction to which the measurements refer, viz: precipitation, neutralization, oxidation etc., curves.

H. Corvazier (5) applied the electrical conductivity method to the analysis of mixtures of sulphuric and nitric acids. By titration with standard barium hydroxide solution the total acidity can be determined after which titration with sodium carbonate will give the barium nitrate and hence the nitric acid.

A. Bruno and P.T. d'Auzay (6) discovered some
differences in the results obtained by Dutoit in
the application of conductivity measurements to wine
analysis and those obtained by the precipitation
of sulphates.

J.F. Snell (7) by formulating a definition
of a standard conductivity for a maple syrup, has
been able to apply conductivity measurements as
a test for purity in maple syrup.

Borris (8) has published a preliminary paper
on conductivity measurements and states that some
applications of the method will appear at a subse-
quent date.

R. Dubrisay (9) has made a study of the
neutralization curves of phenol, chromic acid,
and periodic acid, using a solution of stearic
acid in benzene.

A.G. Dorochevskii and S.V. Dvorzhanchiz (10)
find the electrical conductivity to be a charac-
teristic constant for natural waters and have
applied it as a measure of both temporary and
permanent hardness. In one or two later articles
they have applied conductivity somewhat further
to water analysis.

F. H. van Suuhtelen and A. Itano (11) have
employed the method to several precipitation and
neutralization reactions. The neutralization of
sulphuric acid with sodium hydroxide, the neutral-
ization of lactic and malic acids and the determi-
nation of malic, tartaric, and succinic acids, in
the presence of each other. The precipitation of
chlorine in potassium chloride with silver nitrate,
and the precipitation of barium as sulphate were
studied. They also suggest the use of an
electrometer to do away with the tedium of the
telephone for the manipulator. They claim very
great accuracy for the method as well as simpli-
city in handling.

S. Horiba (12) has applied the conductivity
measurements to the determination of very weak
acids and bases. These determinations were con-
ducted with the aid of empirical formulas deduced
by means of conductivity measurements taken at
25 degrees C.

W. A. Withers and A. L. Field (13) have
applied conductivity measurements to a study of the
reaction between calcium nitrate and dipotassium

phosphate in dilute solution. By this investigation they were able to determine the definite reaction taking place under set conditions and also the amount of hydrolysis undergone by calcium phosphate in different concentrations.

Experimental Part.

This paper is confined entirely to a study of reactions involving precipitations. The particular precipitates considered in the experimental work are: cupric ferrocyanide, cupric hydroxide, cupric carbonate, cupric sulphide, cuprous sulphocyanide and cuprous iodide.

APPARATUS.

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The conductivity measurements were carried out according to the familiar Kohlrausch method. The usual apparatus, consisting of a Wheatstone bridge, resistance box, coil, telephone, storage and connections, was employed. All measurements were carried out in a thermostat at 25 degrees C.

The cell was designed with regard for its possible adaptibility to analytical work. As the experimentation was continued one or two modifications suggested themselves. The first one used was simply a small beaker fitted with a wooden top, through which the electrodes were inserted and held stationary with sealing wax.

The electrodes were platinum disks held ver-
tically in order to prevent the settling of a pre-
cipitate on them and causing irregularities in the
resistance measurements.   In this cell stirring
was effected by agitation, which, of course, gave
trouble in the manipulation as the connections
were frequently broken in attempting to shake the
beaker.

The second cell used was simply a modification
of the first. A somewhat deeper beaker was em-
ployed to allow the use of an electrically operated
stirring device. The stirrer was a glass T tube
rotated by means of a belt from the small electric
motor which stirred the thermostat. The electrodes
were increased in size to about twice the surface
of those used in the first cell, being about 15 mm
diameter.

As the experimental work was continued, greater
dilutions than could be conveniently handled in
small beakers, were found necessary. Also, solu-
tions containing different numbers of electrolytes,
and sometimes different quantities of the same
material, gave rise to such differences in the

conductivity, that a third cell was devised. This
cell, as indicated in the figure, was of sufficient
capacity to admit of considerable change in dilution
as occasion demanded, and the movable electrode
allowed the resistance of the cell to be varied
when the nature of the solution under investigation
required.
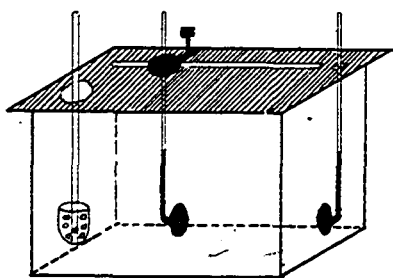
Fig. 1.

The battery jar is
15 x 8 x 11 cms. The
cover is of wood. One
electrode is set and the
other can be moved back
and forth in the slot and made stationary by
means of the clamp. The type of stirrer shown
is employed in order that the stirring may be
sufficiently vigorous to bring such a considerable
volume of solution to a state of intimate mixture
rapidly. The electrodes are about 2 cms in
diameter.

This type of cell was found to be very
satisfactory and could be conveniently used with
any of the reactions studied.

Manipulation.

As stated above, the conductivity measurements were made according to the Kohlrausch method. Each of the readings recorded, was taken only when three consecutive observations, between which the cell was vigorously stirred, showed constant results.

In the curve plots black lines follow actually observed points, interpolated results will be indicated by red.

The gradual addition of reagents was effected by means of standardized pipettes.

Throughout all experiments the copper sulphate solution used was accurately made up to $M/10$ concentration.

Explanation of Curves.

The curves are plotted with ordinates showing bridge readings (relative conductivity), abscissae, amounts of reagent added (measured in cubic centimeters).

The apparatus was so arranged that an increase in bridge reading indicates a decrease in the conductivity of the solution.

Curves.

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The first reaction studied was between copper sulphate solution and potassium ferrocyanide. The potassium ferrocyanide solution was made up and standardized against potassium permanganate.

47.9 cc ferrocyanide = 11.7 cc of potassium permanganate (1.0203 Normal).


Curve 1. (page 13). Fig.2.

10 cc of copper sulphate titrated with potasium ferrocyanide. In the cell before titration the copper sulphate was diluted to about N/50.

cc.	*B.R.	cc.	B.R.
0.	49.20.	21.	40.10.
2.	48.07.	22.	39.85.
4.	46.93.	23.	39.75.
6.	45.85.	25.	39.75.
7.	45.39.	27.	39.11.
8.	45.00.	29.	37.96.
10.	44.13.	31.	36.71.
11.	43.66.	33.	35.60.
14.	42.42.	35.	34.49.
16.	41.81.	37.	33.40.
18.	41.00.	41.	31.65.
19.	40.60.	43.	30.90.
20.	40.21.	45.	30.15.

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* B.R. will be used as abbreviation for Bridge Reading.

Fig. 2.
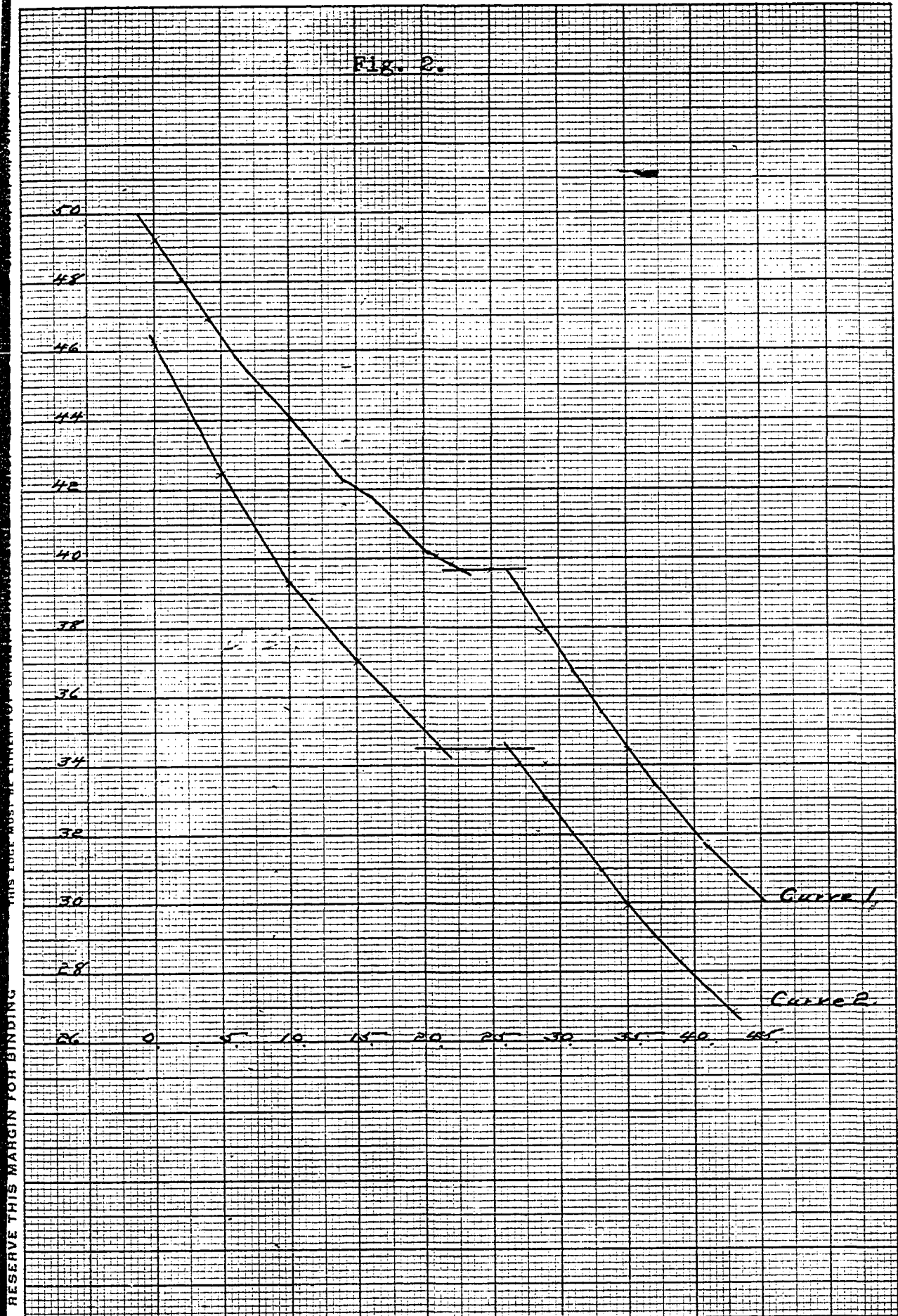
Curve 2. Fig.2. (page 13).

This curve is a duplicate of curve 1. The
difference in bridge readings is caused, of course,
by slight differences in the concentration of the
copper sulphate when diluted in the cell. 10 cc
of the copper solution were added and titrated
with potassium ferrocyanide as above.

cc.	B.R.	cc.	B.R.
0.	46.24.	29.	33.06.
5.	42.45.	31.	32.05.
10.	39.36.	33.	30.95.
15.	37.05.	35.	29.97.
17.	36.35.	37.	29.07.
19.	35.46.	39.	28.28.
21.	34.66.	41.	27.54.
23.	34.46.	43.	26.86.
25.	34.50.	45.	26.17.

The calculated end point in this case is
reached at the addition of 20.1 cc of the ferro-
cyanide.

The two curves are somewhat dissimilar but
apparently, if one or two readings taken in the
neighborhood of the first break in curve 1 are
neglected, a break will occur at about 20.5.

Curves 1 and 2, as may be seen, show two distinct
breaks, neither of which comes at the calculated

end point.

Curve 3. Fig.3 (page 16).

This represents the same reaction as above except that readings were taken more closely together in the immediate vicinity of the two breaks for the purpose of investigating the cause of the apparent horizontal line shown in the curve.

cc.	B.R.	cc.	B.R.
0.	53.30.	21.	42.75.
10.	47.13.	22.	42.61.
15.	45.05.	23.	42.65.
16.	44.75.	24.	42.75.
17.	44.35.	25.	42.74.
18.	43.96.	26.	42.46.
19.	43.58.	27.	42.02.
20.	43.11.		

Curve 4. Fig.3. (page 16.)

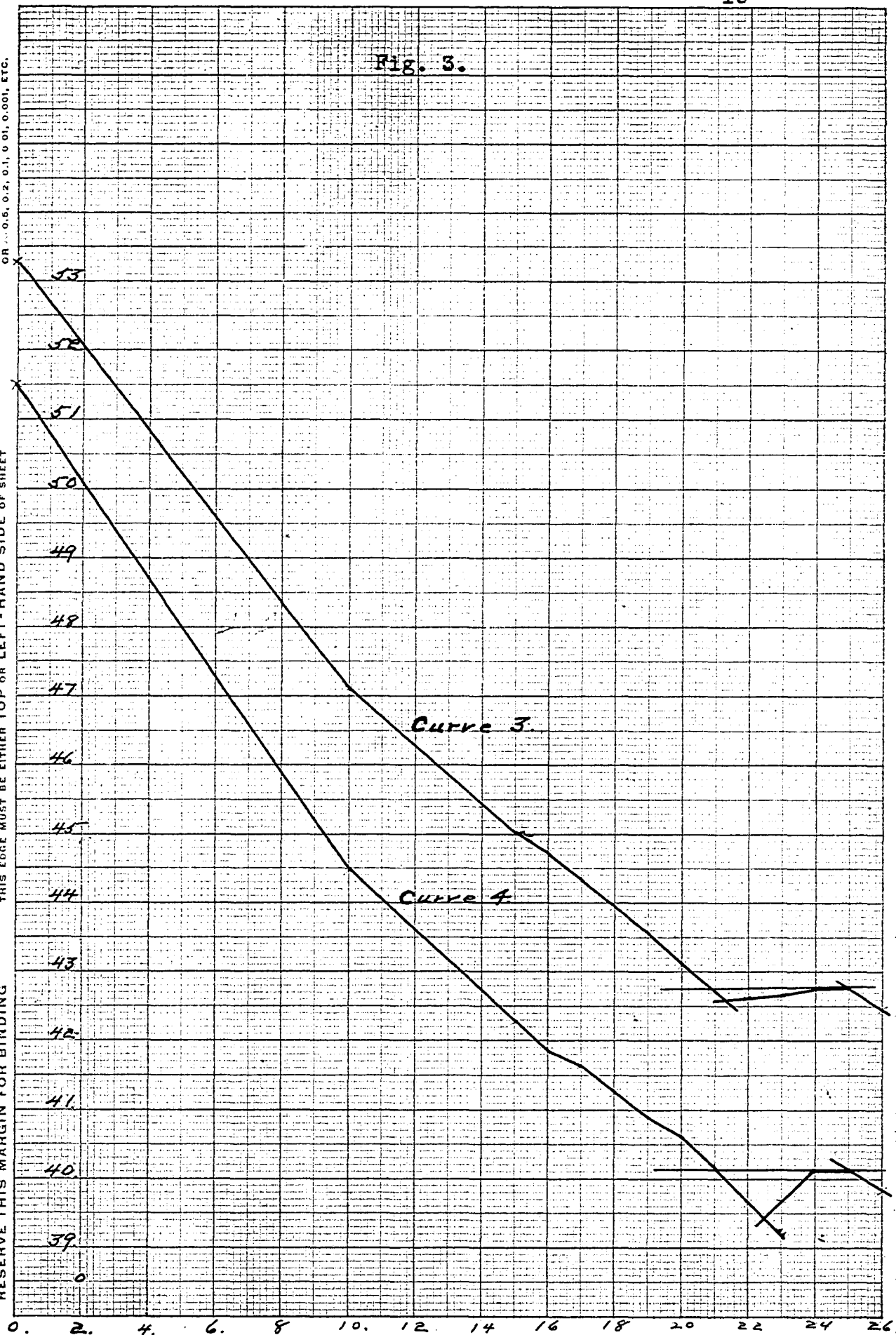| cc.	B.R.	cc.	B.R.
0.	51.50.	21.	40.20.
10.	44.47.	22.	39.67.
15.	42.28.	23.	39.69.
16.	41.85.	24.	40.12.
17.	41.65.	25.	40.12.
18.	41.25.	26.	39.85.
19.	40.90.	27.	39.40.
20.	40.60.		

This curve is a check on 3.

The calculated end point for 3 and 4 is at 20.1.

By interpolation two breaks occur, one at 21, and the other at 25.

Fig. 3.

Curve 3.

Curve 4.

Great difficulty was experienced in getting
constant readings in the foregoing measurements,
particularly in the neighborhood of the calculated
end point in the reaction. What, in curves 1 and
2, appeared to be an approximately horizontal line,
shows in 3 and 4 as a series of distinctly broken
lines and only by interpolation can anything like
concordant results be obtained for the two identi-
cal reactions. A possible cause for these irregu-
larities was ascribed to the difficulty in bring-
ing the mixture to a homogeneous condition after
each addition of the precipitant. In order to
overcome this trouble the first modification in
the cell (described on page 9), was made.

Curve 5. Fig 4. (page 18).

This indicates the reaction in which 5 cc of
the standard copper sulphate were precipitated
with potassium ferrocyanide. The concentration
of the copper solution after being placed in the
cell was approximately N/50.

Fig. 4.
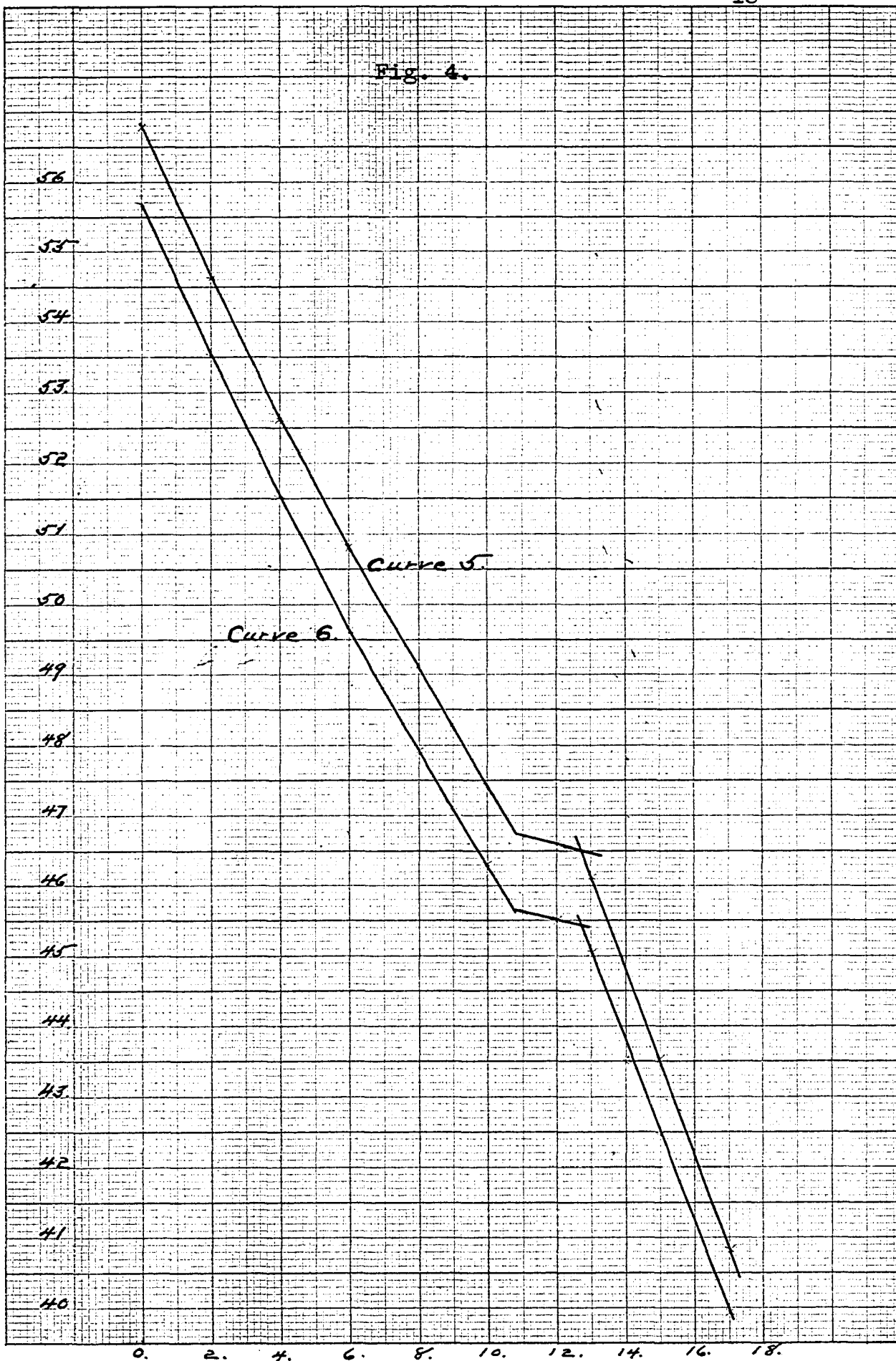
(Curve 5.).

cc.	B.R.	cc.	B.R.
0.	56.80.	10.	47.41.
2.	54.62.	11.	46.70.
4.	52.62.	12.	46.60.
6.	50.80.	13.	46.12.
8.	49.10.	15.	43.50.
9.	48.26.	17.	40.82.

Curve 6. Fig.4. (page 18).

This is a check on the reaction indicated by curve 5.

cc.	B.R.	cc.	B.R.
0.	55.69.	10.	46.30.
2.	53.50.	11.	45.60.
4.	51.51.	12.	45.50.
6.	49.60.	13.	45.05.
8.	47.90.	15.	42.49.
9.	47.09.	17.	39.94.

The calculated end point here is at 10.03.

The observed breaks are at 10.8 and 12.75.

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It will be noticed that these two curves are considerably more regular than than those measured in the first form of cell.   On the other hand, the curves do not show a break corresponding to the reaction end point.

The fact that for a short distance the curve assumes a horizontal direction due to the addition

of small quantities of ferrocyanide failing to cause any change in the conductivity, was ascribed to possible absorbtion. According to Dutoit (14)* several of the ferrocyanides tend to occlude portions of dissolved materials, when precipitated in their presence. This being the case of course the occurrence of the flat part of the curve, and its length, will depend on the concentration of the dissolved materials present in the particular solution and a mathematical relation between the reaction end point and the position of either break in the curve can not be established.

The precipitation of copper ferrocyanide in acid and ammoniacal solutions was next examined.

Curve 7. Fig. 5. (page 21).

5 cc of the copper sulphate solution were titrated with potassium ferrocyanide in the presence of 5 cc of N/10 hydrochloric acid.

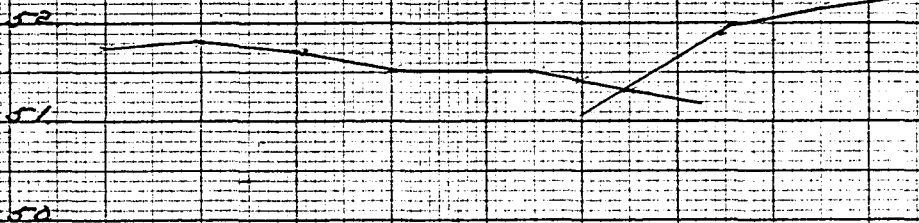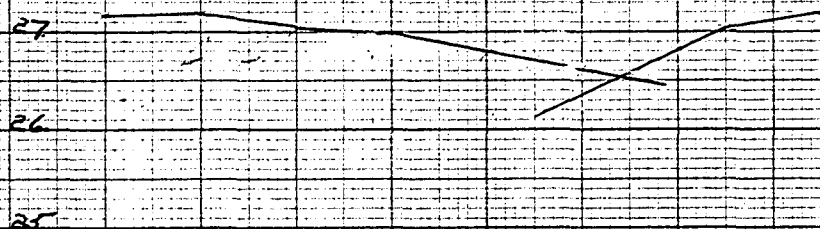| cc.	B.R.	cc.	B.R.
0.	51.75.	10.	51.42.
2.	51.80.	11:	51.32.
4.	51.71.	12.	51.69.
6.	51.51.	13.	51.95.
8.	51.51.	15.	52.15.
9.	51.50.	17.	52.28.

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* See Bibliography.

Fig. 5.

Curve 8. Fig. 5. (page 21).

This is a check on 7. The concentration in
the cell was approximately the same as in 7 but
the resistance in the circuit was changed which
is the reason for the difference in the bridge
readings.

cc.	B.R.	cc.	B.R.
0.	27.16.	10.	26.61.
2.	27.16.	11.	26.58.
4.	27.01.	12.	26.81.
6.	26.98.	13.	27.02.
8.	26.79.	15.	27.15.
9.	26.70.		

The calculated end point in this reaction
is at 10.03. cc.

A break in the curve occurs at 10.8 cc.

The above curves are quite irregular, yet
there is a distinct break at least in the
neighborhood of the point indicated. It will be
noticed that this break coincides with that shown
by curves 6 and 7. The readings became constant
only after a wait of from 3 to 5 minutes of vigorous
stirring.

Curve 9. Fig. 6. (page 24).

This curve follows the precipitation of copper as ferrocyanide, from ammoniacal solution. 5 cc of the copper sulphate solution were diluted in the cell to about N/50 and ammonium hydroxide added until the precipitate of copper hydroxide was just dissolved. The solution was then titrated with the ferrocyanide solution.

cc.	B.R.	cc.	B.R.
0.	44.03.	10.	37.67.
2.	42.60.	11.	36.50.
4.	41.47.	12.	35.30.
6.	40.40.	14.	33.12.
8.	39.38.	16.	31.40.
9.	38.65.		

Curve 10. Fig. 6. (page 24).

cc.	B.R.	cc.	B.R.
0.	41.40.	10.	35.72.
2.	40.08.	11.	34.92.
4.	38.70.	12.	33.99.
6.	37.62.	13.	33.12.
8.	36.70.	15.	31.40.
9.	36.30.		

The calculated end point is at 10.03 cc.

The only break in the curve comes between 9 and 10 cc.

Fig. 6.

Curve 9

Curve 10
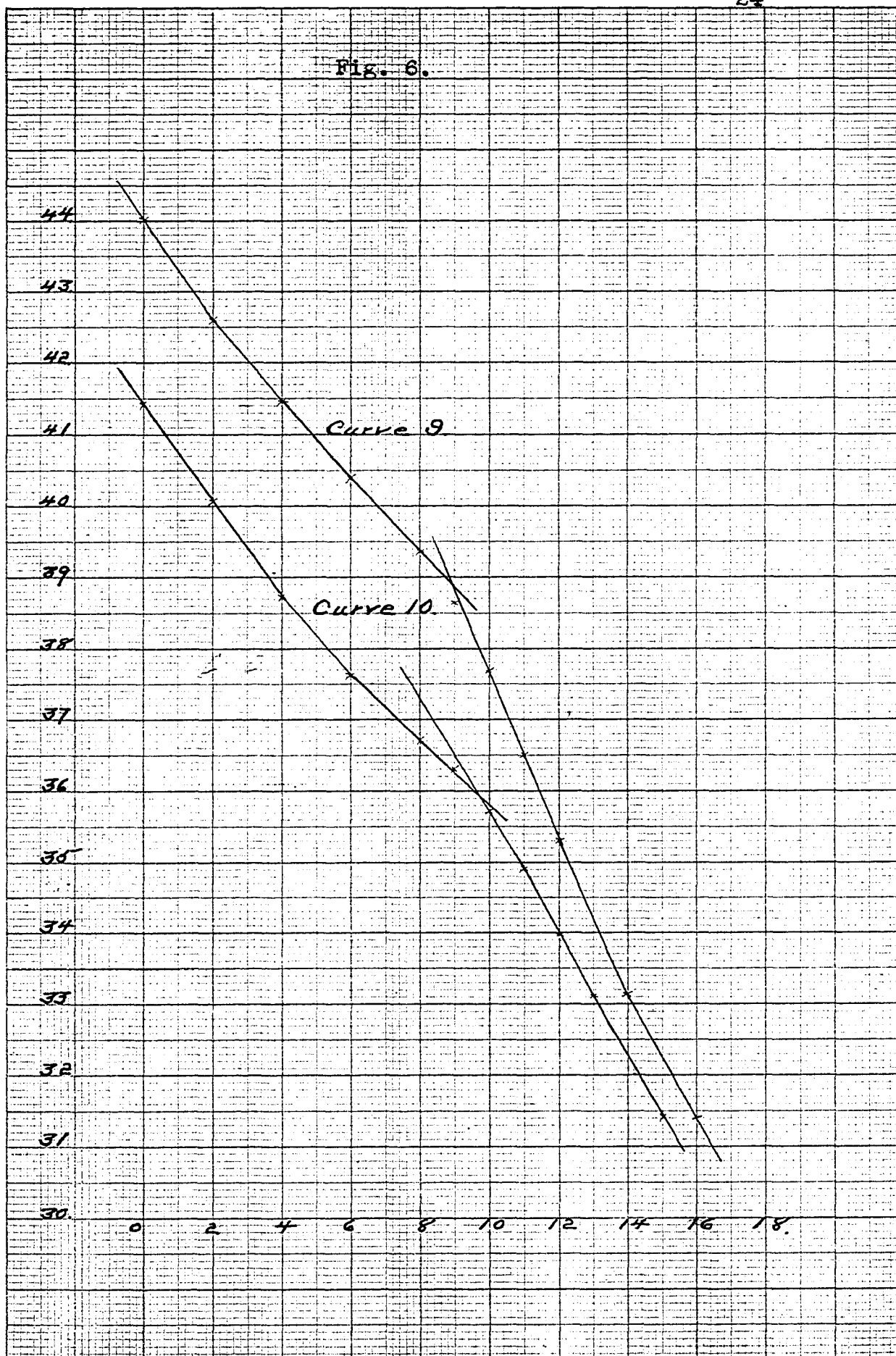
In the foregoing reaction constants for the
bridge readings were more easily obtained than in
the case of either the neutral or acidified solu-
tion. There is, however, no break corresponding
to the calculated end point or to any break occur-
ring in any of the previous curves. Moreover the
two identical reactions failed to give curves
which exhibited breaks at the same point.

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As a brief summary of the curves 1 to 10,
It would seem that the ferrocyanide of copper
does not give a curve which will exhibit a break
at the point at which the precipitation ceases,
theoretically. Dutoit (2)* has indicated this
fact with regards ferrocyanides of some of the
other metals.

Attention might be called, however, to the
fact that there is a correspondence between the
breaks exhibited in Figs. 4 and 5., and it is
possible that further investigation of this
reaction might lead to a factor which would
connect the break with the true end point. The
precipitation from alkaline solution does not give
results of interest.

The next reaction studied was that involving the precipitation of copper as carbonate.

The solution of sodium carbonate used was made up to N/10 and checked with a carefully standardized solution of hydrochloric acid. Methyl orange was used as indicator.

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Curve 11. Fig. 7. (page 27).

5 cc of the copper solution, diluted to about N/50, were titrated with the carbonate solution.

cc.	B.R.	cc.	B.R.
0.	55.05.	10.	48.86.
2.	54.05.	11.	47.85.
4.	52.99.	12.	46.70.
6.	51.81.	13.	45.50.
8.	50.46.	15.	43.12.
9.	49.71.	17.	40.90.

Curve 12. Fig. 7. (page 27).

This curve is a check on 11.

cc.	B.R.	cc.	B.R.
0.	54.56.	10.	48.00.
2.	53.48.	11.	46.91.
4.	52.30.	12.	45.85.
6.	50.98.	13.	44.60.
8.	49.52.	15.	42.21.
9.	48.81.	17.	39.98.

The calculated end point is at 10 cc.

The observed breaks come at 10.3 and 10.1 respectively.

Fig. 7.

Curve 11

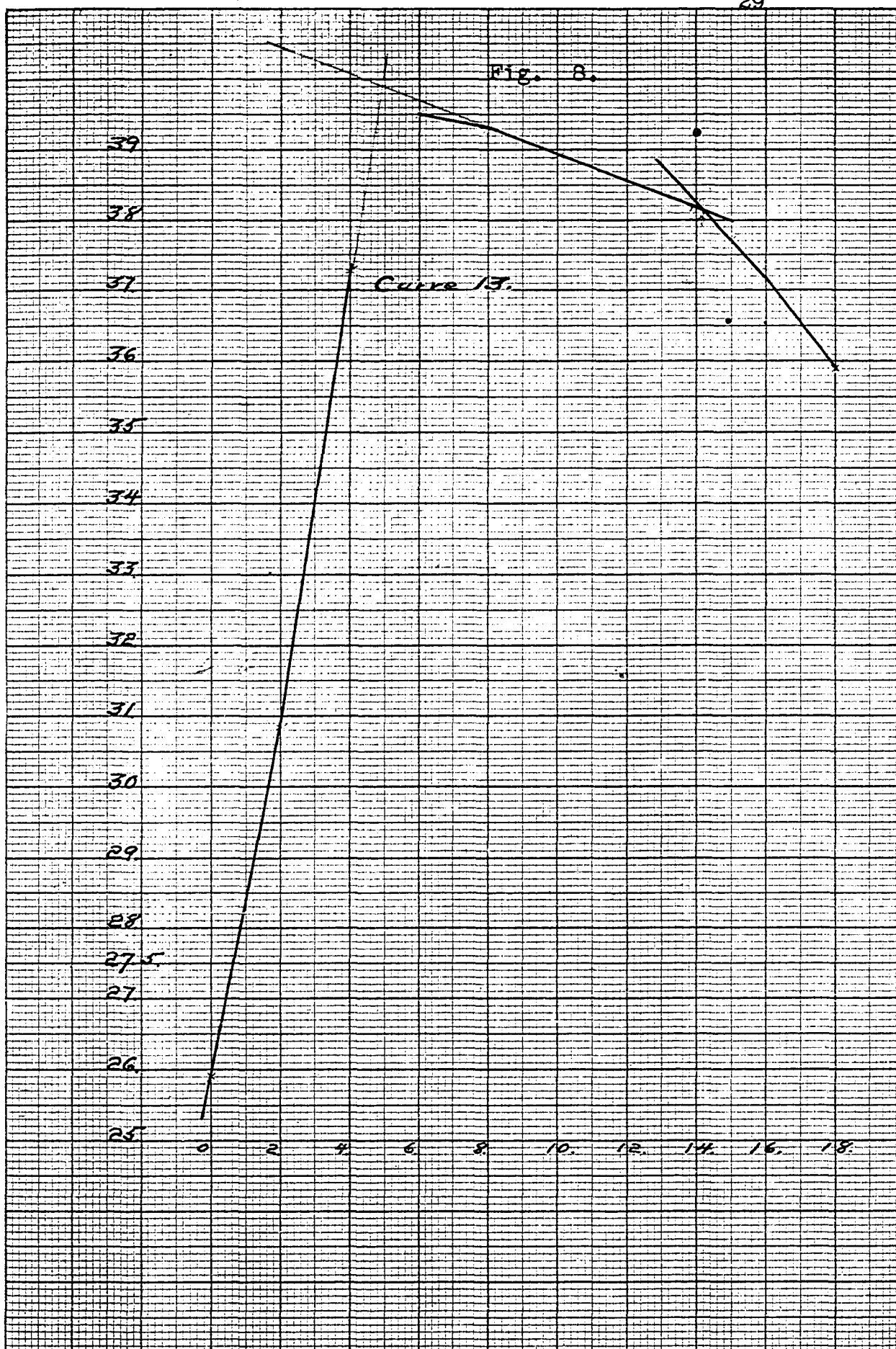Curve 12.
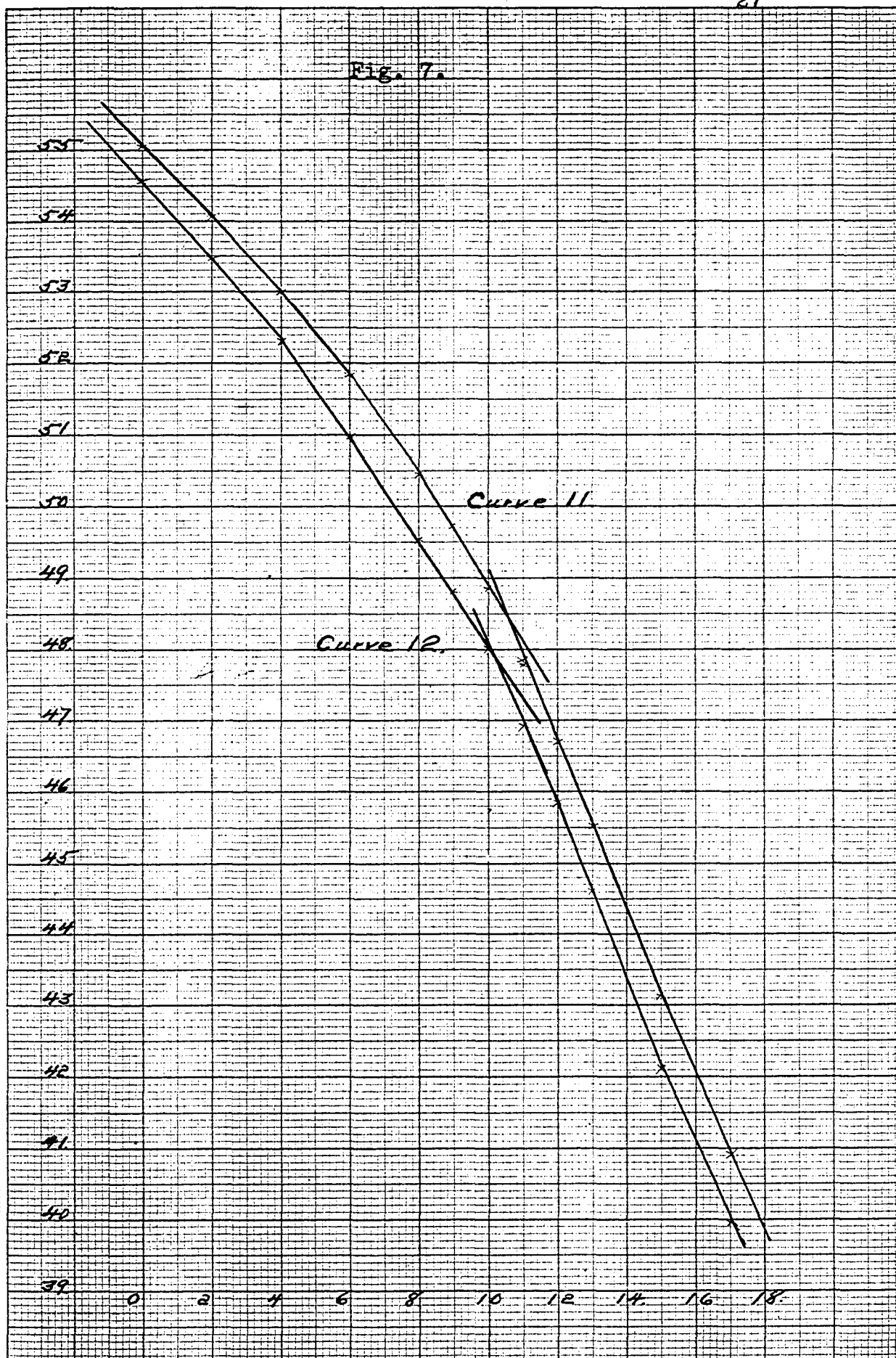
In this reaction constant readings for the con-
ductivity were reached only after continued stirring.
This gradual shift in conductivity before reaching
a constant value is indicative of a secondary reaction
and may possibly be accounted for by formation of
basic copper salts. This, of course, would inter-
fere with the reaction end point and account for
irregularities in the position of the break in curves
representing the reaction.

Curve 13. Fig. 8. (page 29).

This curve follows the reaction involving the
precipitation of copper carbonate from a solution
which is acid. The curve, of course, should show
two breaks, one corresponding to the end point in
the reaction between the carbonate and the acid
present, and the other, the end point in the pre-
cipitation of the copper.

5 cc of the copper sulphate solution were
placed in the cell and 5 cc of N/10 hydrochloric
acid added. The solution was then titrated with
the N/10 sodium hydroxide.

Fig. 8.

Curve 13.

(Curve 13)

cc.	B.R.	cc.	B.R.
0.	25.90.	12.	38.58.
2.	30.85.	13.	38.38.
4.	37.29.	14.	38.11.
6.	39.50.	15.	37.70.
8.	39.30.	16.	37.18.
10.	38.94.	18.	35.90.

The calculated end points occur at 5 and 15 cc. The first observed break occurs at about 4.9 and the second at 14.2.

The break here corresponding to the complete precipitation of the copper again does not agree with the calculated value. The readings were considerably more easily taken as constant values were reached almost immediately after adding the carbonate.
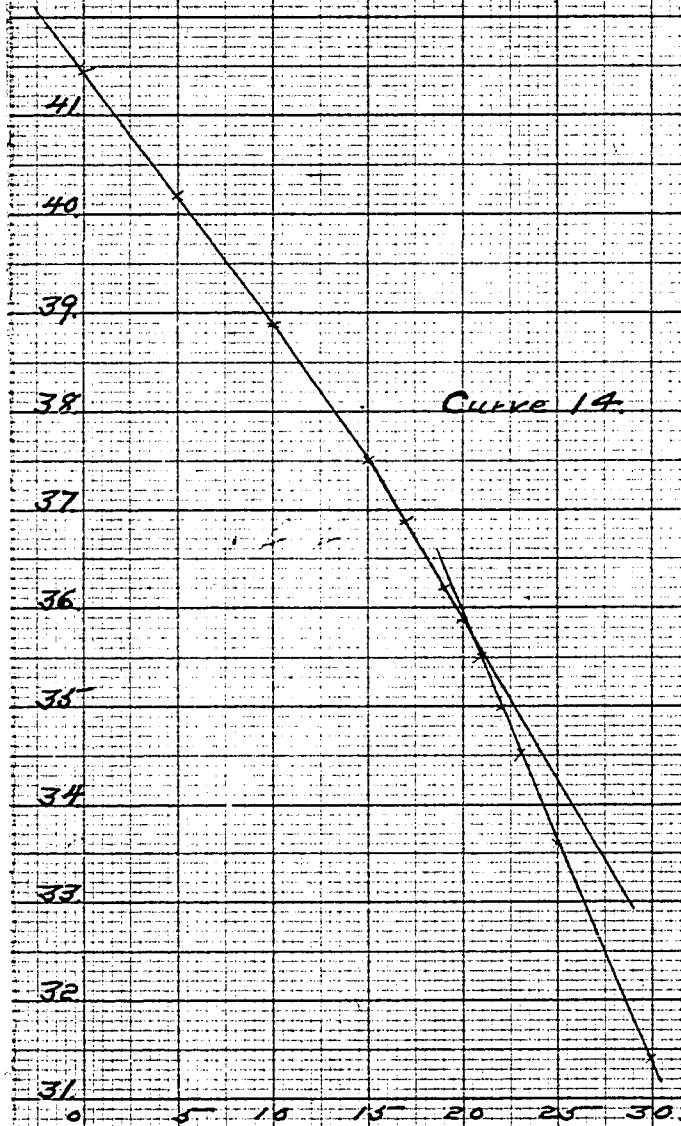

Curve 14. Fig. 9. (page 31).

In this reaction double the quantity of the sulphate was taken to try the effect of concentration on the curve.

cc.	B.R.	cc.	B.R.
0.	41.42.	20.	35.86.
5.	40.20.	21.	35.51.
10.	38.89.	22.	34.98.
15.	37.50.	23.	34.50.
17.	36.89.	25.	33.61.
19.	36.20.	30.	31.40.

Fig. 9.

Curve 14.

The calculated end point is at 20 cc.

The observed break is at 20.2 cc.

The increased concentration seems to bring the

calculated end point and the break closer together.

Still, there is sufficient divergence to prevent

the use of the curve in the determination of copper.

Dutoit (14)* gives as a rule for obtaining the

best results with precipitation curves, that the

precipitant should be considerably more concen-

trated than the solution to which it is added.

He also works with concentrations in the neighbor-

hood of 10 times the dilution of the ones under

consideration.

The effect of doubling the concentration of

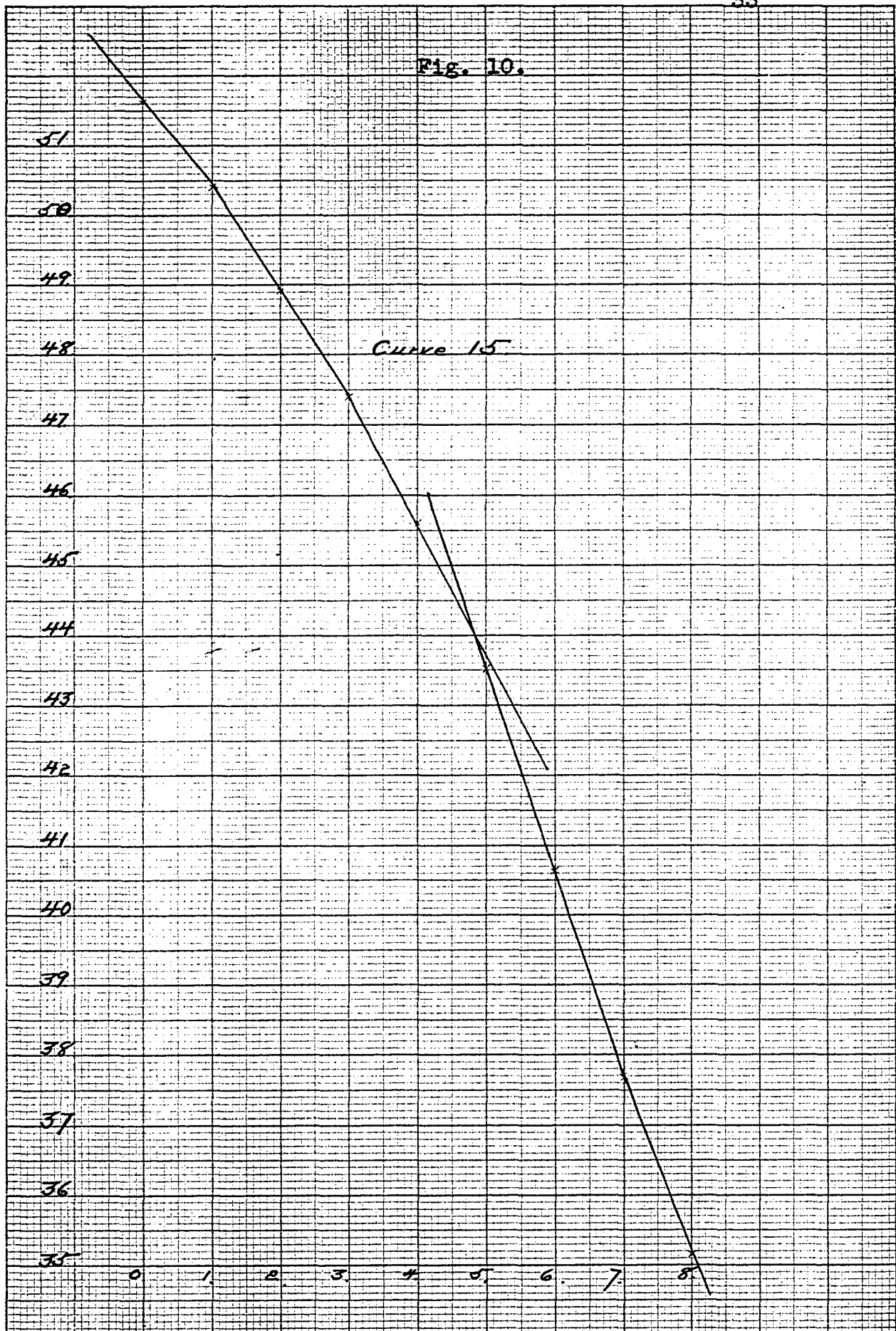the precipitant is noted in curve 15.

Curve 15. Fig. 10. (page 33).

5 cc of the copper sulphate solution were

titrated with N/5 sodium carbonate.

cc.	B.R.	cc.	B.R.
0.	51.63.	5.	43.50.
1.	50.40.	6.	40.65.
2.	48.92.	7.	37.70.
3.	47.40.	8.	35.15.
4.	45.60.		

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* See Bibliography.

Fig. 10.

Curve 15

The calculated end point is at 5 cc.

The observed break occurs at 4.85.

In the foregoing reaction, like the other carbonate precipitations studied, the conductivity readings reached constant values only after repeated stirring. In this curve the two branches show very nearly the same slope. This, of course, prevents an accurate plot for the point of intersection. The irregularities in the readings are probably caused by the relatively great concentration in the cell.
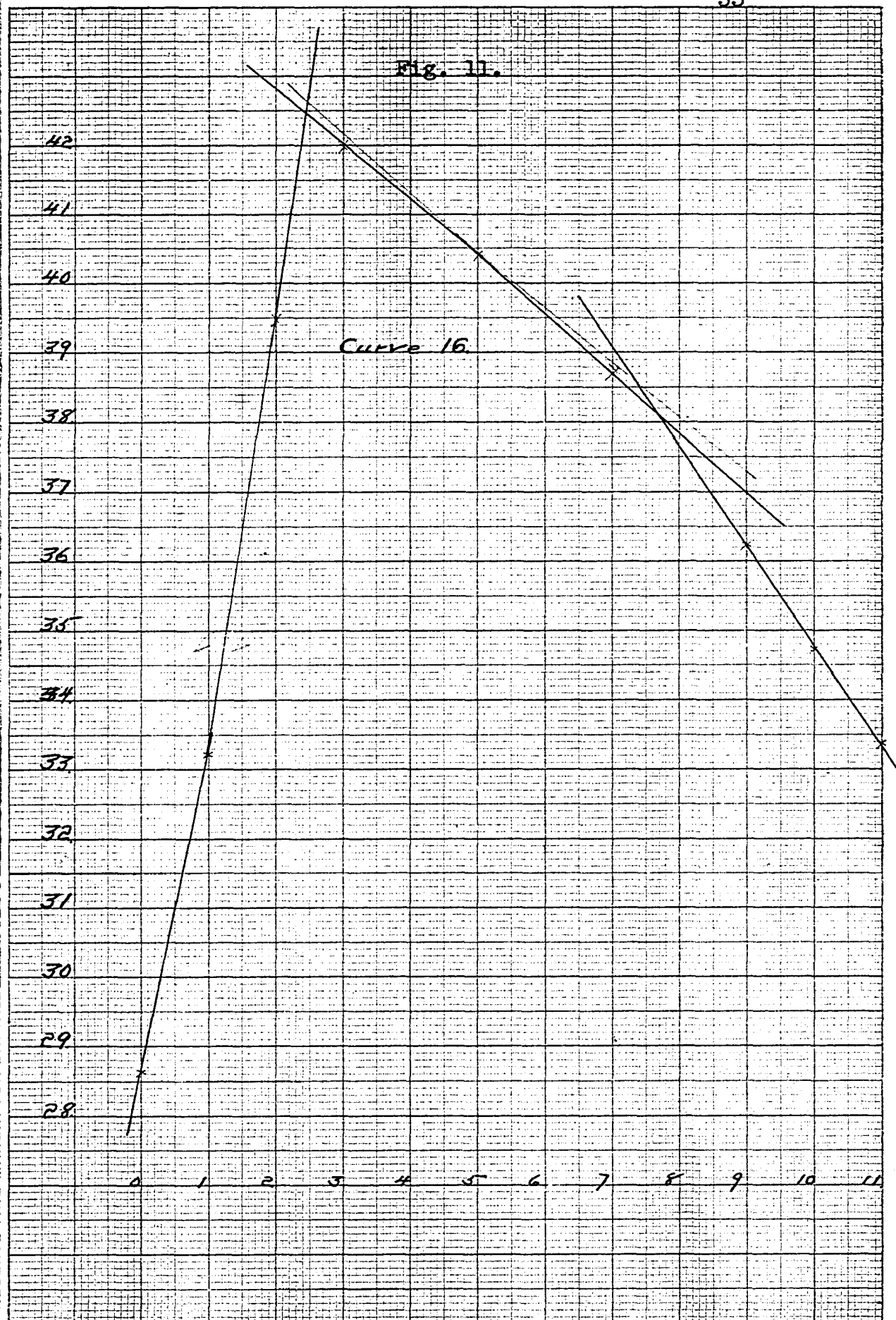

Curve 16. Fig. 11. (page 35).

This curve follows the titration of a solution containing 5 cc of copper sulphate and 5 cc of N/10 HCl.

cc.	B.R.	cc.	B.R.
0.	28.62.	7.	38.70.
1.	33.21.	8.	37.60.
2.	39.50.	9.	36.22.
3.	42.00.	10.	34.72.
5.	40.40.	11.	33.39.

The two calculated end points come at 2.5 and 7.5. The observed breaks are at 2.44 and 7.57.

Fig. 11.

Curve 16.

Briefly returning to the curves 11 to 16, it will be observed that, although the breaks tend to follow closely the calculated reaction end points, there is a sufficient deviation to exclude the possibility of their application to a determination of copper. Furthermore, the direction of the error, or difference, varies and consequently does away with any possible determination of a factor which would connect the break with the end point.

Another difficulty is encountered with the similarity in the slopes of the two branches of the curve. This of course prevents accurate plotting.

The reaction is studied somewhat further later on in the experiments with the modified cell, shown in Fig. 1.

The Precipitation of Copper as Hydroxide.

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A solution of sodium hydroxide was prepared from metallic sodium and purified water to insure freedom from carbon dioxide.

This was carefully standardized against N/10 hydrochloric acid (using alizarine as indicator).

The factor was 1.0785 x N/10.

Curve 17. Fig. 12. (page 38).

This follows 5 cc of the N/5 copper sulphate solution, titrated with the above hydroxide solution.

cc.	B.R.	cc.	B.R.
0.	55.19.	10.	41.22.
2.	55.30.	11.	38.09.
4.	55.30.	12.	35.50.
6.	55.20.	13.	33.45.
8.	49.89.	15.	29.90.
9.	45.09.		

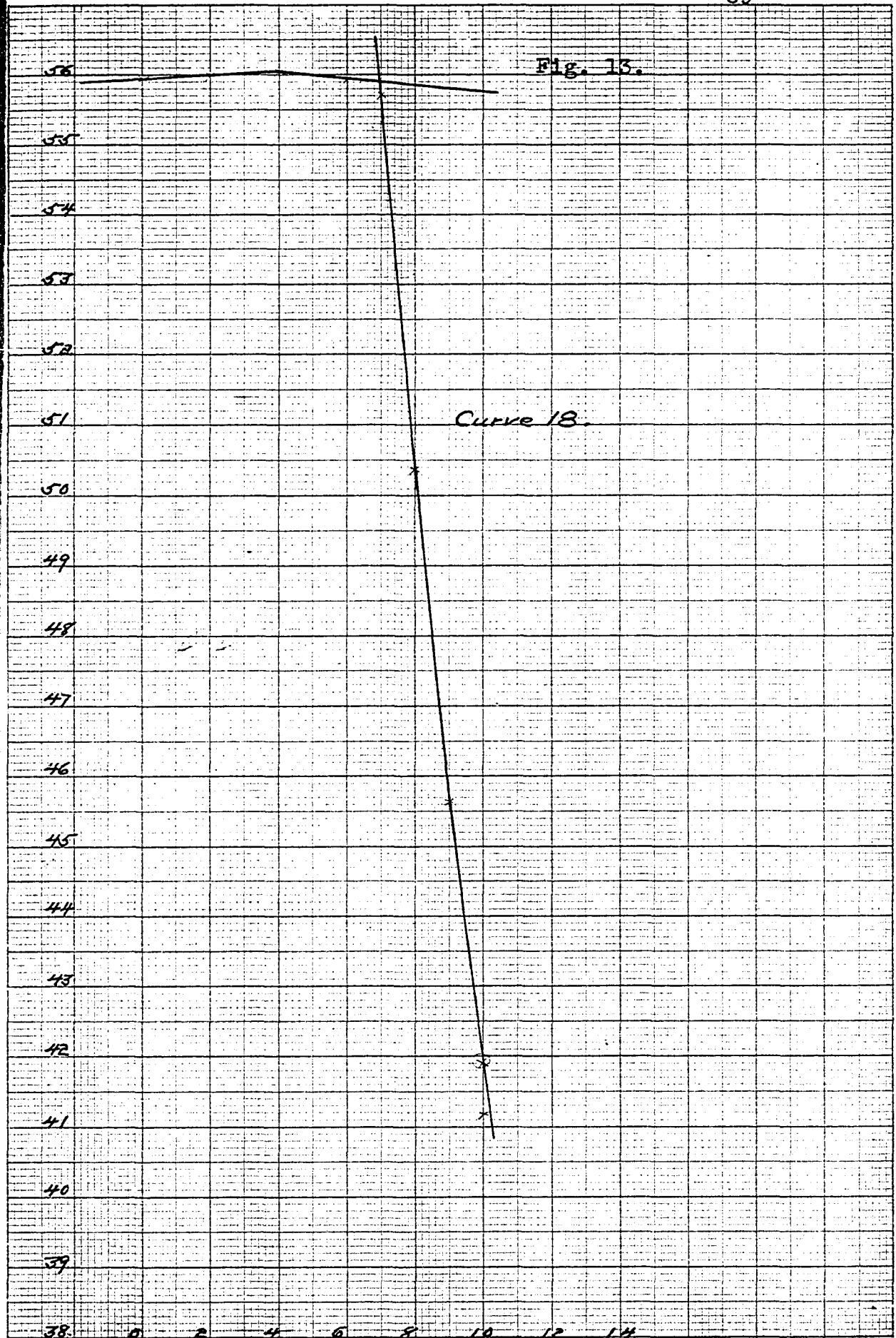
Curve 18. Fig.13. (page 39).

This is a check on 17. This curve is drawn on a separate page on account of the intersection of it with 17.

Fig. 12.

Curve 17.

Fig. 13.
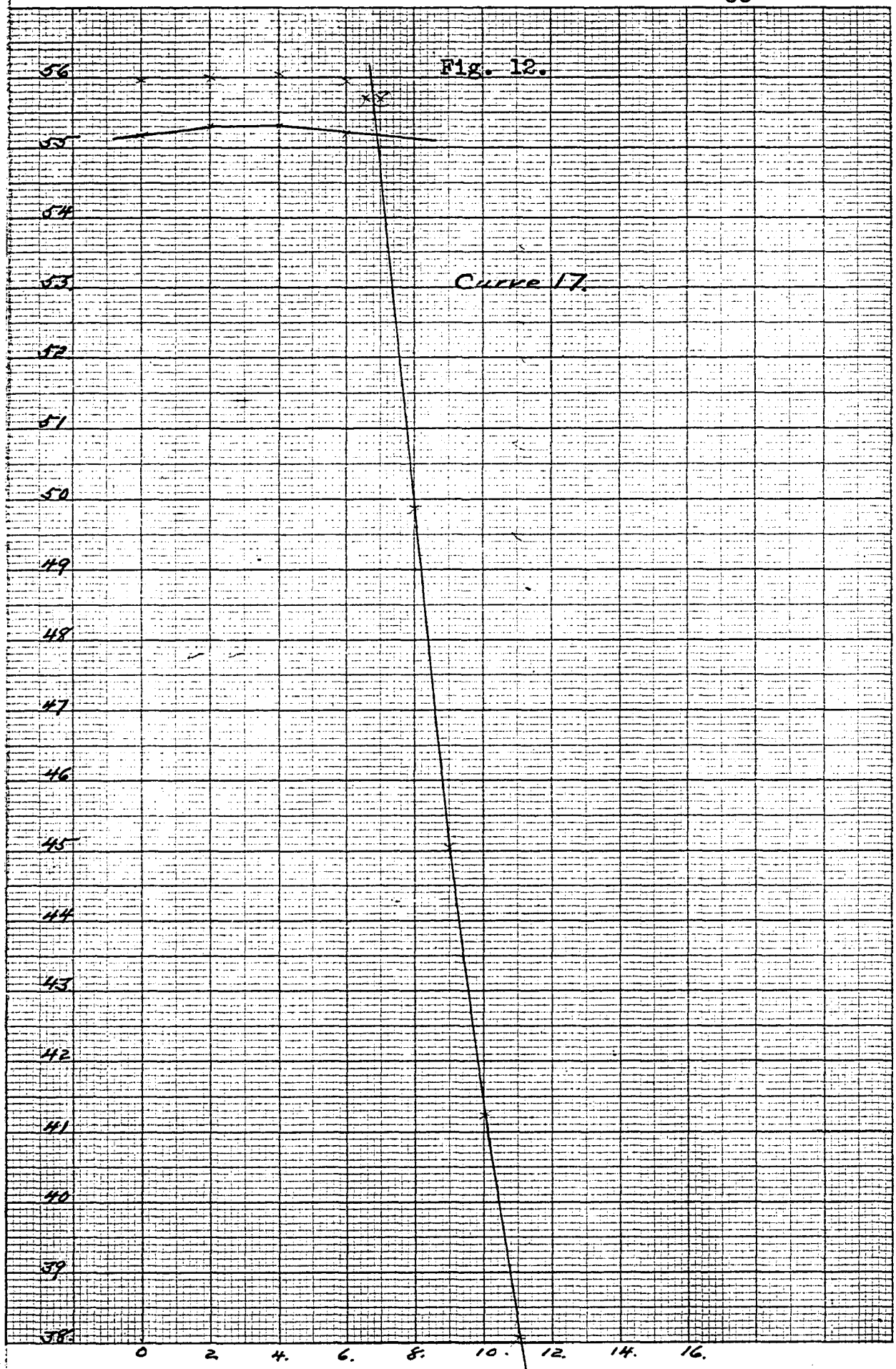
Curve 18.

(Curve 18).

cc.	B.R.	cc.	B.R.
0.	55.96.	8.	50.38.
2.	56.00.	9.	45.65.
4.	56.04.	10.	41.90.
6.	55.96.	12.	36.10.
8.	50.38.	14.	31.92.

The calculated end point is at 9.27 cc.
The observed break is at 6.9 cc.

The above curves check quite closely but the break does not agree with the end point in the precipitation. Dutoit (2)[*] has found this to be true for hydroxides in general.

A secondary reaction in which a basic salt is formed would give a deviation in the direction observed in the two curves.
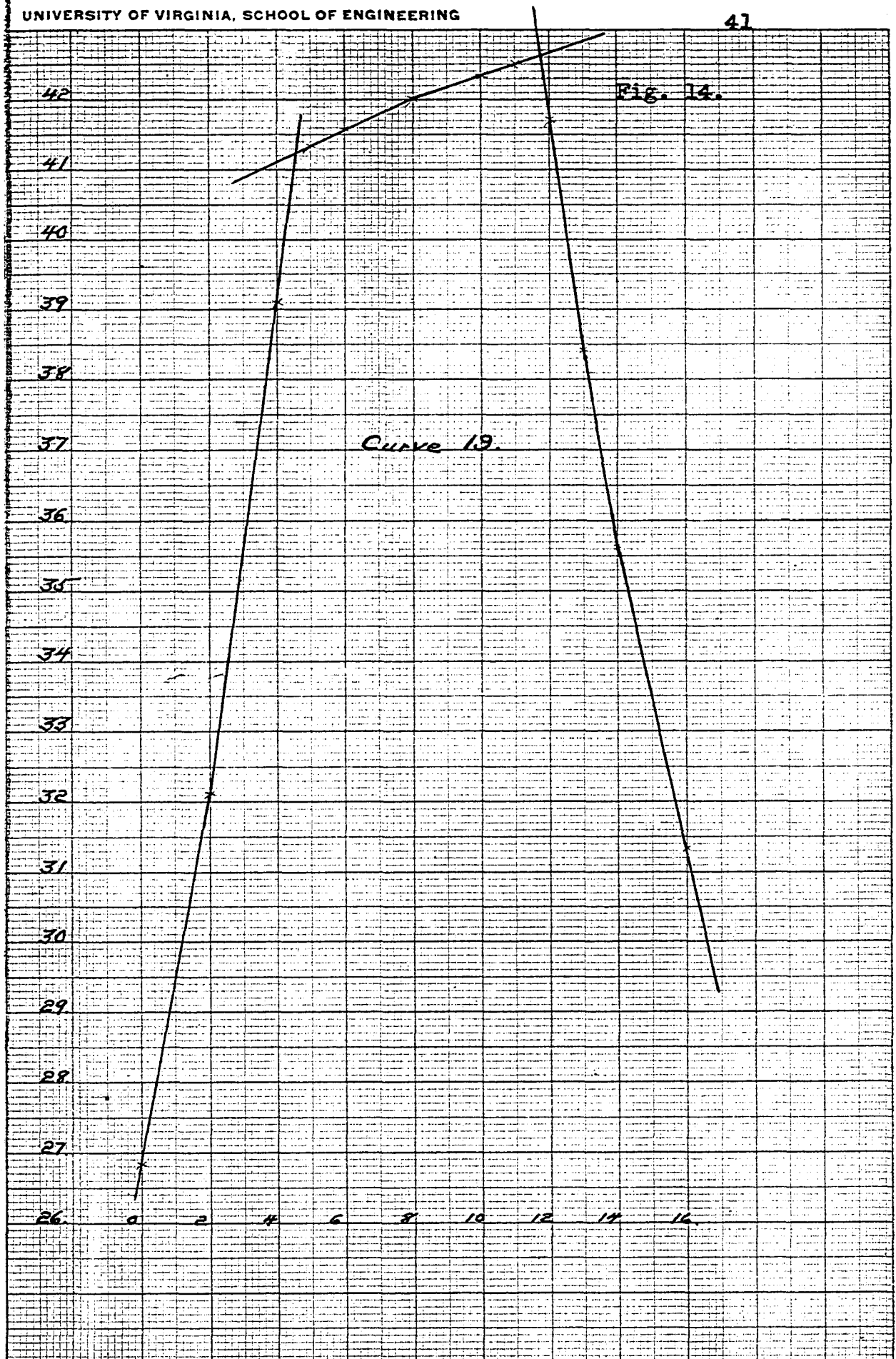

Curve 19. Fig. 14. (page 41).

An acidified solution of copper sulphate is here titrated with sodium hydroxide. 5 cc of the sulphate were taken and 5 cc of N/10 HCl added.

cc.	B.R.	cc.	B.R.
0.	26.82.	10.	42.32.
2.	32.12.	11.	42.50.
4.	39.10.	12.	41.70.
5.	41.34.	13.	38.41.
6.	41.59.	14.	35.64.
8.	42.00.	16.	31.32.

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[*] See Bibliography.

Fig. 14.

Curve 19.

42

41

40

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27

26

0 2 4 6 8 10 12 14 16

(curve 19)

The two calculated breaks in this curve should appear at 4.13 and at 13.40.

The observed breaks are at 4.6 and 11.8.

The fact that the break corresponding to the neutralization of the acid present comes somewhat beyond the calculated neutral point, might be expected as a result of the partial hydrolysis of the copper sulphate. On the other hand the second break should come at 11.03, which is obtained by adding the observed end point obtained in curves 17 and 18, to the theoretical neutral point for the acid added. Since observation does not confirm this, it is apparently evident that these curves can not be duplicated to agree with each other.

It is therefore probably necessary to abandon this reaction for the purpose desired.

The Precipitation of Copper as Cuprous Iodide.

------------------o----------------

A solution of potassium iodide was made up as follows: 4.1500. gms of the iodide were weighed out and brought to 500 cc of solution.

Curve 20.   Fig. 15.   (page 44).

This curve follows 5 cc of the copper solution titrated with the potassium iodide.

cc.	B.R.	cc.	B.R.
0.	54.80.	10.	41.12.
2.	51.11.	11.	40.34.
4.	48.00.	12.	39.55.
6.	45.40.	14.	38.30.
8.	43.11.	16.	37.10.
9.	42.00.		

The calculated end point is at 10 cc.

A break in the curve occurs at 9.3 cc.

------------ ----------------------

This reaction proceeds very slowly, from 10 to 15 minutes being necessary for the reaction to come to a point of equilibrium after each addition of iodide.   The slopes of the two branches of the curve differed so slightly that there was some doubt as to whether the plotted break was actually an intersection or simply resulted from a gradual increase in the curvature of the line.

Fig. 15.

Curve 20.
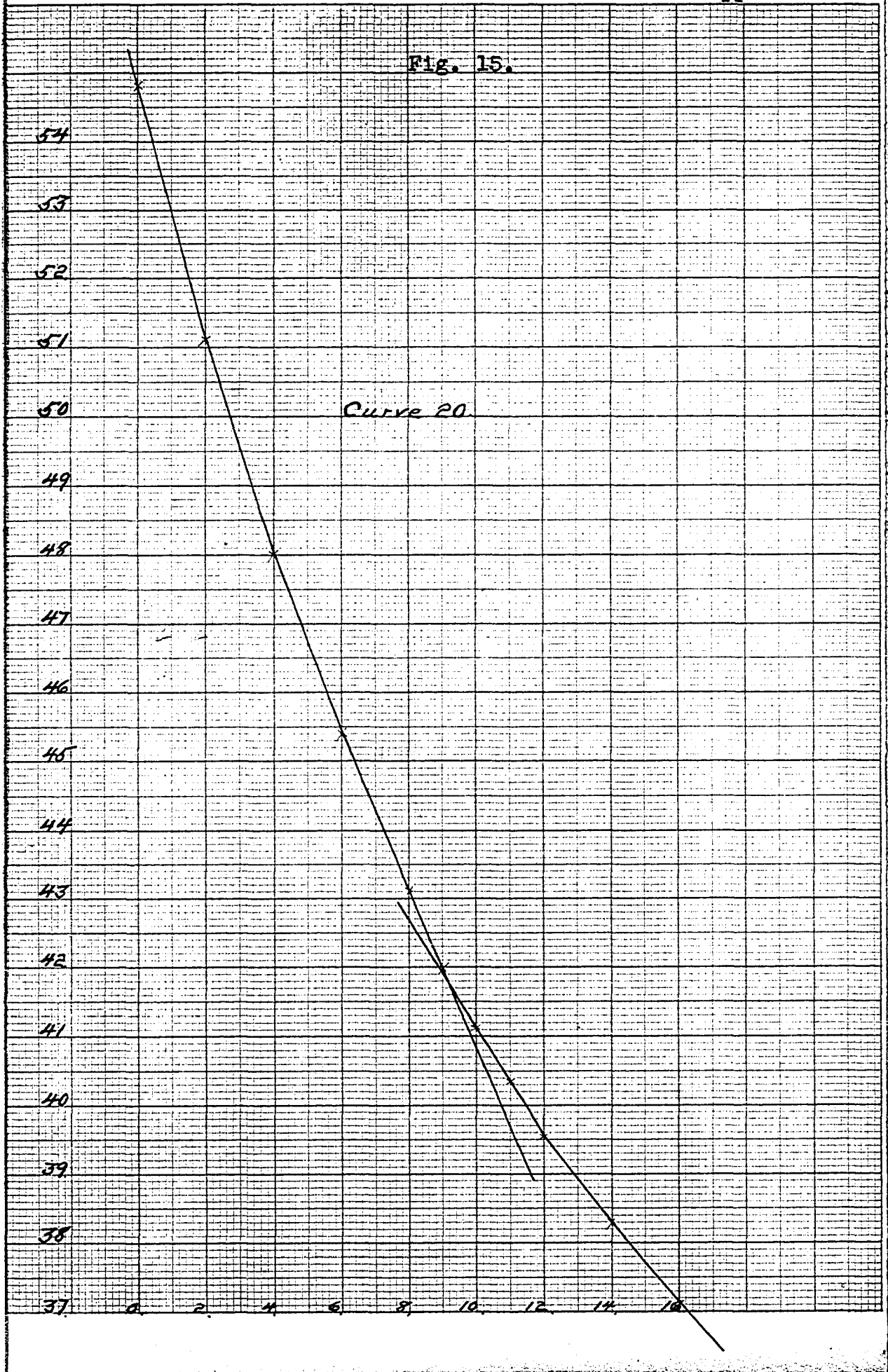
Qualitative examination of the reaction indicated that it could be hastened only by adding a considerable excess of the iodide or by raising the temperature to the neighborhood of the boiling point.

The necessity of such conditions render conductivity measurements of the reaction impossible.

The Precipitation of Copper as Cuprous Sulphocyanide.

------------------o------------------

A solution of ammonium sulphocyanide was made up and carefully standardized. The strength of the solution was 5.208 x N/10.

Curve 21. Fig. 16. (page 47).

5 cc of copper sulphate were saturated with sulphur dioxide and titrated with the sulphocyanide.

cc.	B.R.	cc.	B.R.
0.	24.13.	3.	23.70.
1.	23.95.	4.	23.80.
2.	23.75.	5.	23.80.

This curve shows a break at 5.2 cc. The calculated break should come at 1.9. cc.
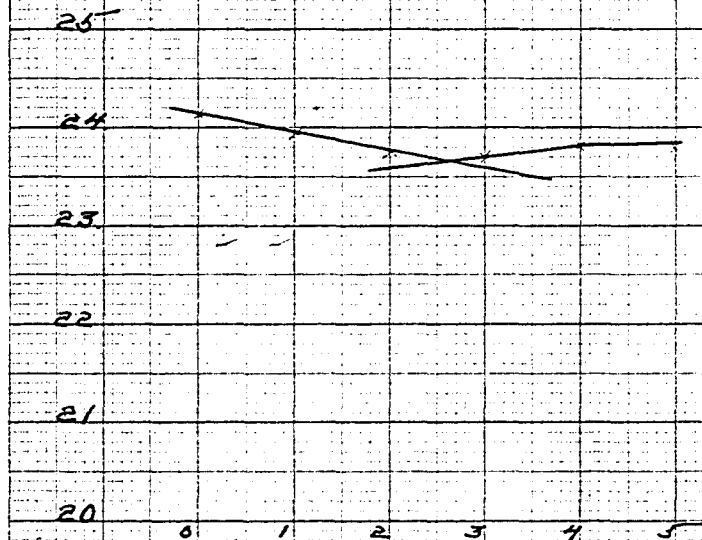

In the above reaction it was really impossible to get readings for the conductivity. The above represent only an approximately constant result obtained after repeated stirring.

At this point the reactions involved in the well known Volhard volumetric method for copper were suggested as a possible solution of the difficulty.

Fig. 16.

Curve 21

The method of procedure adopted was to saturate the copper solution with sulphur dioxide, add an excess of the ammonium sulphocyanide and titrate with standard silver nitrate solution.

The great inconstancy in the readings taken in 21 seemed to be partly caused by the gradual escape of the sulphur dioxide. The apparatus was according modified to admit of a constant addition of the gas, thus keeping the solution saturated.

Curve 22. Fig. 17. (page 49).

This curve follows the reaction in which 10 cc of copper sulphate were reduced, 3 cc of ammonium sulphocyanide added, and the solution titrated with N/10 silver nitrate.
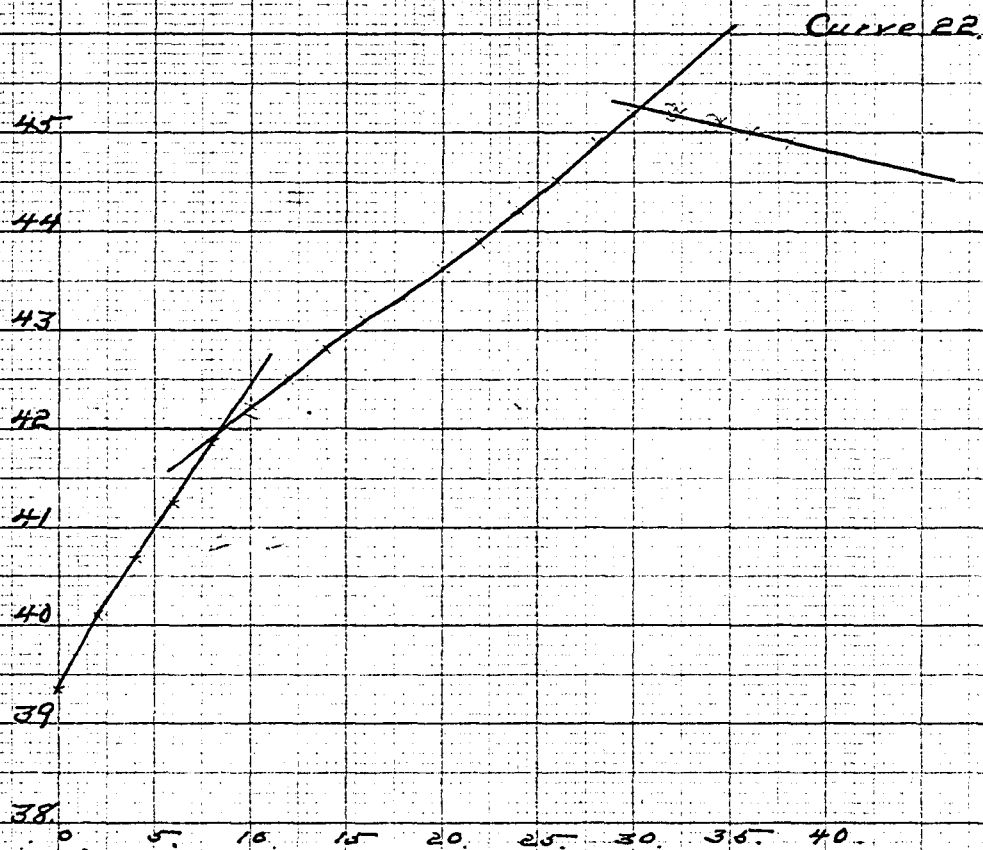
cc.	B.R.	cc.	B.R.
0.	39.35.	20.	43.61.
2.	40.10.	22.	43.90.
4.	40.66.	24.	44.22.
6.	41.22.	26.	44.50.
8.	41.89.	28.	44.90.
10.	42.21.	30.	45.20.
12.	42.50.	32.	45.20.
14.	42.80.	34.	45.10.
16.	43.10.	36.	45.00.
18.	43.33.	38.	44.90.

The calculated end point for the precipitation of silver sulphocyanide is at 5.624.

A break in the curve comes at 8.5. cc.

Fig. 17.

Curve 22.

In this curve the conductivity measurements were obtained with almost as much difficulty as in the preceding one. After stirring duplicate readings were gotten in only a few cases. The cause for this seemed to be the tendency for the spongy platinum, with which the electrodes had been plated, to absorb the sulphur dioxide.

There was a secondary reaction noticeable between the silver nitrate and the sulphur dioxide. The second break in the curve probably indicates the end point in this.

This reaction was next studied with the solution free from excess sulphur dioxide. The technique described by Edgar (15)[*] was used.
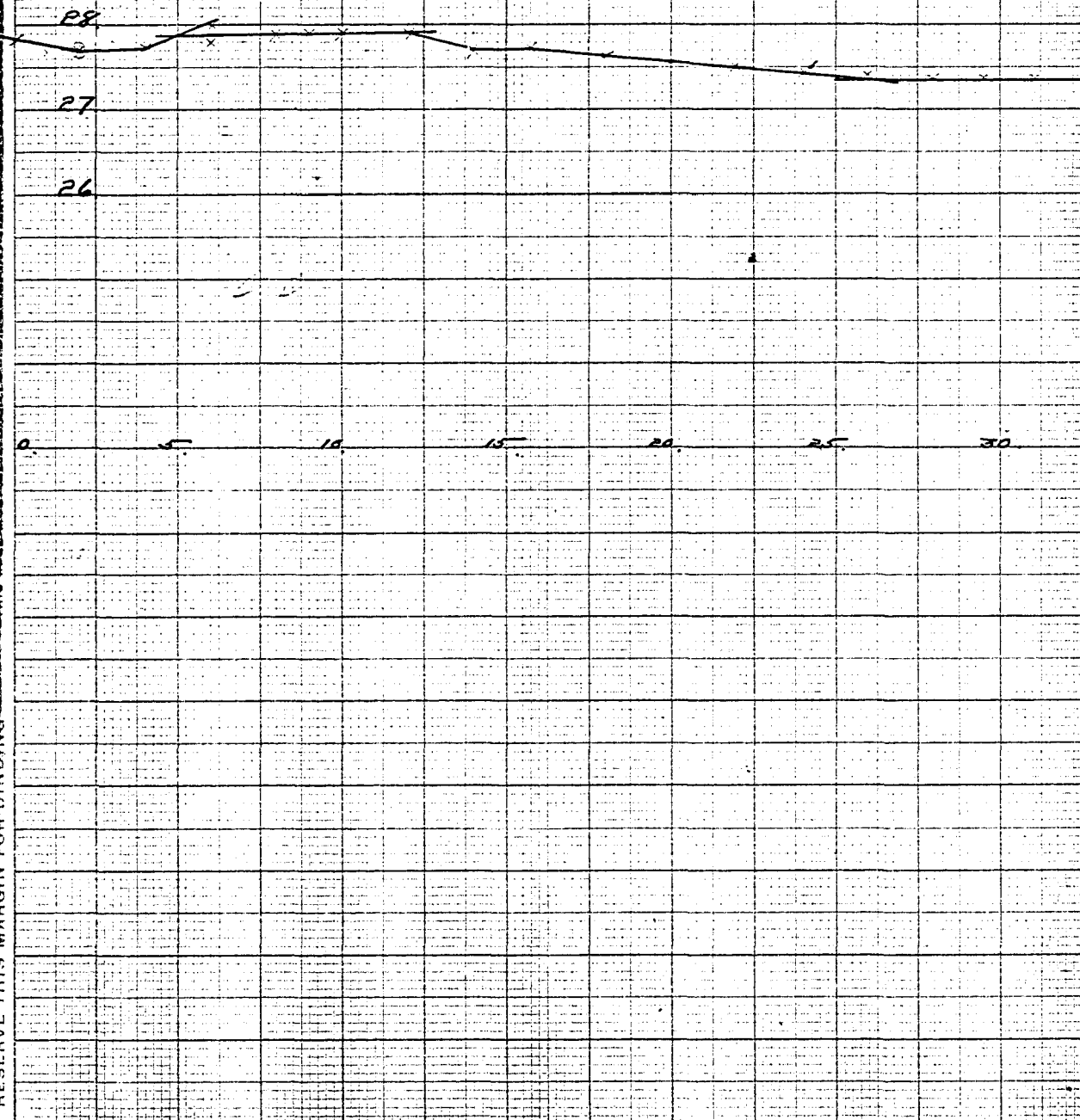

Curve 23. Fig. 18. (page 51).

10 cc of copper sulphate solution were saturated with sulphur dioxide, 3 cc of ammonium sulphocyanide added, and then boiled for about 10 minutes, a current of carbon dioxide being passed through it continuously. The excess sulphocyanide remaining in the solution was titrated with silver nitrate.

[*] See Bibliography.

Fig. 18.

Curve 23.

·(curve 23).

cc.	B.R.	cc.	B.R.
0.	27.82.	18.	27.65.
2.	27.70.	20.	27.59.
4.	27.75.	22.	27.50.
6.	28.00.	24.	27.45.
8.	27.90.	26.	27.45.
10.	27.90.	28.	27.40.
12.	27.90.	30.	27.39.
14.	27.70.	32.	27.39.
16.	27.75.	34.	27.39.

The calculated end point is at 5.62.
The observed break is at 5 cc.

The branches of this curve show slopes so nearly identical that it is doubtful whether the points indicated are the true intersections. Since the other curves representing the same reaction are totally different in form, it is probable that in this case the sulphur dioxide was not completely driven off.

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At the second break in the curve a color change began to be noticeable in the cell. This seemed to indicate that a second reaction involving the reduction of the excess silver nitrate, was taking place. After this point the readings became less regular.

Curve 24. Fig. 19. (page 53).

This is a repetition of the above reaction in which 5 cc of the copper solution and 2 cc of sulphocyanide were used.

Fig. 19.
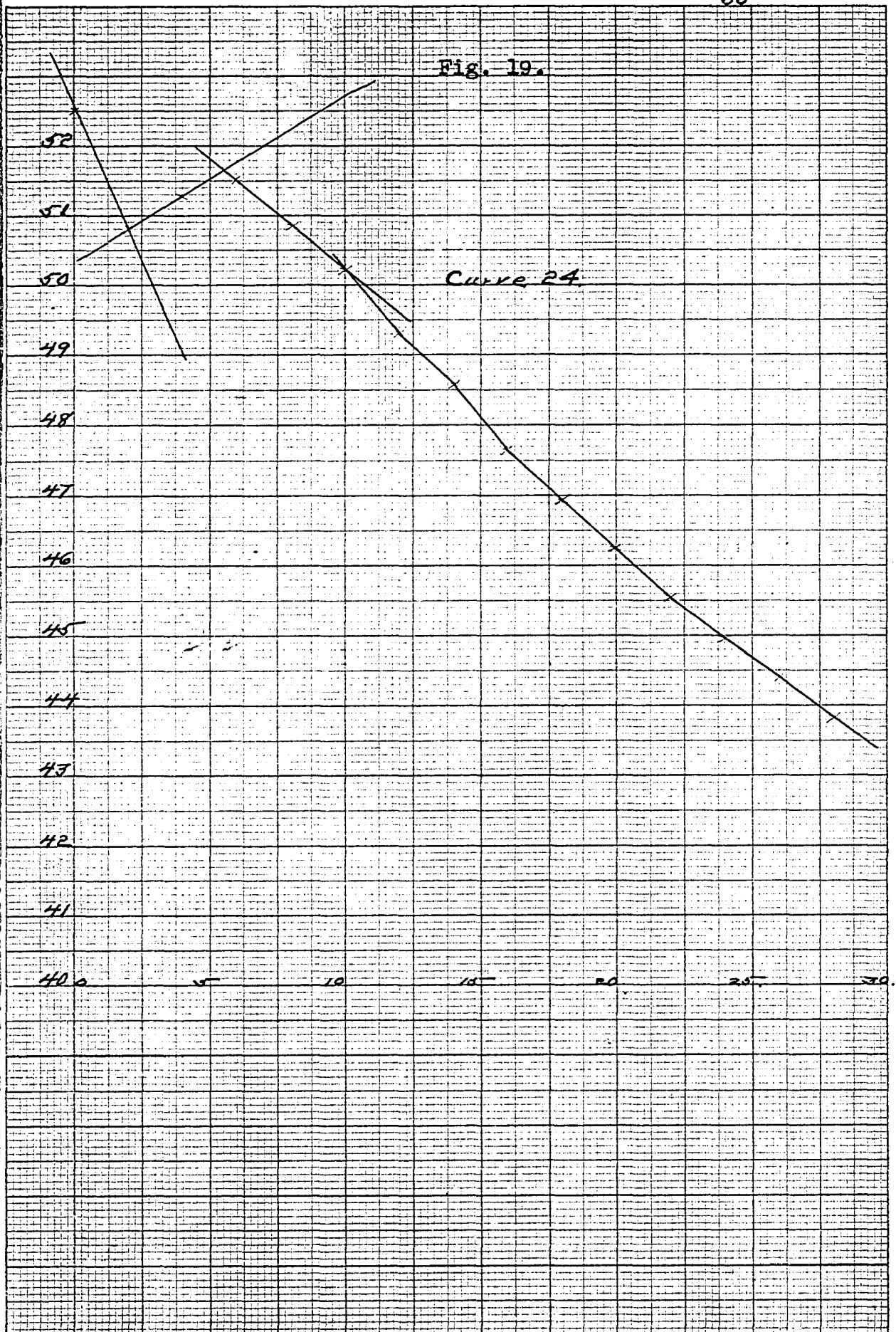
Curve 24

(Curve 24).

cc.	B.R.	cc.	B.R.
0.	52.50.	16.	47.67.
2.	50.80.	18.	46.92.
4.	51.29.	20.	46.25.
6.	51.50.	22.	45.55.
8.	50.85.	24.	44.96.
10.	50.21.	26.	44.40.
12.	49.30.	28.	43.82.
14.	48.59.		

The calculated end point is at 5.41.cc.

A break in the curve occurs at 5.5.

The color began to change at the reading corresponding to 8 cc.

If the second break is considered the calculated and observed points fall close together. The third break is probably indicative of the beginning of the secondary reaction. The first break could not be explained.

Curve 25. Fig. 20. (page 55).

This was run as a check on 24.

cc.	B.R.	cc.	B.R.
0.	38.00.	10.	38.72.
2.	38.50.	12.	38.20.
4.	39.00.	14.	37.71.
6.	39.29.	16.	37.28.
8.	39.00.	18.	36.90.

The calculated point for the final precipitation is at 5.41. The observed point is at 5.4.

Fig. 21.

Curve 25.

In the foregoing at the addition of 8 cc a slight color change became evident. At 10 and 12 cc the conductivity was slow to assume a constant value, falling off gradually before reaching a point of eqilibrium.

It will be noticed that the first break shown in curve 24 does not occur in the check. There is a break in both at 10 cc.


It is quite evident from the curves just shown that the addition of a certain excess of silver nitrate starts a secondary reaction. In order, therefore, that the desired reaction may be measured it will be necessary to obtain two points between the final precipitation of the silver sulphocyanide and the starting point of the secondary change.

The following curves were plotted to determine with what degree of accuracy varying quantities of the copper sulphate could be measured.

It is understood, of course, in every case the reduction was effected by means of sulphur dioxide and the solution freed from excess as referred to above.

Fig. 22.

Curve 26.
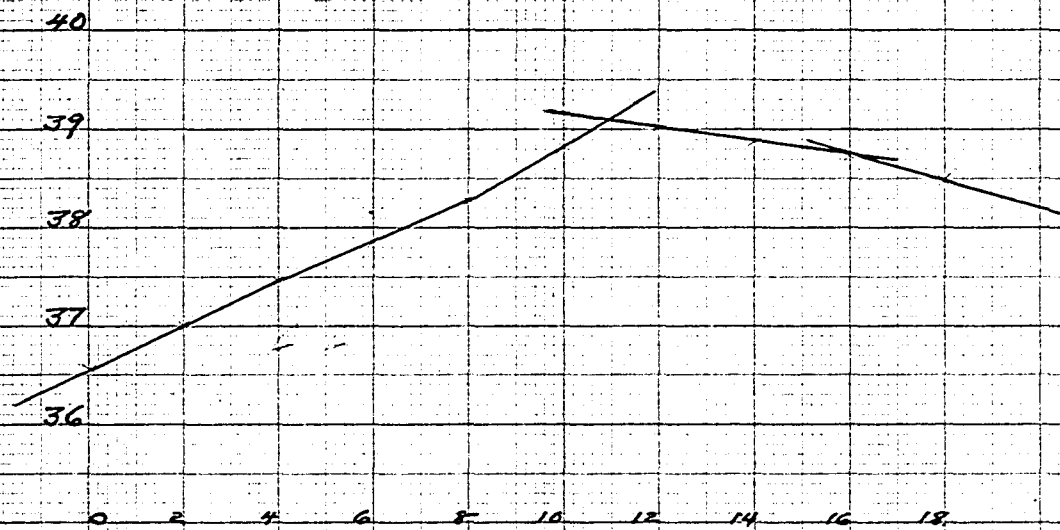
Curve 26.   Fig. 22.   (page 57).

5 cc of copper sulphate and 3 cc of ammonium
sulphocyanide were used.   Titration with silver
nitrate.

cc.	B.R.	cc.	B.R.
0.	36.56.	10.	38.81.
2.	37.00.	12.	39.01.
4.	37.45.	14.	38.89.
6.	37.87.	16.	38.75.
8.	38.29.	18.	38.50.

Calculated end point at 10.62.

Observed end point at 10.9.

Curve 27.   Fig. 23   (page 59).

This represents 6 cc of the copper solution
and 2 cc of the sulphocyanide.

cc.	B.R.	cc.	B.R.
0.	38.70.	6.	39.40.
2.	39.10.	8.	39.08.
4.	39.60.	10.	38.90.

Calculated end point 4.41.

Observed   "   "   4.44.

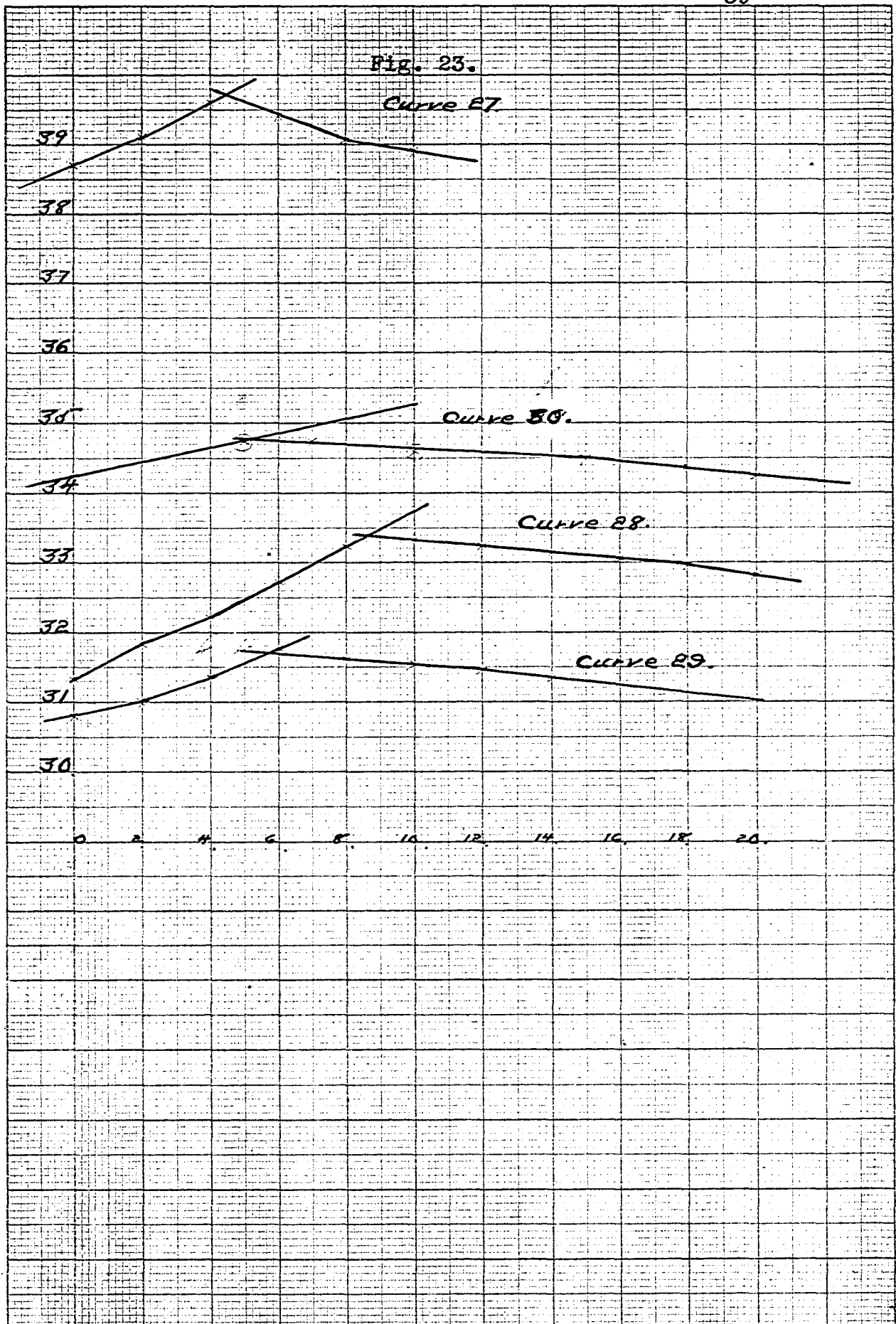---

Curve 28. Fig. 23. (page 59).

Here 7 cc of copper sulphate solution and
3 cc of ammonium sulphocyanide were used.

Fig. 23.

(curve 28).

cc.	B.R.	cc.	B.R.
0.	31.32.	12.	33.25.
2.	31.81.	14.	33.19.
4.	32.21.	16.	33.05.
6.	32.72.	18.	32.99.
8.	33.22.	20.	32.82.
10.	33.31.		

The calculated end point is 8.62.

The observed " " 8.62.

Curve 29. Fig. 23. (page 59).

10 cc of copper sulphate solution and 3 cc of the sulphocyanide.

cc.	B.R.	cc.	B.R.
0.	30.80.	8.	31.62.
2.	31.00.	10.	31.53.
4.	31.37.	12.	31.48.
6.	31.77.	14.	31.35.

Calculated end point at 5.62.

Observed " " 5.70.

The color began to change at 8 cc. After this the readings reached constant values more slowly.

Curve 30. Fig. 23. (page 59).

20 cc of copper sulphate and 5 cc of ammonium sulphocyanide were used.

(curve 30).   cc.   B.R.   cc.   B.R.
                 0.   34.24.   15.   34.50.
                 5.   34.75.   20.   34.26.
                10.   34.61.

Calculated end point 6.04.

Observed   "   "   5.8

The color of the precipitate began to change at the addition of 5 cc.

The agreement between the calculated and observed results in the reactions represented by curves 24 to 30 is quite close.   However, as the concentration in the cell is increased, the end point in the precipitation reaction and the beginning of the secondary reaction occur closer and closer together.   Since some distance between these is necessary for the graphical estimation of the desired end point, it might be expected that in rather high concentrations, as in curve 30, the calculated and observed results should show some difference.

Dutoit (14)[*] has stated that the proper concentration for obtaining the most satisfactory results with precipitation curves is from .05 to

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[*]   See Bibliography.

.001 Normal.

Van Suchtelen and Itano (11),[*] apparently with-
out reference to Dutoit's work, found .001 Normal
to be the best concentration for the solution
in the cell and .01 normal, for the concentration
of the precipitant.

Greater dilutions will be discussed later in
this paper.

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[*]See Bibliography

The Precipitation of Copper as Sulphide.

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The first solution of sodium sulphide employed
was made up as follows:· 200 cc of sodium hydroxide
(free from carbon dioxide), 1.0785 X N/10, was
saturated with hydrogen sulphide and an equal volume
of the same hydroxide added.

It will be noticed that this solution was
prepared under conditions which should give rise
to the formation of the hydrosulphide rather
than the normal salt.   The curves obtained from
the use of this solution were interesting on account
of the fact that they showed how qualitative explan-
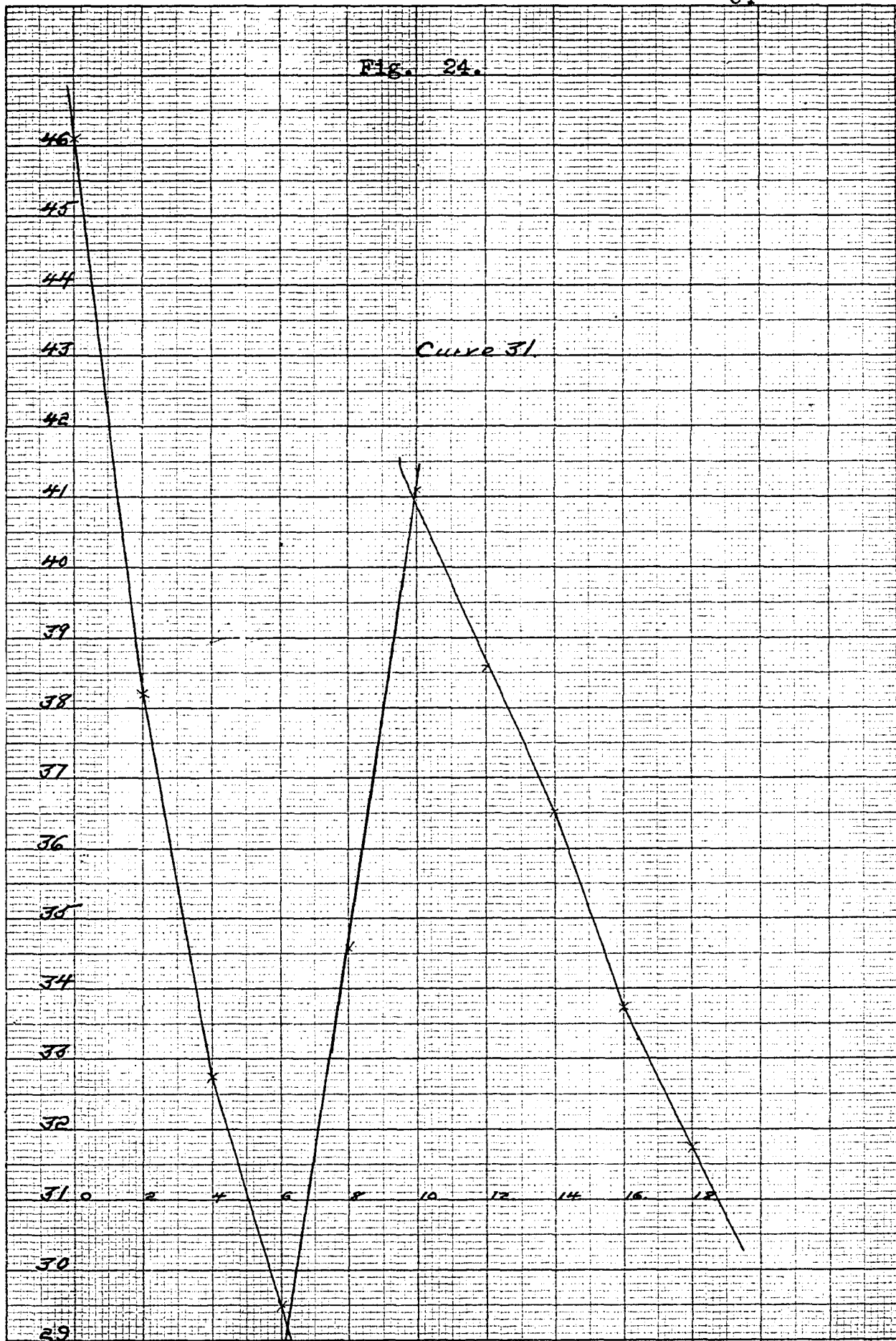ations of reactions may be arrived at through con-
ductivity measurements.

Curve 31. Fig. 24. (page 64).

This represents the titration of 5 cc of the
copper solution with the above sulphide solution.

cc.	B.R.	cc.	B.R.
0.	46.10.	10.	41.10.
2.	38.20.	12.	38.59.
4.	32.75.	14.	36.01.
6.	29.50.	16.	33.75.
8.	34.60.	18.	31.78.

Fig. 24.

Curve 31

Curve 32. Fig. 25.   (page 66).

This was run as a check on 31.

cc.	B.R.	cc.	B.R.
0.	50.20.	10.	43.38.
2.	40.90.	12.	39.90.
4.	34.71.	14.	37.11.
6.	31.09.	16.	34.80.
8.	36.80.	18.	32.80.

Curve 33. Fig. 26. (page 67).

Here 10 cc of the copper sulphate solution were taken. Titration as above.

cc.	B.R.	cc.	B.R.
0.	38.38.	16.	26.59.
2.	33.32.	18.	29.40.
4.	29.50.	20.	31.60.
6.	26.65.	22.	30.18.
8.	24.41.	24.	28.95.
10.	22.69.	26.	27.85.
12.	21.75.	28.	26.90.
14.	24.04.		

The calculated end point in curves 31-32 is at 6.45.
The observed   "   "   "   "   "   "   "   " 6.2

The calculated end point in curve 33 is at 12.90.
The observed break in the curve is at 11.7.

The peculiar shape of the curves can be explained by a consideration of the method of
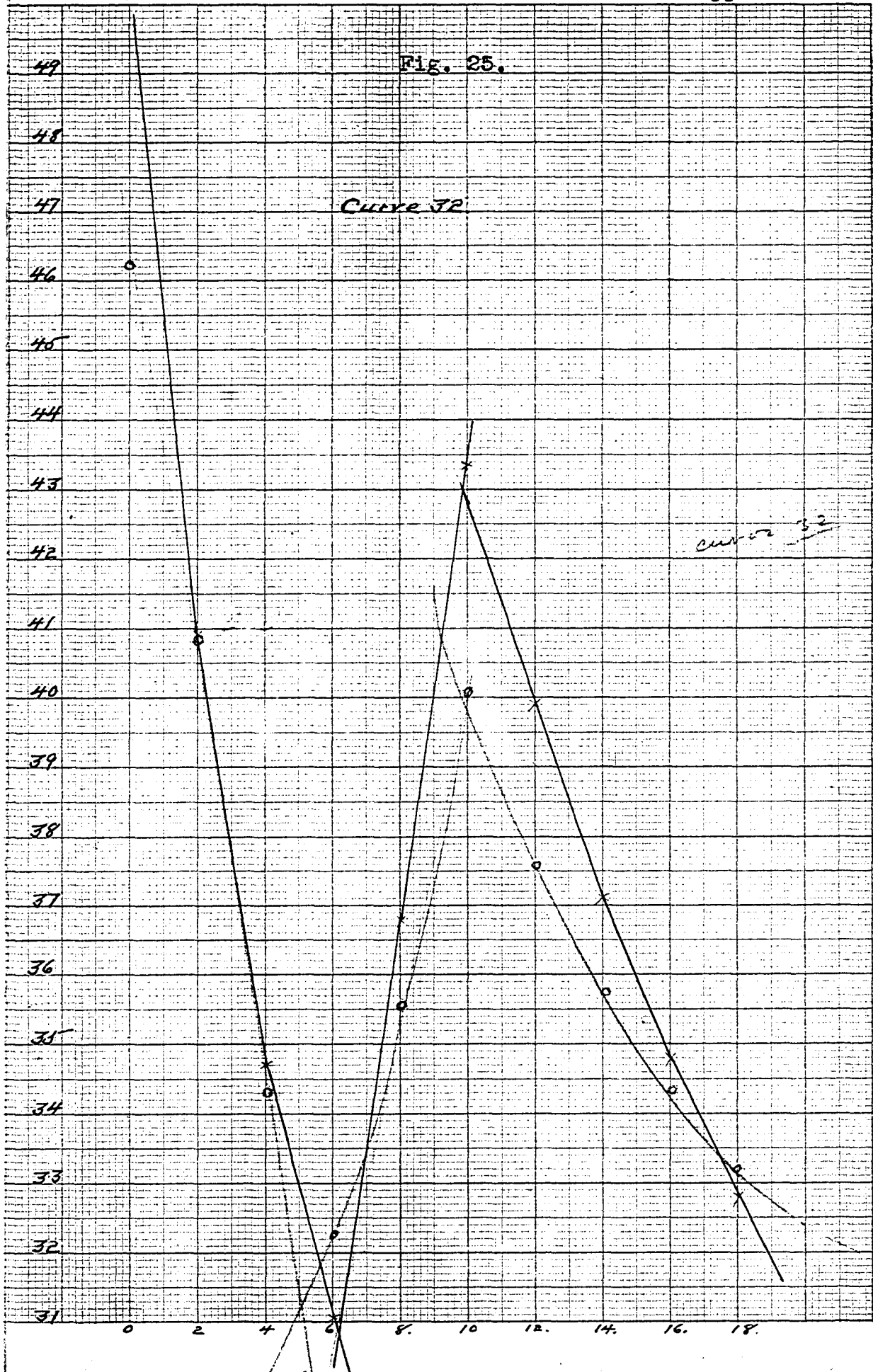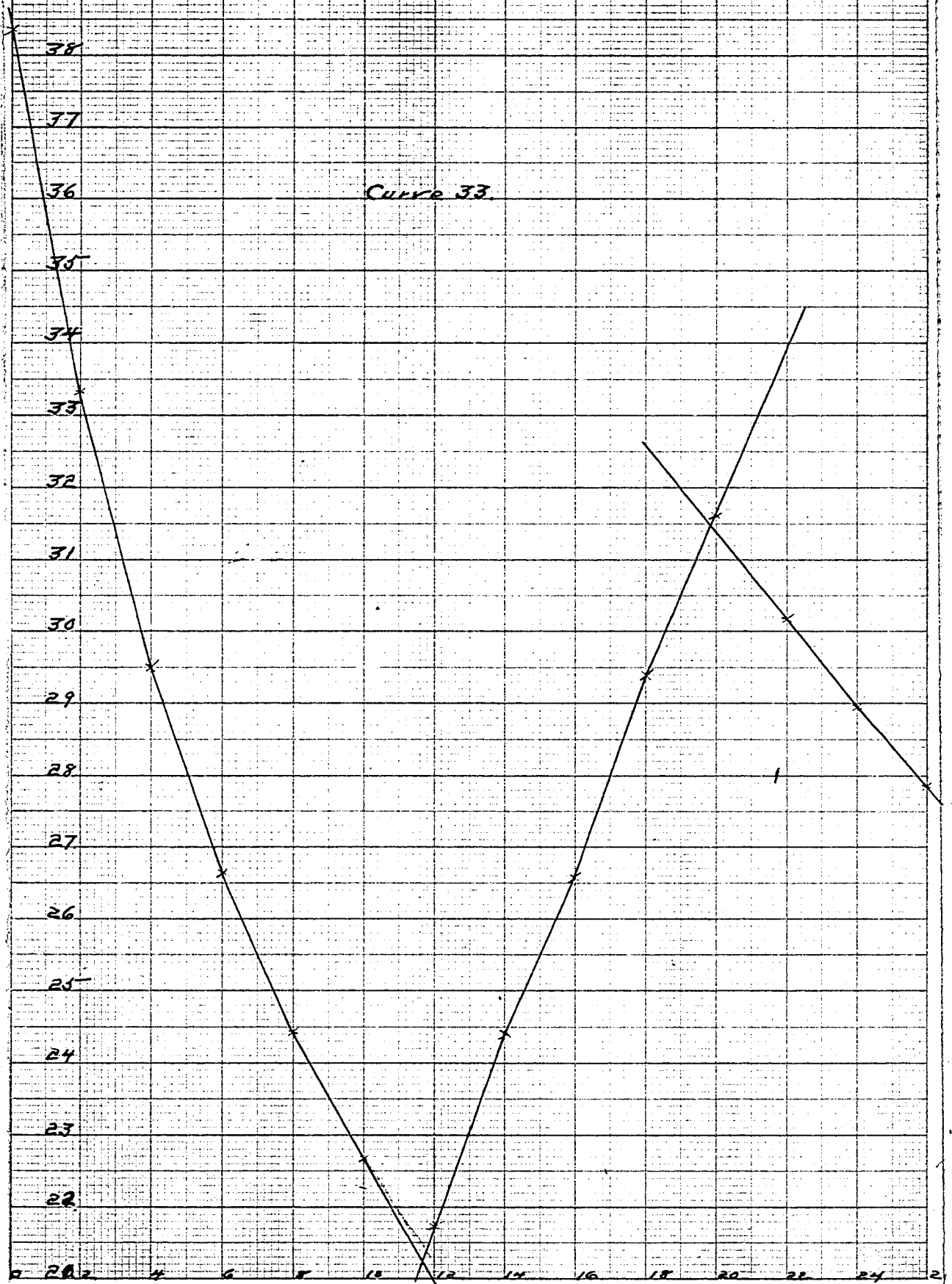
Fig. 25.

Curve 32

curve 32

Fig. 26.

Curve 33.

preparing the sodium sulphide solution. It will

be noticed that the concentration of the sodium

hydroxide was such as to give rise to the formation

of the hydrogen sulphide of sodium rather than the

normal. The first reaction taking place, therefore,

on mixing this solution with the copper sulphate,

would be that involving the precipitation of

the copper as sulphide and the attendant formation

of hydrogen ions in the solution. The high mobility

of the hydrogen ion explains the rapid increase

in the conductivity indicated by the deep slope

of the first line in the curve. When the last

of the copper has been precipitated additional

quantities of the sodium sulphide will diminish

the hydrogen ion content on account of the low

dissociation of hydrogen sulphide. This explains

the second branch of the curve. Finally, when

the continued addition of the sulphide solution

has brought the concentration of the hydrogen ions

to that constant corresponding to the dissociation

of hydrogen sulphide at the given temperature and

dilution, the conductivity ceases to diminish and

any further addition of the sulphide will simply

increase the ionic content of the solution and accordingly give rise to a gradual increase in conductivity.

The agreement of the breaks in these curves with each other is quite good. The reaction end point, however, is not indicated by the breaks.

A solution of normal sodium sulphide was prepared as follows: 333 gms of solid sodium hydroxide were dissolved to make a liter of solution. This was divided in half and one half was saturated with hydrogen sulphide until constant and approximately theoretical weight was reached. The other half was then added and the solution let stand to crystallize. (Treadwell-Hall, Quantitative Analysis, Page 225.)

12 gms of these crystals were roughly weighed out and dissolved to make 500 cc of solution.

The solutions employed in standardizing the sulphide were as follows:

Iodine solution   1.345 x N/10.

Sodium thiosulphate 1.043 x N/10.

The sodium sulphide solution was standardized at
1.65 x N/10.

Curve 34. Fig. 27. (page 71).

This follows 10 cc of the copper sulphate
solution titrated with the above sulphide.

cc.	B.R.	cc.	B.R.
0.	39.40.	10.	31.68.
2.	37.70.	12.	28.69.
4.	36.20.	14.	25.02.
6.	34.75.	16.	22.25.
8.	33.38.	18.	20.02.

The calculated end point is at 12.12.

The observed   "   "   "   " 9.9

It will be noticed in this curve that
there is an apparent irregularity in the reading
taken at 10 cc. This is assumed from the
noticeable change in the direction of curvature
of the line. If the line had continued the
general direction indicated by the points at
16 and 14, the break would come in the
neighborhood of 11 cc.

Curve 35. Fig.28. (page 72).

Fig. 27.

Curve 34

Fig. 28.
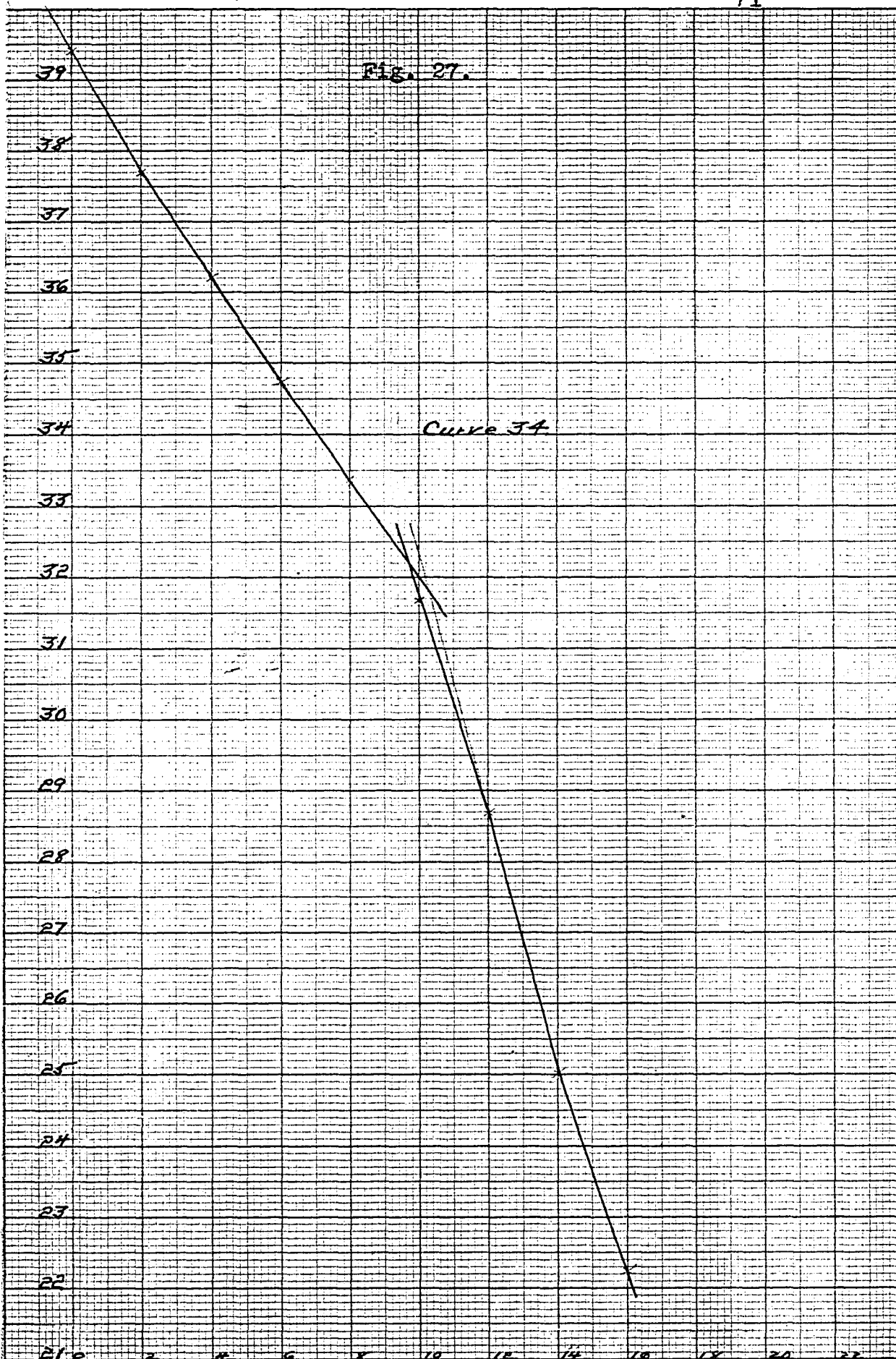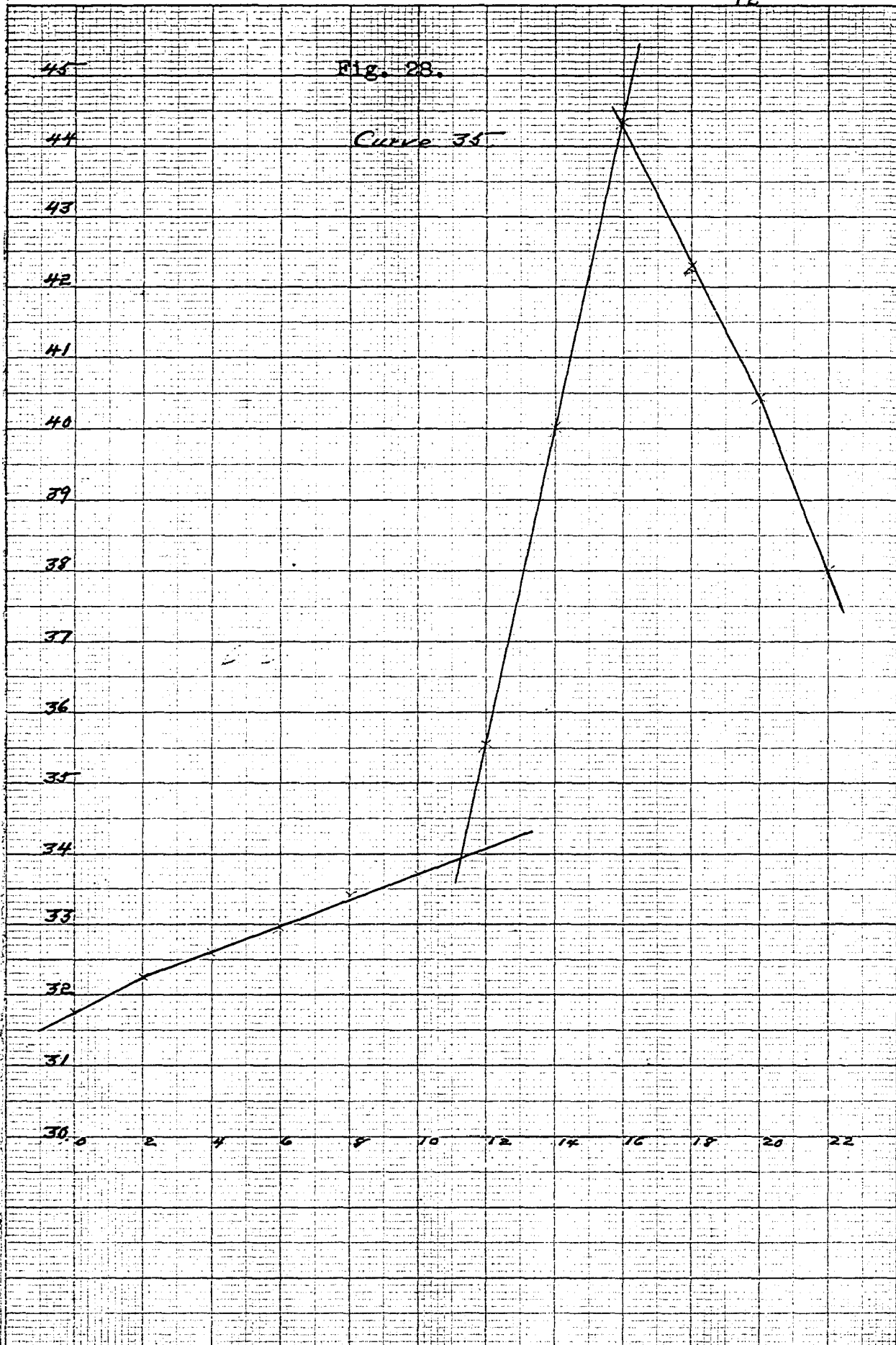
Curve 35

(curve 35).   This shows 10 cc of the copper solution, titrated
with sodium sulphide solution, in the presence of
10 cc of N/10 hydrochloric acid.

cc.	B.R.	cc.	B.R.
0.	31.77.	12.	35.55.
2.	32.25.	14.	40.00.
4.	32.60.	16.	44.35.
6.	32.95.	18.	42.30.
8.	33.40.	20.	40.45.
10.	33.70.	22.	38.00.

The calculated end point is at 12.12 cc.

The observed   "   "   "   "   11.3.

The presence of the acid seemed to make the
readings reach a constant value more rapidly.

It will be noted that the end point in the
above reactions does not coincide with the break
in the curve. Dutoit (2)* has stated that the
reactions involving the precipitation of sulphides
do not admit of measurement by the method of
conductivity.

This reaction was studied somewhat further
in a subsequent experiment.

A study of the curves traced up to this point shows that the only reaction which will admit of direct application as an analytical method for copper is that involving the precipitation of cuprous sulphocyanide with an excess of standard ammonium sulphocyanide and the subsequent titration of the excess with silver nitrate.

While the end points calculated for this reaction agree very well with observed breaks in the curves, it is necessary for practical purposes to obtain somewhat more regular lines in the curves in order that graphical interpolation will show the accurate end point without the necessity of taking so many points.

Consequently a study of the reaction at greater dilutions was made and the apparatus shown in Fig. 1. (page 10.) was employed.

Curves 36 to 40 are some preliminary experiments run with the new cell. Some of the reactions already studied were used in order that comparison with previous work might be made.

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In all of the work with this cell the volume of the material taken was brought approximately to 500 cc. The first reaction considered was a repetition of the precipitation of copper as sulphide.

The strength of the sulphide solution used was 1.483 X N/10.

Curve 36. Fig. 29. (page 76).

This shows 10 cc of the copper sulphate titrated with the above sodium sulphide solution.

cc.	B.R.	cc.	B.R.
0.	47.10.	12.	38.79.
2.	46.10.	14.	33.80.
4.	44.48.	16.	30.07.
6.	43.80.	18.	27.12.
8.	42.60.	20.	24.75.
10.	41.28.		

Calculated end point 13.4

Observed   "   "   11.4.

Curve 37. Fig. 30. (page 77).

Here 10 cc of the copper solution were titrated with the sodium sulphide solution in the presence of 10 cc of N/10. hydrochloric acid.
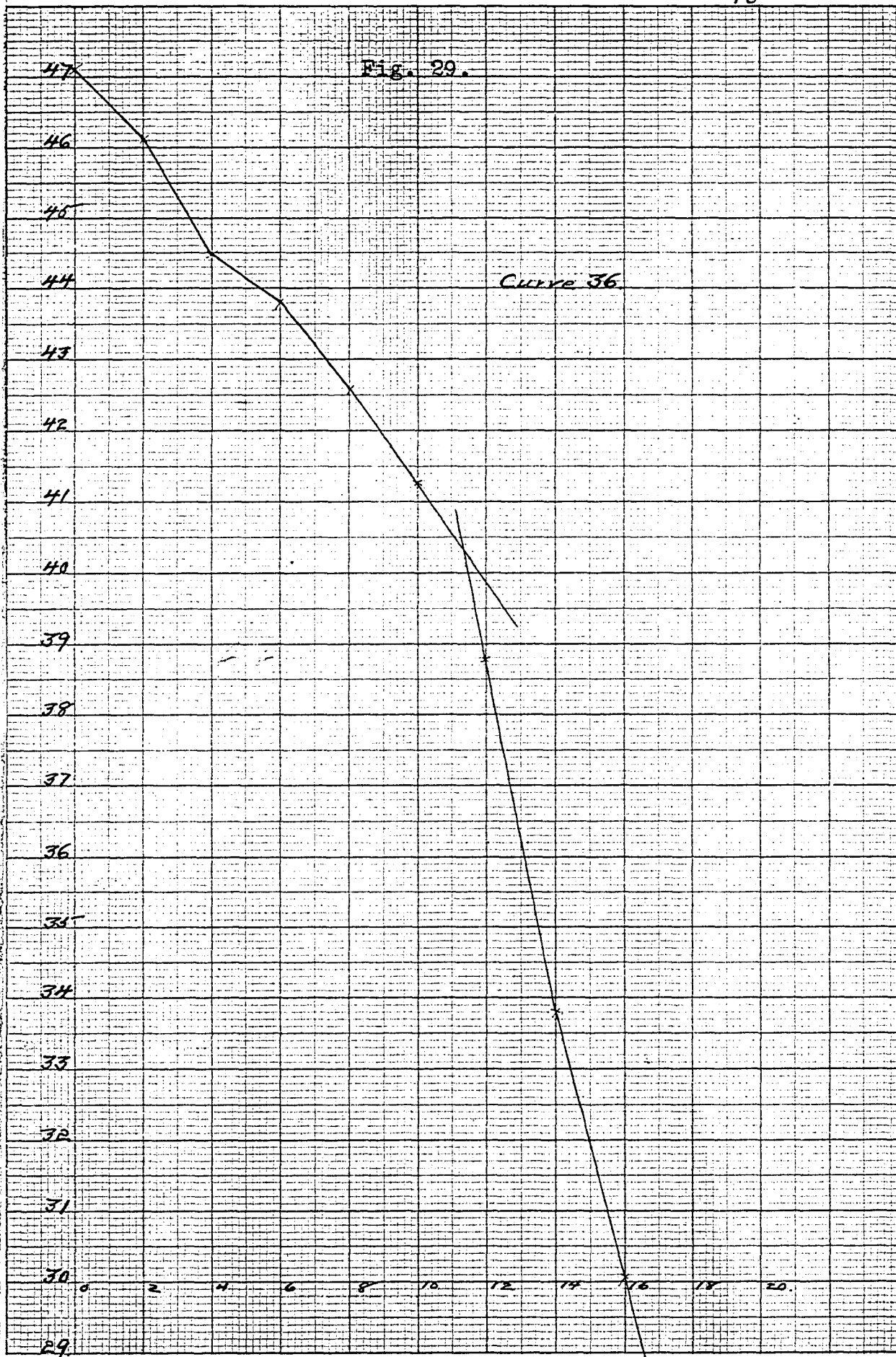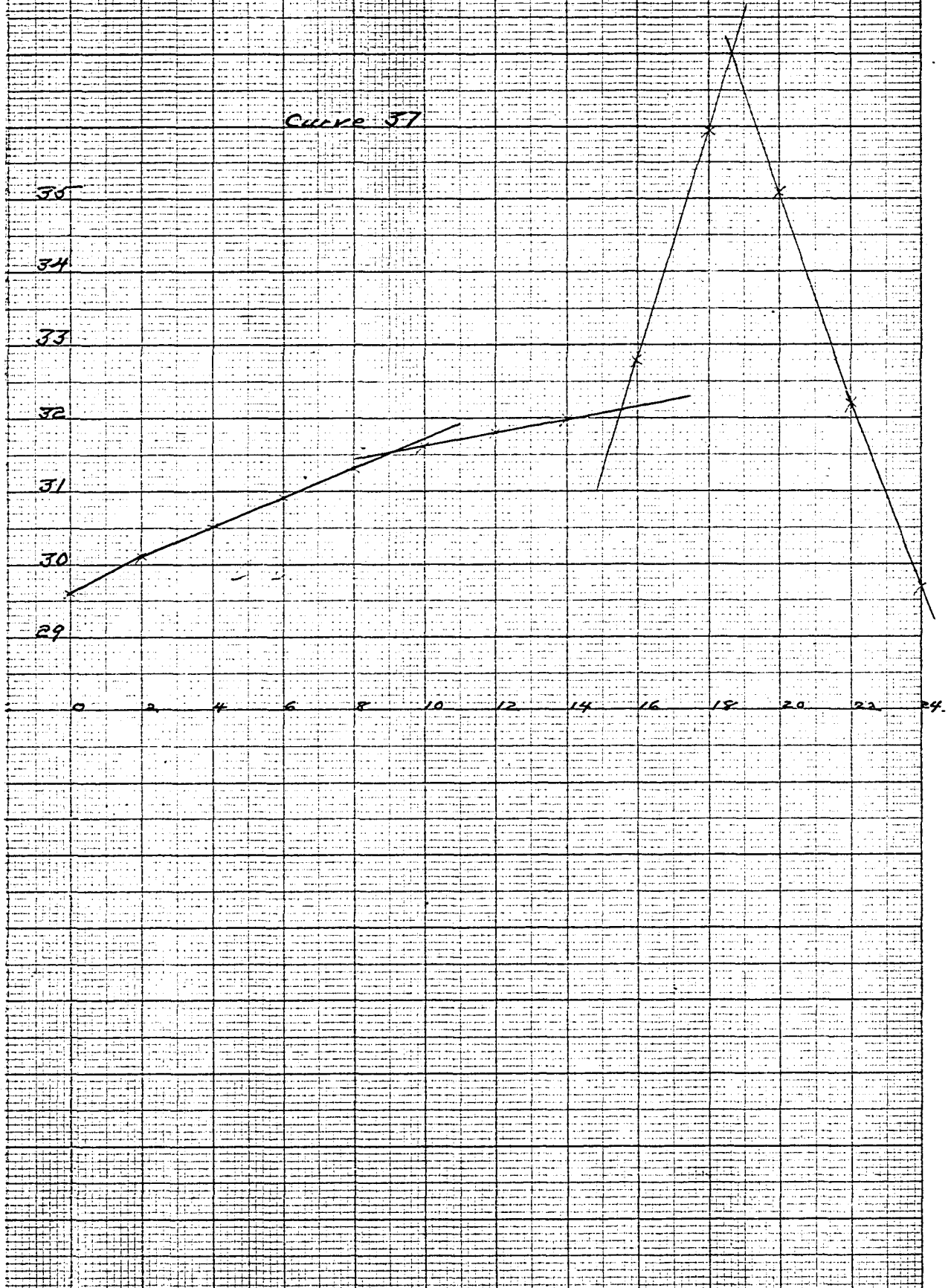
Fig. 29.

Curve 36

Fig. 30.

Curve 37

(curve 37).

cc.	B.R.	cc.	B.R.
0.	29.60.	14.	32.00.
2.	30.10.	16.	32.80.
4.	30.51.	18.	35.95.
6.	30.91.	20.	35.10.
8.	31.30.	22.	32.20.
10.	31.60.	24.	29.70.
12.	31.80.		

Calculated end point at 13.4 cc.

Observed   "   "   "   15.5 cc.

An attempt to obtain a curve following the precipitation of copper sulphide in the presence of ferric chloride gave readings indicative of a secondary reaction. Qualitative investigation showed that the copper sulphide reacted quite rapidly with the ferric salt to give elementary sulphur, copper chloride, and ferrous chloride. This reaction proceeds at such a rate as to make measurements of the conductivity impossible.

The above curves do not differ materially from those obtained in the other form of cell.

It might be noted, however, that the manipulation was somewhat facilitated by the greater

dilution as the readings for the conductivity
reached a constant value more rapidly and with
less stirring.


A conductivity curve for the precipitation
of copper hydroxide in the presence of ferric
chloride could not be obtained. This might be
anticipated from a consideration of the relative
solubilities of copper and ferric hydroxides.
The first addition of sodium hydroxide apparently
gave rise to the formation of both bases but
immediately a secondary reaction between the
copper hydroxide and the ferric salt caused a
gradual change in the conductivity and made
measurements impossible.

Curve 38. Fig. 31. (page 80).

This shows the precipitation of copper as
carbonate at greater dilution. 10 cc of the
copper sulphate solution were used. The sodium
carbonate solution was .1 N.

Fig. 31.
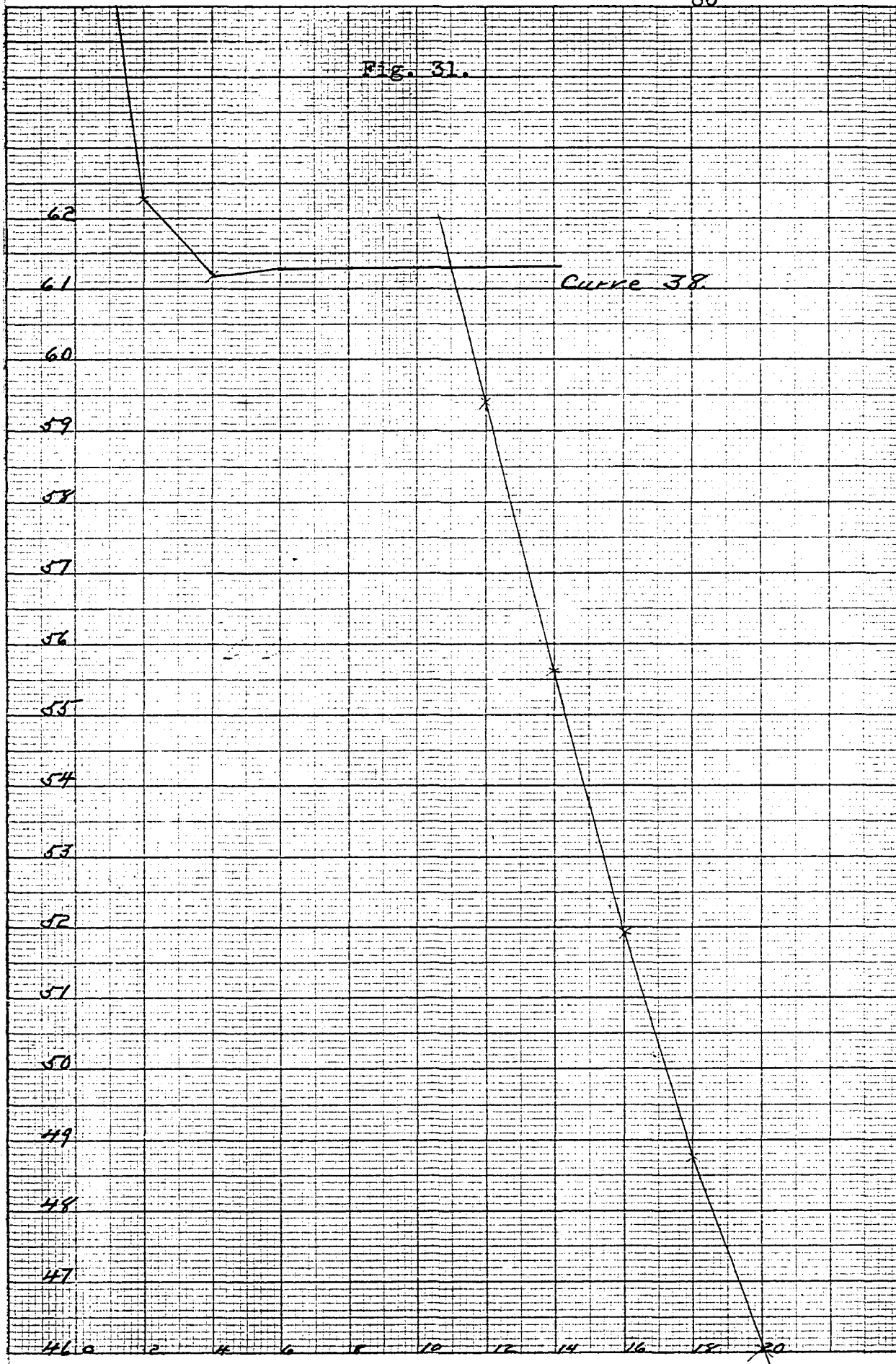
Curve 38.

(curve 38).

cc.	B.R.	cc.	B.R.
0.	78.80.	12.	59.40.
2.	62.29.	14.	55.62.
4.	61.20.	16.	51.94.
6.	61.29.	18.	48.75.
8.	61.30.	20.	46.05.
10.	61.30.		

Calculated end point at   10 cc.

Observed   "   "   11 cc.

It will be remembered that the end point in this
reaction appeared somewhat past the calculated
point in the experiments with the other cell.
Dilution seems to increase this difference between
the theoretical and experimental results.

In this case dilution does not serve to
aid the manipulation. The readings were very
irregular and slow to assume constant values.

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The following curves are devoted to a more
detailed study of the reaction already discussed
in curves 23 to 30. The technique suggested by
Edgar and previously described in this paper (page 50),
was employed.   In all cases the measured quantities
of materials introduced into the cell were brought
to a volume of about 500 cc before titration.

Curve 39. Fig. 32. (page 83).

The quantities for this reaction were as follows:

     5 cc of N/5 copper sulphate.

     5 cc of 4.464 X N/10 ammonium sulphocyanide.

Titration with silver nitrate.

cc.	B.R.	cc.	B.R.
0.	29.80.	14.	29.80.
2.	29.80.	16.	29.80.
4.	29.80.	18.	29.51.
6.	29.80.	20.	28.90.
8.	29.80.	22.	28.30.
10.	29.80.	24.	27.80.
12.	29.80.		

Calculated end point 17.32.

observed   "   "   17.19.

Curve 40   Fig. 32.

Curve 39
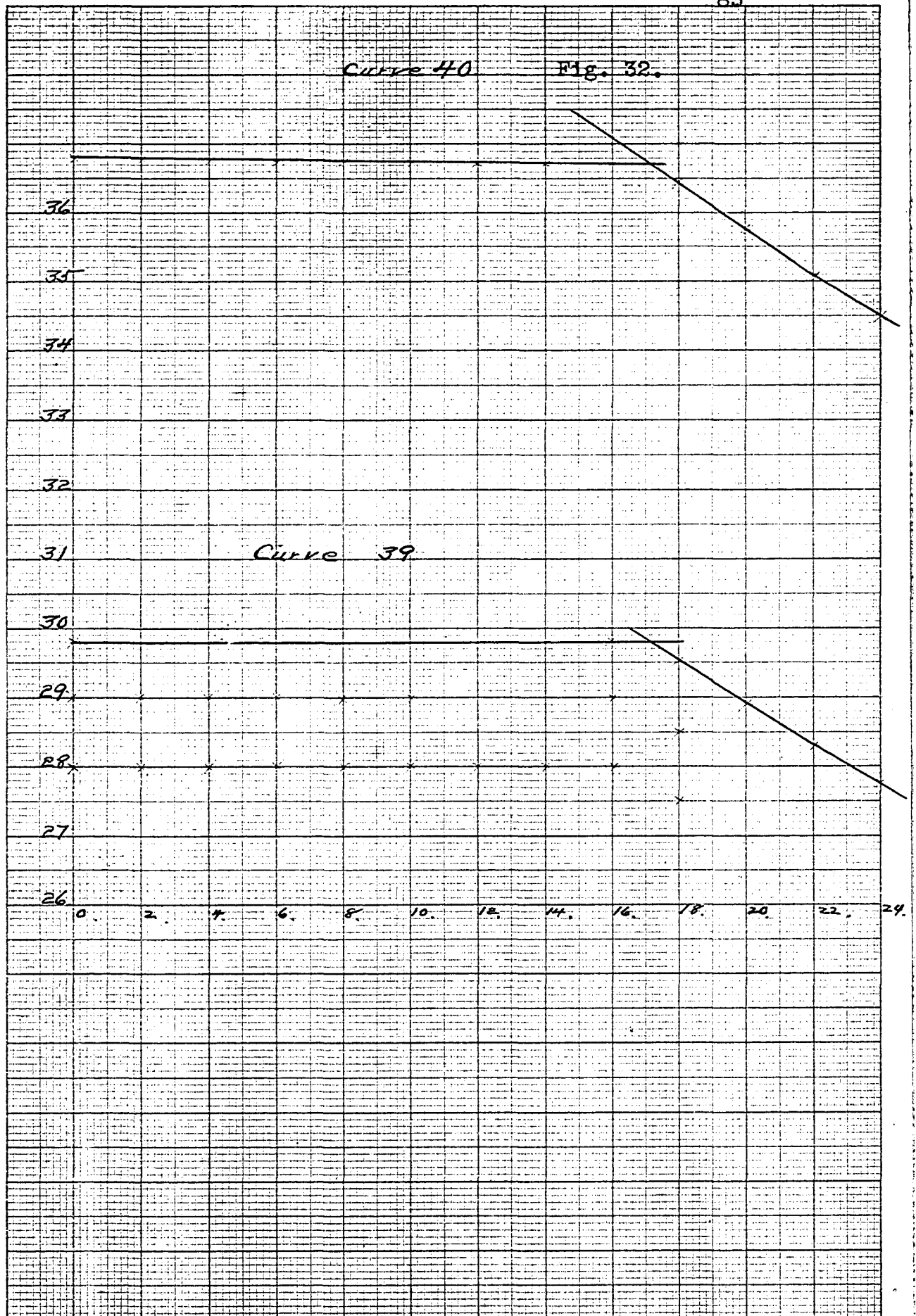
Curve 40. Fig. 32. (page 83).

This is a check on 39.

cc.	B.R.	cc.	B.R.
0.	36.80.	14.	36.72.
2.	36.79.	16.	36.71.
4.	36.78.	18.	36.45.
6.	36.76.	20.	35.79.
8.	36.75.	22.	35.10.
10.	36.74.	24.	34.50.
12.	36.73.		

Calculated end point 17.32.

Observed   "   "   17.19.

The next two reactions were run with varying

amounts of the sulphate.

Curve 41. Fig. 33. (page 85).

7 cc of copper sulphate solution and 5 cc of

ammonium sulphocyanide were used in this reaction.

Titration with silver nitrate.

cc.	B.R.	cc.	B.R.
0.	32.20.	12.	32.20.
2.	32.20.	14.	32.20.
4.	32.20.	16.	32.00.
6.	32.20.	18.	31.50.
8.	32.20.	20.	30.99.
10.	32.20.	22.	30.50.

Calculated end point 15.32.

Observed   "   "   15.33.

Fig. 33.
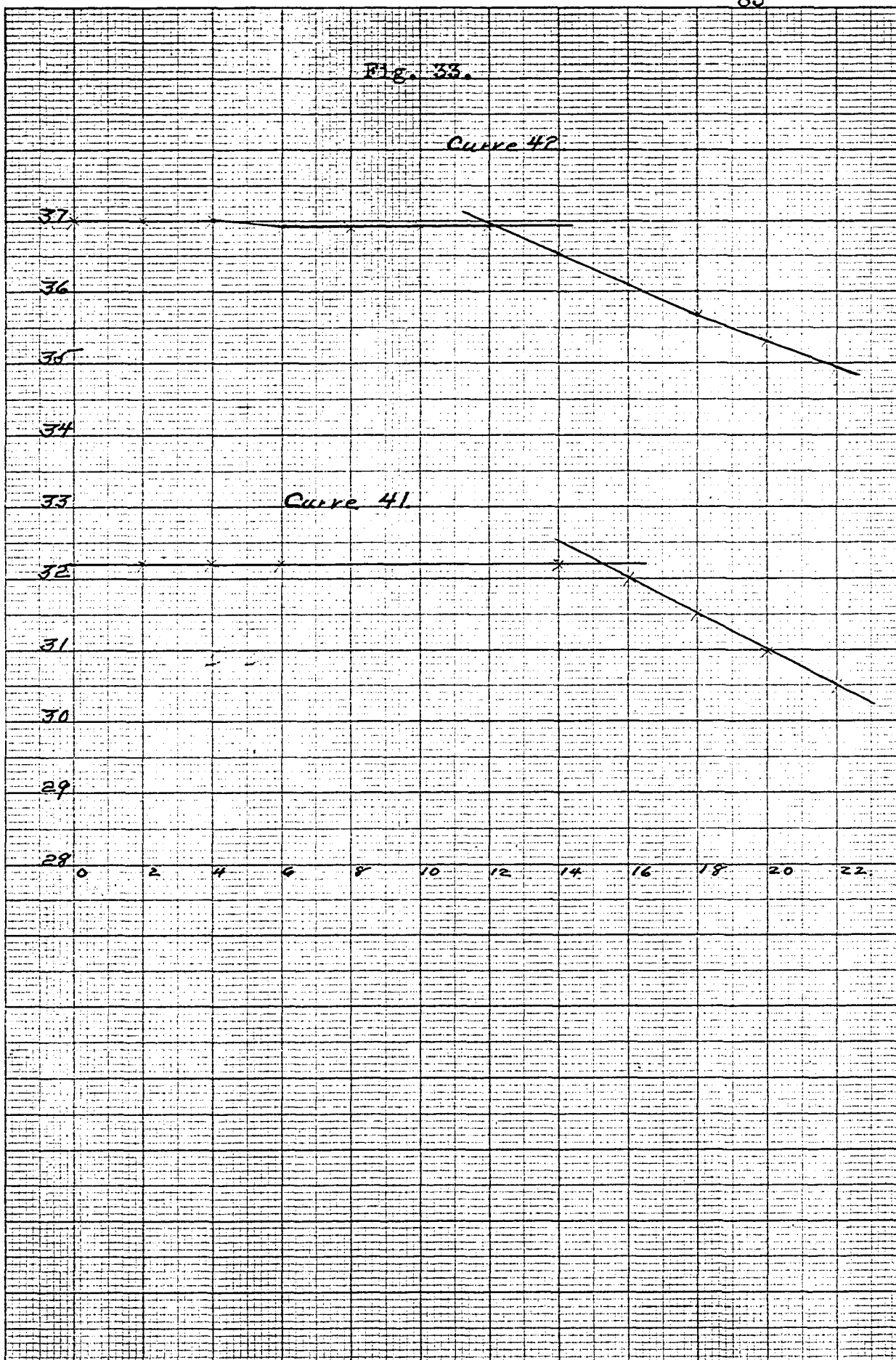
Curve 42

Curve 41

Curve 42. Fig. 33. (page 85).

Here 10 cc of copper sulphate solution were taken. 5 cc of ammonium sulphocyanide (4.464 X N/10.) Titration with silver nitrate.

cc.	B.R.	cc.	B.R.
0.	37.00.	12.	36.90.
2.	37.00.	14.	36.56.
4.	37.00.	16.	36.10.
6.	36.90.	18.	35.70.
8.	36.90.	20.	35.32.
10.	36.90.	22.	34.96.

Calculated end point 12.32.

Observed " " 12.3ø

The irregularity in the curve between 4 and 6 cc was probably due to a temperature change in the thermostat.

The agreement between the calculated results and the breaks in the above curves is quite sufficient to admit of a utilization of this method for the determination of copper.   There is however, a distinct tendency for the second branch to show curvature after a relatively small excess of the silver solution has been added. This fact, of course, necessitates an increased number of readings in order to insure an accurate plot of the point

of intersection.

Secondly, if the above method is to be applied
to the analysis of copper ores, its value in time
saving will be greatly enhanced if it can be shown
that the presence of certain other materials, more
especially iron, will not effect the nature of the
conductivity curve.

Thirdly, if a reaction might be found that
would serve for the estimation of the iron or
other main constituent present, in the same solution
after the copper had been determined, the method
would be doubly practical. This last phase of the
problem opens a considerable field for investigation
and this paper does not attempt to go into it.

The above mentioned points have not been
investigated at this time. A few preliminary
experiments, which will be described in the
rest of the paper, were tried in the hope that
they might suggest a possible direction through
which the questions presented might be cleared
up.

The difficulty in plotting these curves, as
has been previously stated, was apparently caused
by the appearance of a secondary reaction after
a rather small excess of the silver nitrate solution
had been added.   It seemed possible that this
trouble might be avoided by the addition of smaller
excess of the ammonium sulphocyanide and titrating
with a more highly diluted solution of the silver
nitrate.   The following curve shows the result
of this procedure.

Curve 43.   Fig. 34.   (page 89).

This reaction is between 7 cc of copper
sulphate, 2 cc of ammonium sulphocyanide and
titration with N/100 silver nitrate.

cc.	B.R.	cc.	B.R.
0.	41.70.	14.	42.05.
2.	41.77.	16.	42.10.
4.	41.84.	18.	42.18.
6.	41.90.	20.	42.24.
8.	41.90.	22.	42.22.
10.	41.99.	24.	42.20.
12.	42.00.	26.	42.20.

The calculated end point is at 19.28 cc.

There is a slight inflection in the curve
in the neighborhood of 21 cc but if there be a

Fig. 34.

Curve 43
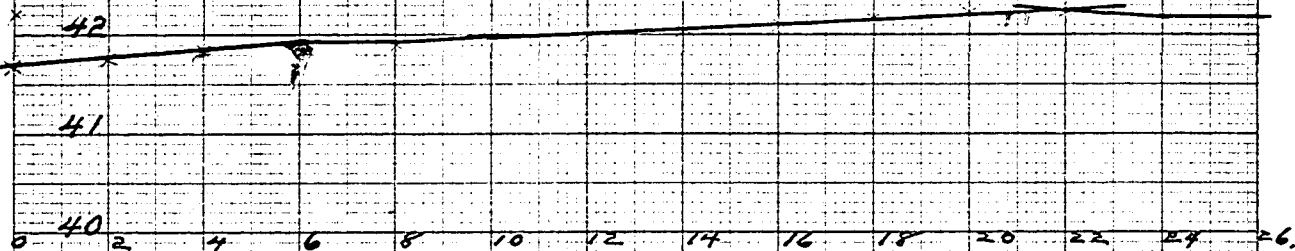
a break the slopes of the two lines are so nearly
the same that plotting would be impossible.

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The reaction was next repeated in the presence of
an iron salt.

_____

Curve 44. Fig. 35. (page 91).

The quantities used were: 5 cc of copper sulphate,
5 cc of ammonium sulphocyanide (4.464 X N/10), and
5 cc of approximately N/10 ferric chloride. Titration
with N/10 silver nitrate·

cc.	B.R.	cc.	B.R.
0.	25.47.	16.	25.15.
2.	25.32.	18.	25.11.
4.	25.32.	20.	25.11.
6.	25.30.	22.	25.10.
8.	25.25.	24.	24.63.
10.	25.20.	26.	24.15.
12.	25.19.	28.	23.71.
14.	25.15.	30.	23.29.

The calculated end point is in the neighborhood
of 22 cc. The observed break is at 22 cc.

_____

In the above reaction the iron is apparently
without material effect on the curve. The break

Fig. 35.

Curve 44
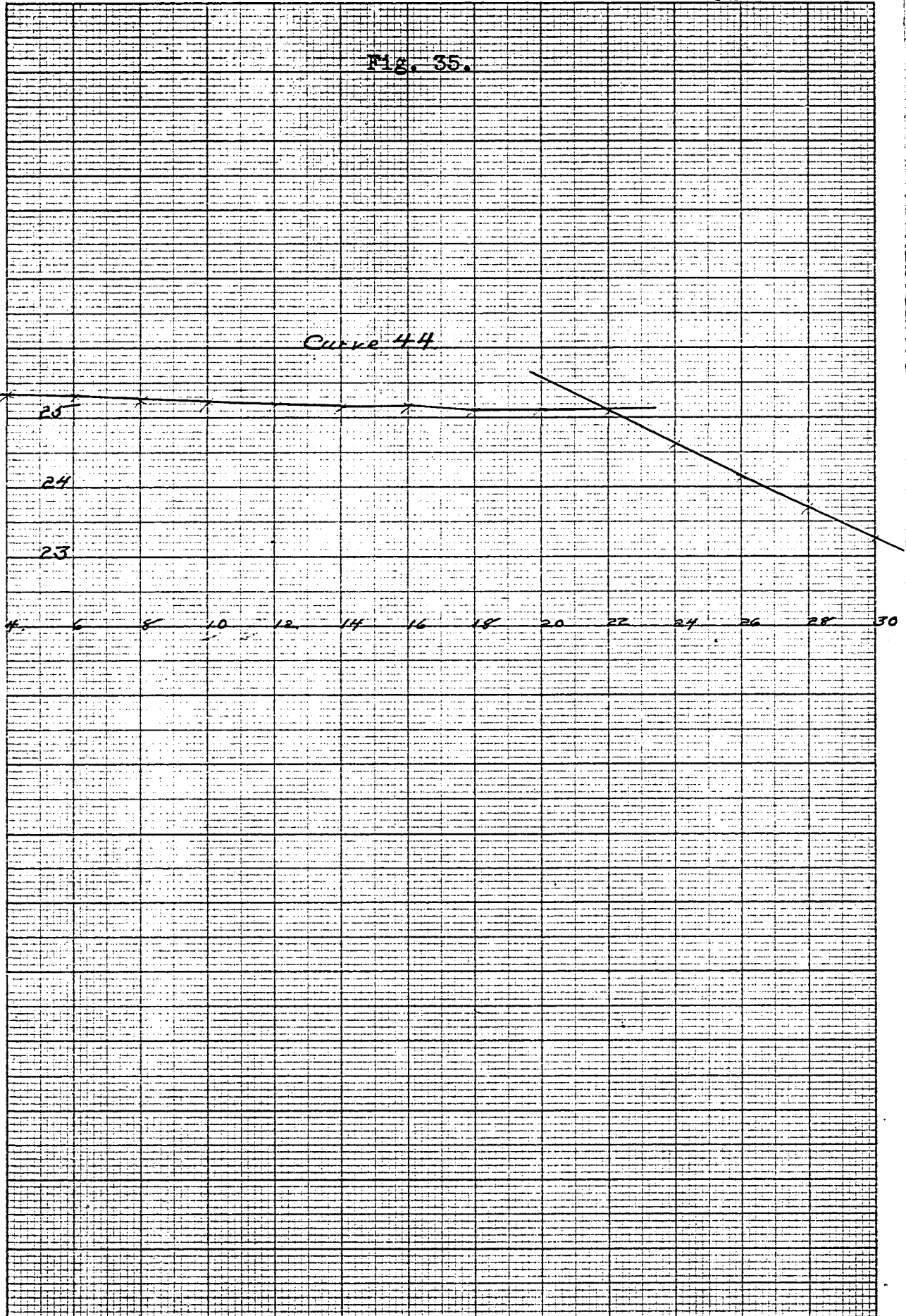
indicates, of course, the end point in the precipitation
of the chlorine present as well as the sulphocyanide.

As an analytical method it would be necessary
to rid the solution of chloride, probably with
sulphuric acid, and so a number of curves are shown
in which the reaction was carried out in the
presence of varrying quantities of ferric alum.

Curve 45. Fig. 36. (page 93).

In this 5 cc of copper sulphate and 5 cc of
ammonium sulphocyanide (4.464 X N/10) were titrated
in the presence of 5 cc of ferric alum (about N/10).

cc.	B.R.	cc.	B.R.
0.	36.45.	12.	36.65.
2.	36.50.	14.	36.65.
4.	36.56.	16.	36.70.
6.	36.60.	18.	36.52.
8.	36.65.	20.	36.10.
10.	36.65.	22.	35.65.

The calculated end point is at 17.32.

The observed   "   "   "   "   17.0.

The readings between 8 and 16 cc were irregular.

Curve 46. Fig. 36. (page 93).

This is a check on 45.

Fig. 36.
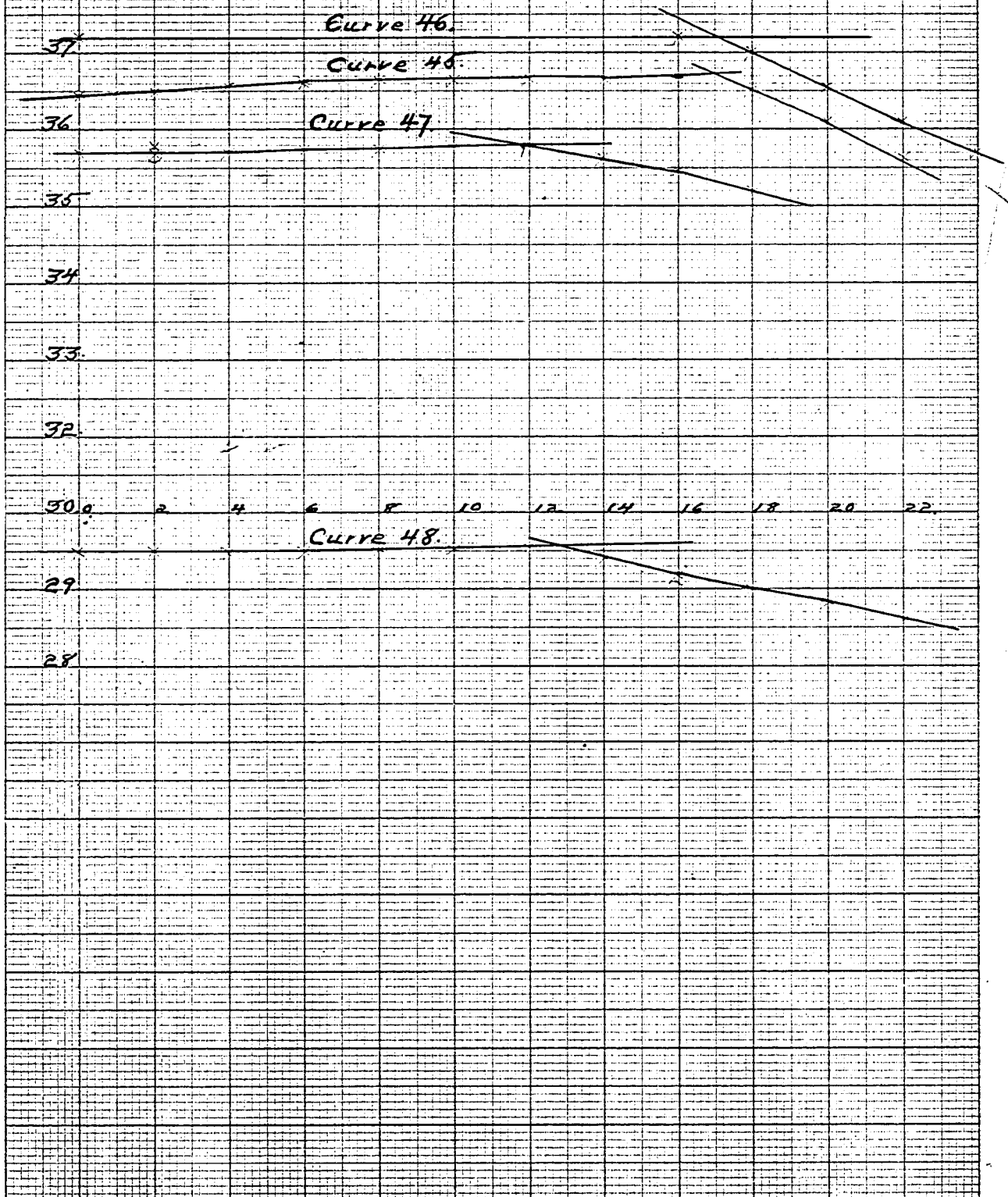
Curve 46.
Curve 46
Curve 47
Curve 48.

(curve 46).

cc.	B.R.	cc.	B.R.
0.	37.20.	16.	37.20.
2.	37.20	18.	37.00.
4.	37.20.	20.	36.55.
6.	37.20.	22.	36.10.
8.	37.20.	24.	35.70.
10.	37.20.	26.	35.30.
12.	37.20.		

Calculated end point at 17.32.

Observed " " " 17.1.

Curve 47. Fig. 36. (page 93).

10 cc of copper sulphate, 5 cc of ammonium
sulphocyanide (concentration as above) and
10 cc of ferric alum solution were used in this
reaction.

cc.	B.R.	cc.	B.R.
0.	35.70.	10.	35.79.
2.	35.70.	12.	35.80.
4.	35.72.	14.	35.65.
6.	35.75.	16.	35.49.
8.	35.75.	18.	35.22.

Calculated end point 12.32.

Observed end point 11.8.

After reduction the above was allowed to stand
over night before titration. The color gave
evidence of slight oxidation.

Curve 48.   Fig. 36.   (page 93).

This is a duplicate of curve 47.

cc.	B.R.	cc.	B.R.
0.	29.50.	12.	29.55.
2.	29.50.	14.	29.40.
4.	29.50.	16.	29.19.
6.	29.50.	18.	29.00.
8.	29.51.	20.	28.81.
10.	29.53.	22.	28.62.

The calculated end point is at 12.32.

The observed   "   "   "   "   12.65.

At 8 cc the precipitate collected together.

From the above it can be seen that the presence of iron in the solution tends to shift the break in the curve away from the calculated end point.   As has been stated this is merely a statement of the problem and no attempt has been made to investigate the cause of the difference.

Since the iron in the above reaction is necessarily reduced to the ferrous state at the time of the precipitation of the excess sulphocyanide, it occurred that a curve might be obtained for the precipitation of ferrous

Ferricyanide. Solutions of ferric alum and potassium
ferricyanide were prepared (approximately N/10) and
a curve was obtained as follows:

5 cc of ferric alum solution were reduced with
sulphur dioxide, freed from excess by boiling and
simultaneously saturating with carbon dioxide, and
titrated with the potassium ferricyanide.

Curve 49. Fig. 37. (page 97).

cc.	B.R.	cc.	B.R.
0.	50.60.	12.	49.95.
2.	50.50.	14.	49.80.
4.	50.40.	16.	49.45.
6.	50.40.	18.	48.70.
8.	50.28.	20.	48.04.
10.	50.10.	22.	47.40.

A break in the curve occurs at 15.4. The
solution was not standardized as subsequent
measurements failed to give qualitative results
that accorded.

Curve 50. Fig. 38. (page 98).

This shows 7 cc of copper sulphate, 4 cc of
ammonium sulphocyanide and 5 cc of the ferric
alum solution used in 49., titrated first with
silver nitrate and then with the above potassium
ferricyanide solution.

Fig. 37.

Curve 49
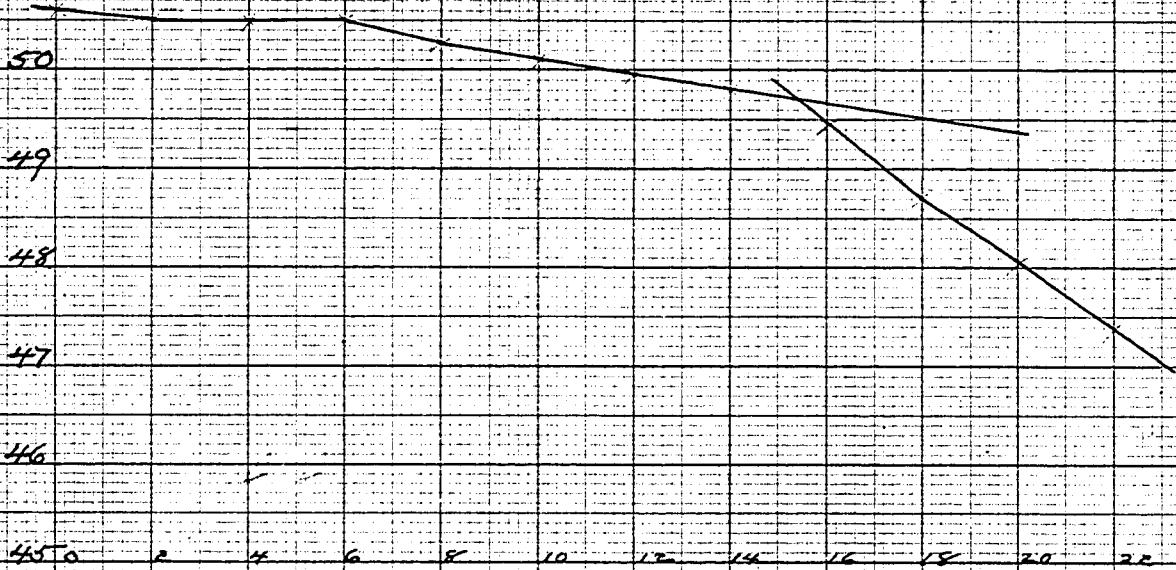
Fig. 38.
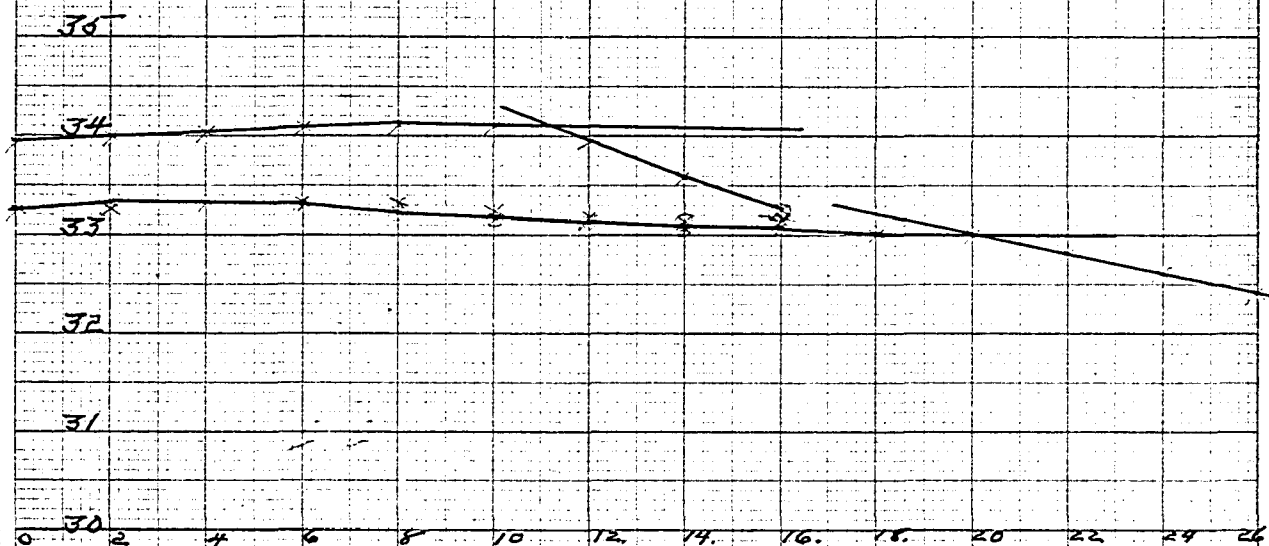
Curve 50

(curve 50).

Titration with silver nitrate.

cc.	B.R.	cc.	B.R.
0.	33.95.	10.	34.10.
2.	34.00.	12.	33.95.
4.	34.05.	14.	33.60.
6.	34.10.	16.	33.25.
8.	34.10.		

In this curve the break is calculated to come at 10.87. The observed break is at 10.6.

Titration with potassium ferricyanide.

cc.	B.R.	cc.	B.R.
0.	33.25.	14.	33.10.
2.	33.32.	16.	33.10.
4.	33.32.	18.	33.02.
6.	33.31.	20.	33.00.
8.	33.25.	22.	32.82.
10.	33.20.	24.	32.64.
12.	33.15.	26.	32.40.

From curve 49 a break should occur at 15.4. A break can be observed at 20.

There was distinct evidence of a secondary reaction in the second case above. Until a considerable excess of the ferricyanide had been added the blue color of the ferrous ferricyanide faded out quite rapidly. This indicates at once that the particular reaction under consideration is inapplicable. A check on the above was run as indicated in the next curve.
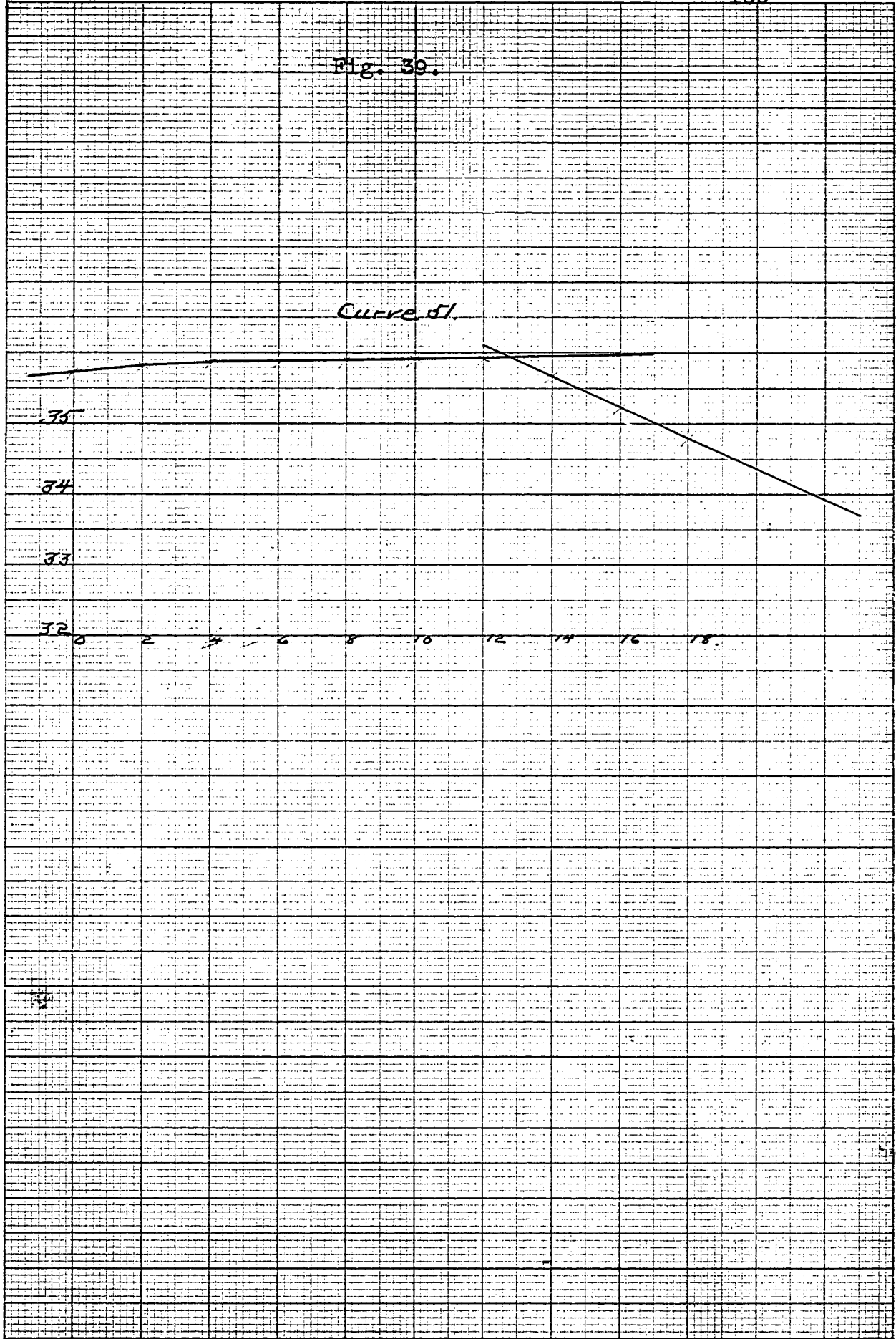
Fig. 39.

Curve 51.

Curve 51.   Fig. 39.   (page 100).

Here 5 cc of copper sulphate, 4 cc of the
sulphocyanide and 5 cc of the ferric alum solution
were used.   Titration, first with silver nitrate,
then with potassium ferricyanide.

Titration with silver nitrate.

cc.	B.R.		cc.	B.R.
0.	35.73.		10.	35.92.
2.	35.83.		12.	35.92.
4.	35.87.		14.	35.69.
6.	35.89.		16.	35.24.
8.	35.90.		18.	34.80.

Calculated end point 12.87.

Observed   "   "   12.79.

The titration with the ferricyanide was
attempted but the secondary reaction was so
definite and the readings for the conductivity
so irregular that the measurements were not
recorded.

Discussion of Precipitation Curves in General.

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If two solutions, containing substances which on
mixing will exhibit a chemical reaction involving
the precipitation of one of the possible products,
are brought gradually together and simultaneously
measurements of the electrical conductivity of the
solution are made, a graphical result may be
obtained if lines are constructed through the
points located by plotting the conductivity
measurements as ordinates and the volumes of reagent
added, as abscissae, which in general will be a
curve showing a more or less well defined point
of inflection.   This point of inflection
usually occurs at an abscissa corresponding to
the addition of chemically equivalent quantities
of materials, or in other words, to the end point
of the reaction.

From this it follows that an accurate determination
of this point of inflection may be utilized as an
indicator and applied to the quantitative measure-
ment of many reactions.

The accuracy with which the abscissa can be located will depend on two things. First, the angle at which the two lines intersect. As this approaches a right angle, the intersection becomes more well defined and can consequently be more easily read. Secondly, the construction of the lines themselves depends on the degree of curvature which they exhibit. Straight lines cannot only be more accurately drawn but will also admit of interpolation of the intersection, thereby diminishing the number of measurements necessary.

With these statements in mind a few general rules for the selection of reactions to which this method is applicable may be formulated and some prediction can be made as to conditions under which the curves may be most satisfactorily drawn.

Suppose that .2 cc of .1 N potassium chloride is added, .1 cc at a time, to 100 cc of .001 N silver nitrate. Conductivity measurements taken after each addition and plotted as indicated above, will give a curve of the general order
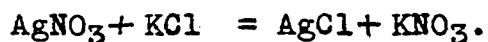
shown in Fig. 40.
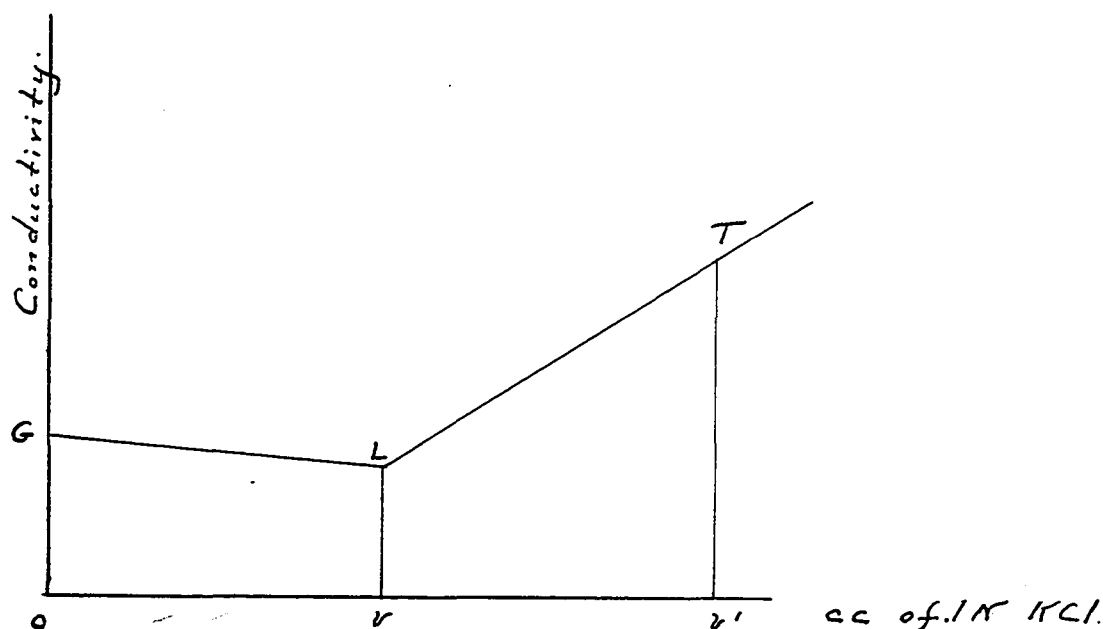
Fig. 40.

The ordinate OG represents the conductivity of
the silver nitrate solution. At this concentration
the dissociation is practically complete and hence

$$OG = \alpha (V_{Ag} + V_{NO_3}).$$

in which V_{Ag} and V_{NO_3} are the migration velocities
of the Ag and NO_3 ions, respectively.

At the point v the equation:

$$AgNO_3 + KCl = AgCl + KNO_3.$$

shows the solution to contain only potassium nitrate,,
since the silver chloride is completely insoluble.

The ordinate vL is therefore given by the equation:

$$vL = -\alpha(V_K + V_{NO_3})$$

where V_K and V_{NO_3} are the ionic mobilities as shown by the subscripts.

In reality the concentration α is no longer .001 N but about .000999, the total volume of the solution having been brought to 100.1 cc. This slight difference, however, may be neglected.

v' is the point corresponding to the addition of .2 cc and the ordinate v'T is given by:

$$v'T = \alpha(2V_K + V_{NO_3} + V_{Cl}).$$

From the discussion it can be seen that all of the data necessary for the calculation of the angle GLT are known, viz; the speeds of the ions, the measurements of the ordinates and abscissae.

For example the tangent of the angle will be

$$\tan GLT = \frac{-\alpha(V_{Ag} + V_{Cl}).0v}{\overline{0v}^2 + \alpha^2(V_K - V_{Ag})(V_K + V_{Cl})}.$$

The general equation for any double decomposition reaction involving complete precipitation of one of the products, follows from the above.

If the reaction be of the type

$$AB + CD = AD + CB.$$

and a,b,c,and d are used to represent αV_A, αV_B, αV_C, and αV_D, respectively. Calling the length of the line corresponding to the number of cc necessary for complete reaction, m. The tangent of angle A is given as follows:

$$\tan A = \frac{-(a+d)m}{m^2+(c-a)(c+d)}$$

From this formula it can be seen that:

1. A is independent of b.

2. A varies inversely with d.

3. A varies directly with c so that $c > \frac{a+d}{2}$. It reaches a minimum value when $c = \frac{a+d}{2}$.

4. A increases as m is increased.

From this mathematical discussion seven rules have been derived by Dutoit (2)[*] which direct the application of the method.

1. The radical of the salt which does not help to form the insoluble compound has no influence on the sharpness of the point of inflection of the curve.

2. The sharpness of the point of inflection is greater when the anion of the precipitant shows great velocity.

This is not of very great importance since the
mobilities of the various acid anions do not show
very marked differences in value.

3. The sharpness of the point of inflection is
greater when the ion of the reagent which does
not enter into insoluble combination, has a low
velocity.

4. The presence of foreign materials, electrolytes
or otherwise, which take no part in the reaction,
does not influence the point of inflection.

5. The solution to be analyzed should be as
dilute as possible.

For practical purposes from .01 to .02 N
is probably most satisfactory.

6. The reagent should be as concentrated as
possible.

This can be seen in the figure as shortening
the line Ov.

7. When the precipitate formed is appreciably
soluble it is necessary to avoid taking readings
in the immediate vicinity of the end point.
Observation of this rule will, however, allow

the application of this method to reactions which could not be used even in gravimetric analysis.
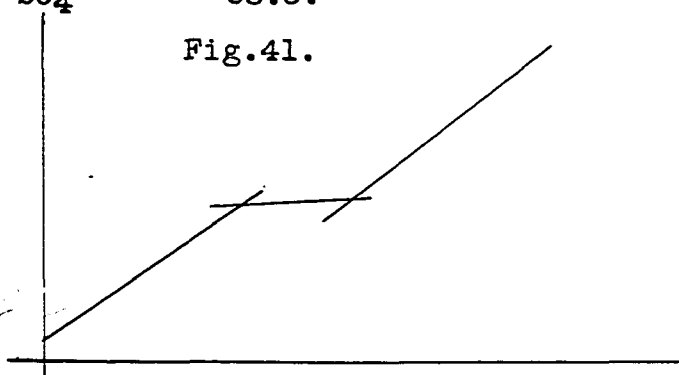
Discussion of Curves Studied.

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Precipitation of Cupric Ferrocyanide.

Equivalent conductance of ions involved:

Cu	45.9[*]
K	64.5
$Fe(CN)_6$	95.0
SO_4	68.5.

Fig.41.

The general type of curve exhibited is shown in the figure.

The angle of intersection would be too obtuse to permit an accurate graphical representation of the reaction end point were it not for the double break occurring. A comparison of the ionic speeds given shows that the intersection angle should be rather great on account of the relative values for the copper and potassium ions, although the ferrocyanide ion should tend to oppose this by increasing the slope of the second branch.

On the other hand the nature of the angle

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[*] A.A. Noyes and K.G. Falk, J, Amer. Chem. Soc. 34,479.

would not account for the great difference between
the calculated and observed results. Nor should
this source of error give results which agree
so well among themselves, but rather should cause
an irregular error in the point of intersection.

The short and approximately horizontal branch
of the curve was considered only briefly. The assumption that it is caused by the property of adsorption
which is shown by a number of the ferrocyanides,
seems to explain at least the appearance of the
irregularity and is in accord with the fact
that the length of the branch is increased by
an increased quantity of the precipitated ferrocyanide.

Although this reaction does not lend itself
immediately as one which might be employed in
analysis through the application of the conductivity
method, the possible duplication of observed
results suggests that further investigation might
lead to the determination of a factor which
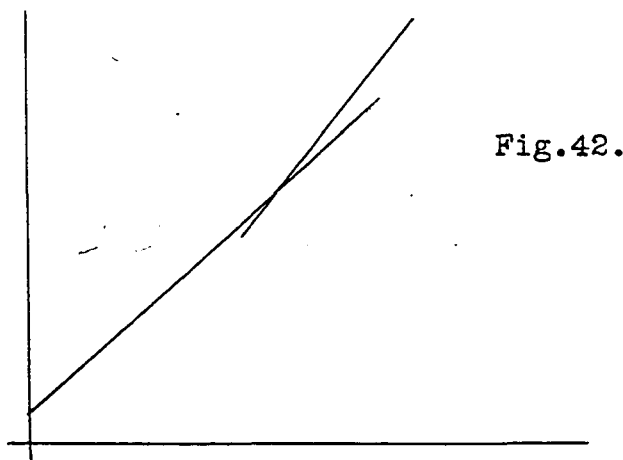would render the reaction useful.

Precipitation of Cupric Carbonate.

Equivalent Conductance of ions involved:

Cu	45.9.
Na	43.4.
CO_3	70.0.
SO_4	68.5.

- - - - - - - - - -

Fig. 42. gives the general type of curve obtained.

Fig.42.

The point of intersection shown in this curve is

again uncertain on account of the size of the angle.

It will be noted that the agreement between the

observed and calculated end points, however is much

more close than in the ferrocyanide. The error

does not occur consistantly as should be expected

if it is entirely caused by difficulties in

the graphical location of the observed end point.

It is quite possible that concentrations of the substances might be chosen that would considerably diminish the angle of intersection, thereby increasing the accuracy with which the reaction might be used.

Reference to the mathematical formula given previously in this paper, will show that c is less than the average of a and d, which is not the condition pointed out to be the minimum for the angle of intersection.

In conclusion, the fact that carbonate solution s can be so easily prepared and standardized, coupled with the fair agreement between the conductivity method and calculated results, might warrant some little further investigation of the empirical effect of dilution on the curve.

Precipitation of Cupric Carbonate from Acid Solution.

Equivalent Conductance of ions:

Cu   45.9.
Na   43.4.
CO$_3$ 70.0.
H   335.5.

The general type of curve is as follows:
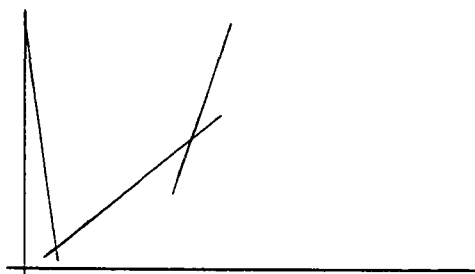
The first break in this curve should correspond

to the complete reaction of the acid present with

the sodium carbonate added, the second should

come at the point at which the last of the copper

is precipitated.

Reference to Fig. 11 page 35, will show a

curve in which the two points are calculated at

2.5 and 7.5 respectively. The observed values

agree fairly closely in spite of the difficulties

encountered in taking readings. Comparison with

curves 14 and 15 seems to indicate that the

presence of small quantities of acid facilitates

the measurements of this reaction.

This fact occurs advantageously as solutions in which copper is to be determined are usually necessarily acid.

Precipitation of Cupric Hydroxide.

Equivalent conductance of the ions involved:

Cu	45.9
SO_4	68.5
Na	43.4
OH	174.0

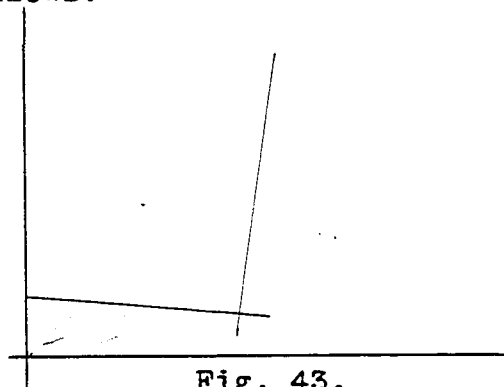The general type of curve obtained with this reaction is as follows.

Fig. 43.

The sharp break in the curve can be anticipated from the ionic conductances involved. Experiment shows, however, that the point of inflection does not correspond to the calculated reaction end point.

The only explanation which could be offered for this observed difference was the possible partial formation of one of the basic salts of copper in the course of the reaction.

The results of the experiments showed that this particular reaction would not be of interest in the present work and it was accordingly abandoned.

The Precipitation of Cupric Sulphide.

Equivalent conductance of the ions involved.

Cu   45.9.
SO$_4$ 68.5.
Na   43.4.
S   **
(OH)   (174)

The value for the equivalent conductance of the
S ion was not given in any tables available. The
fact that sodium sulphide hydrolyzes to such a
great extent makes it probable that the predominant
ion was the hydroxyl and its conductance is con-
sequently given.

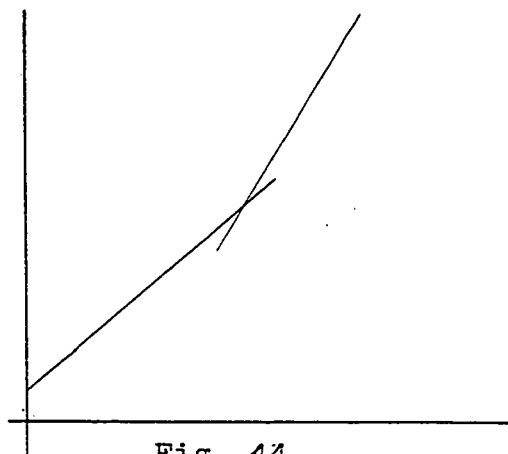The figure shows the general type of curve
obtained.

Fig. 44.

The results obtained for this reaction were also
negative. A difference of about 2 cc of 1.5 X
N/10 sodium sulphide between the observed and
calculated quantities, was found. This of course,

could not be explained by the wide angle of inter-
section alone. The direction of the error might
suggest that the formation of some other com-
bination of the ions present, such as the hydro-
sulphide of copper, was an influencing factor.
However, the curve showed itself to be inappli-
cable as a method for the estimation of the
copper in the solution and investigation of
the causes was not attempted.

Curves for the reactions involving the precipitation
of cuprous iodide and cuprous sulphocyanide could
not be obtained. The first reaction proceeded at
such a slow rate that readings could not be taken.
The second gave irregular readings, apparently on
account of the necessary presence of the reducing
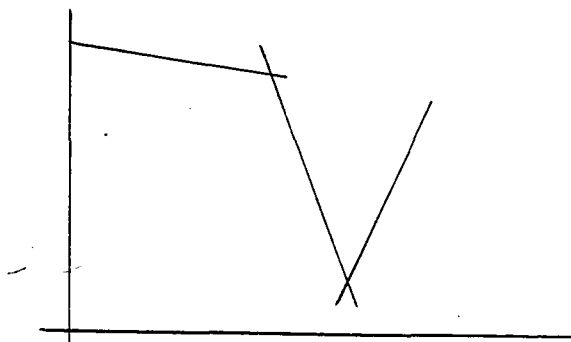agent. Attempts to free the solution from this
proved unsuccessful.

The Precipitation of Copper as Sulphide in Acid
Solution.

Equivalent conductance of ions:

Cu	45.9
Na	68.5
S	(not given in tables).
OH	174.
H	335.5.

The general type of curve is shown in the figure.

The first line of this curve corresponds to the
precipitation of the copper, the second indicates
the reaction between the acid present and the
sodium sulphide excess.

Curve 35. page 72·, shows a measurement of
the reaction in which the calculated end point
for the precipitation of the copper should be
at 12.12 cc. The observed point is at 11.3.

The influence of the presence of acid is an
important factor in determining the practical
value of these measurements as has been mentioned

previously.

A comparison with curve 34 shows that the
acid again apparently facilitates the measurement
of the reaction although the disagreement between
the observed and calculated values still seems
to suggest that this particular reaction is en-
tirely inapplicable to the purpose desired.

The precipitation of silver sulphocyanide is shown
in curves 21 to 30 and again in 32 to 50.   The
accuracy with which the end point in this reaction
can be determined graphically makes it applicable
indirectly to the estimation of copper.

After reduction, the copper is precipitated
by an excess of standard ammonium sulphocyanide
and the excess is then titrated with a solution
of silver nitrate.

The equivalent conductance of the ions involved
is as follows:

NH_4 64.0.
SCN 56.7
Ag 54.0
NO_3 61.8

The type of curve obtained is shown in the figure.
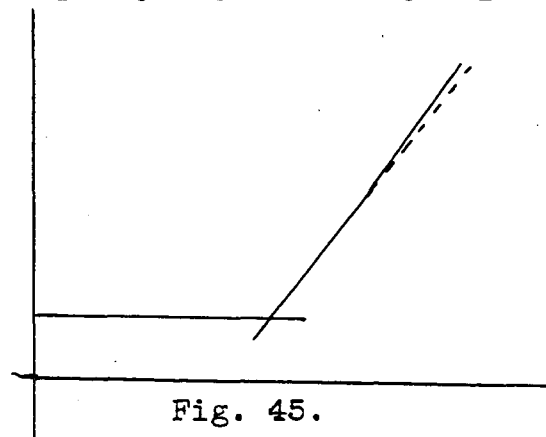

Fig. 45.

The curve shows two points of inflection.   In

the figure the second break is slightly exaggerated in order to make it visible on the curve drawn to the small scale.

The first break corresponds accurately to the theoretical end point in the precipitation of the silver sulphocyanide. The second break is caused by the appearance of a secondary reaction involving the reduction of the excess silver salt to metal silver by the cuprous sulphocyanide.

The accuracy with which this reaction can be measured is to .01 cc of a N/10 solution.

A sharp break in the curve is shown when concentrations of .05 N and .1 N for the sulphocyanide and silver nitrate, respectively, are used. The ions do not show differences in conductance which should afford a very small angle of intersection, however, for practical purposes the angle is quite well defined and can be measured with no inconvenience.

It is of interest that the particular concentration used in the curves 43 to 50 gave an approximately horizontal line for the first branch of the curve. Referring to the mathematical

formula deduced on page 106 we see that for this
case the angle of intersection is independent of
the value of m. This is of distinct advantage
because larger quantities of copper can be taken
provided the initial dilution is sufficiently
increased, without affecting the accuracy of
the determination of the end point. This
should prove convenient in the utilization of
this reaction for analytical work.

The second break in the curve is a
disadvantage. The interpolation of the point
desired depends on the extension of the line
occurring between the two breaks and since this
line is short, it becomes necessary to make
several measurements in the neighborhood of
the reaction end point. This increases the
time necessary for conducting the manipulation.
This secondary reaction was observed to depend
on the concentration of the silver nitrate in
the solution and it was suggested that a
greater dilution of the reagent, provided the
excess of sulphocyanide was diminished, might
lengthen the necessary line. Experiment showed

that the increase in the total dilution of the cell
caused irregularities which more than counterbalanced
any advantage which might result from the use of
more highly diluted silver nitrate.

This difficulty, of course, could be overcome
by filtration, i.e., by filtering the solution
free from the precipitate of copper sulphocyanide.
On the other hand, filtration not only requires
time but is apt to introduce error and it is
quite possible that the taking of a few more
conductivity readings would be more convenient
and accurate than resorting to filtration.

The writer was forced to leave the direct
application of this method to the determination
of copper in ores for a later investigation.
It seems possible from the results obtained in
the foregoing that a method may be arrived at
which will avoid one or two filtrations, found
to be necessary in other volumetric processes.
The experimental confirmation of this fact would
add much value to the work already done.

SUMMARY.

The points developed in this investigation may be briefly stated as follows:

1. The precipitations of copper as cupric hydroxide, cupric sulphide, cuprous iodide, and cuprous sulphocyanide, can not be measured by electrical conductivity.

2. The curve following the precipitation of cupric ferrocyanide shows two distinct breaks, neither of which corresponds to the reaction end point. The agreement in the occurrence of the first break in different experiments suggests the possibility of the determination of a factor which would render the reaction applicable to the analysis of copper. The second break probably indicates adsorbtion of the precipitant by the cupric ferrocyanide.

3. Irregularities between observed and calculated end points for the reaction involving the precipitation of copper as carbonate are caused by the wide angle formed by the

intersection of the two branches of the curve.

4. By precipitating cuprous copper with an excess
of ammonium sulphocyanide and then titrating
with silver nitrate, it is found that copper
can be determined volumetrically, using
electrical conductivity as an indicator.

5. A cell is devised with adjustible electrodes
which enable it to be quickly and conveniently
adapted to the study of any of the different
reactions through a considerable range of
concentration. The capacity of the cell
allows relatively larger quantities of a
solution to be taken which makes it
possible to use more highly diluted reagents
without greatly effecting the total concen-
tration. The use of a dilute reagent, of
course, reduces the error attendant on the
measurement of volumes.

ACKNOWLEDGMENT.

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