ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

PROGRESS REPORT

April 1 to May 25, 1954

ABSORPTION STUDIES

FOR

TRAY EFFICIENCY RESEARCH PROGRAM

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Summary

In the period from April 1 to May 25, 1954, fifty-four runs were made, absorbing carbon dioxide from air with water at 18°C and substantially at atmospheric pressure. The first forty-three of these samples were taken simultaneously from each tray. The data show the cross-overs in composition and efficiency which seem to be inherent in bubble tray tests, and we believe further study of the data is necessary before even preliminary reporting. Beginning with the forty-fourth run, samples were taken only for obtaining performance of the second active tray from the top. Eleven such runs are reported here with a brief discussion of analytical methods and vapor-liquid equilibrium data.

Work Planned for May 25 to June 30

The following operation is planned for the period May 25 to June 30 with the same

(1) carbon dioxide absorption at low gas rates and high water rates for the 3-1/2-inch weir height,
(2) absorption of ammonia from air over the same range of gas and water rates used for carbon dioxide, and
(3) humidification of air.

When these data are complete, the weir height will be changed to two inches. Sufficient data to show the effect of submergence will be taken with the above systems.

Experimental Procedure

In the absorption runs, the following items were sampled or recorded:

Rates
Water flow in (city water is used throughout)
Air flow in
Carbon dioxide flow before mixing with air

Composition
Runs 1-43, liquid entering and leaving each tray
vapor entering column and leaving tray 3
Runs 44- , liquid and gas samples as shown in Fig. 1

Pressure and Temperature
Measured at all rotameters and in the column

Froth Heights and Densities, Pressure Drops
These have all been measured separately in comprehensive
air-water tests. These have been completed for two weir
heights, 2 and 3-1/2 inches.

In the original plan of the tests, simultaneous samples were to be
taken on each plate in the column so that the performance of each plate might
be measured. The data could then be averaged by means of plots of efficiency,
composition, or other criteria as functions of absorber conditions. This
procedure was used in the first forty-three runs and proved clearly the often-
repeated statement that mass-transfer data are inherently uncertain. These
data still require more evaluation and processing before even a preliminary
presentation.

It now seems a better procedure from the standpoint of conservation
of time and effort to take several successive samples so that the operation
of a single tray may be accurately determined. The top tray, number 5, is
currently used for entrainment separation. Fresh water is introduced in the
downcomer from tray 5. The top active tray is number 4 and neutralizes the
inherent alkalinity of the water. The next tray, number 3, is then supplied
with water in which the factor of chemical reaction is not present to com-
plicate the mass-transfer mechanism. Since, of the remaining trays, number
3 has the highest concentration of carbon dioxide in the liquid phase, it
is used as the test tray. The assumption of neutralization of basic con-
stituents in city water on the top tray seems reasonable in view of the
kinetic data of Faurholt[3] for reaction between carbon dioxide and hydroxyl
ions. However, the assumption is being verified by tests on tray number 2,
although accurate data are more difficult to obtain owing to smaller concen-
trations of carbon dioxide.

Sample Points and Tray Arrangement
Used in Runs 1-54, CO_2-Water

TopTray - 5

Fresh water in

2

Tray 4

1

• Sample points

• 5

3

• Tray 3

4
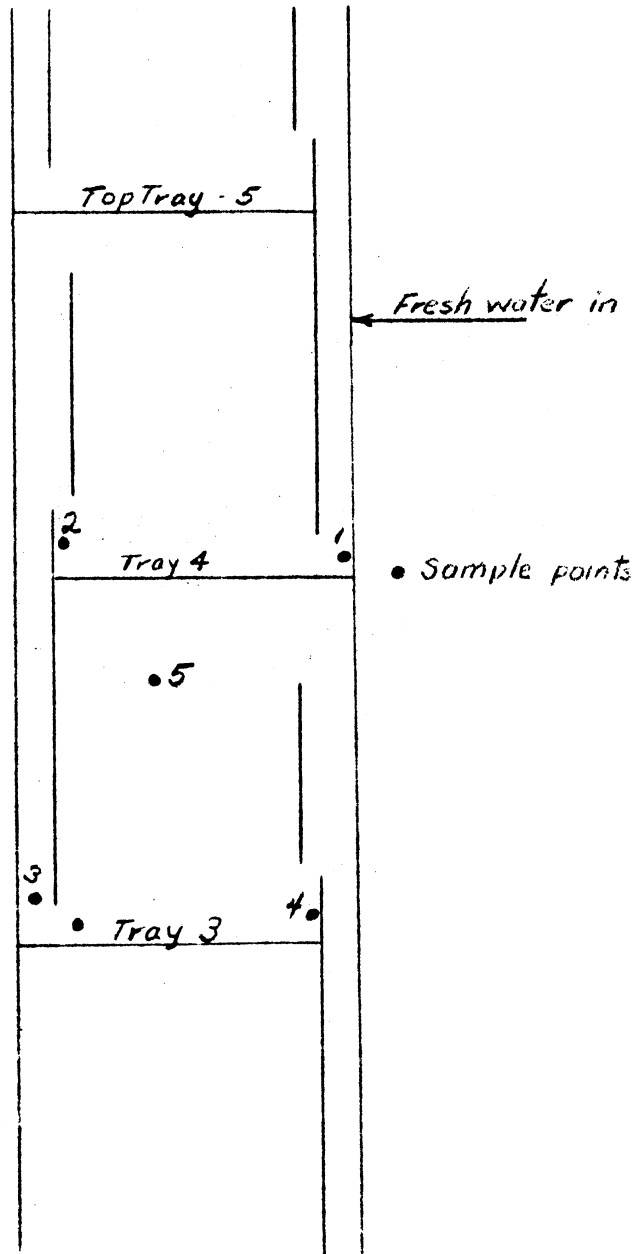
Weir height   3½ in.
Splash Baffle:
4 in from tray, 1 in from weir

FIGURE 1

Beginning with run number 44, tests were limited to tray number 3 and samples were taken at the sampling points shown in Fig. 1. The purpose of each point is as follows:

Sampling Point

1. Bottom of downcomer from tray 1. The liquid sample should be only fresh water. The sampling point is in the same position as the one in the downcomer from tray 4. The presence of any carbon dioxide indicates back-mixing from the liquid on the tray.

2. Liquid leaving tray 4.

3. Liquid leaving downcomer and entering tray 3. Any difference between here and point 2 indicates transfer in the downcomer or back-mixing from tray 3.

4. Liquid leaving tray 3, the test tray.

5. Vapor leaving tray 3. There is a negligible change in carbon dioxide content in the gas passing through the tower, and this sample is used to check the composition computed from gas rotameter readings. So far these have agreed within 0.5 percent.

Additional sampling points and taps are available for making lateral and longitudinal traverses on the tray. This will be done in the course of testing.

The eleven runs, 44-45, made on tray 3 are summarized in Table I. Only the Murphree liquid efficiencies are reported here and are shown in Figs. 2 and 3 as functions of superficial vapor velocity and the "F" factor. The efficiencies are substantially lower than those reported for desorption of carbon dioxide in the North Carolina State College, Raleigh, North Carolina. These data for tray 3 are also consistent, in general, with runs 1-43. Information from the two schools must be compared on the same basis before any conclusions are made.

It is planned to make desorption runs at Michigan to test the possibility that there is a difference between absorption and desorption. However, there is a difference in the tray layouts used. The upstream weirs were removed from the Michigan tray because the presence of the weir caused a peculiar hydraulic jump at the higher liquid rates. This phenomenon was obviously enough to induce a serious artificial effect on mass transfer at varying liquid rates, and the weirs were therefore removed. The splash baffles have been left in the Michigan column. Without these baffles the gradient across the tray was excessive. At high rates the top of the froth was at an angle of almost 30° from the horizontal.

TABLE I

SUMMARY OF RUNS 44-45
Weir length = 7.375 in.

Carbon Dioxide Absorption

Run No.	Air Rate			Water Rate		Concentration of Carbon Dioxide					E_{ML}
	cfm	ft/sec*	F=vρ	gpm	gpm/in. weir	in water mol % x 1000			in air		
						leaving tray 4		entering tray 3	mol %	partial pressure mm Hg	
44	115	3.2	0.71	9.2	1.25		1.28	1.063	2.60	19.4	0.339
45	115	3.2	0.71	9.2	1.25		1.33	1.09	2.60	19.4	0.406
46	115	3.2	0.71	9.2	1.25		1.34	1.07	2.60	19.2	0.46
47	115	3.2	0.71	4.6	0.62		1.314	1.167	2.57	19.4	0.236
48	115	3.2	0.71	18.4	2.5		1.198	0.855	2.76	20.4	0.418
49	77	2.1	0.47	18.4	2.5		1.16	0.835	2.84	21.0	0.354
50	77	2.1	0.47	9.2	1.25		1.235	0.95	2.75	20.4	0.363
51	173	4.7	1.05	9.2	1.25		1.11	0.915	2.19	16.2	0.398
52	173	4.7	1.05	4.6	0.62	0.902	1.132	0.990	2.47	16.7	0.274
53	115	3.2	0.71	4.6	0.62	0.981	1.218	1.06	2.53	18.8	0.247
54	77	2.1	0.47	4.6	0.62	0.90	1.15	1.00	2.52	18.7	0.212

*Superficial air velocity based on cross-section area between splash baffle and downcomer, 0.606 sq ft.

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Absorption of Carbon Dioxide in Water
Murphree Tray Efficiency E_{ML}
vs.
Superficial Gas Velocity

Gas velocity based on superficial area, 0.606 sq ft
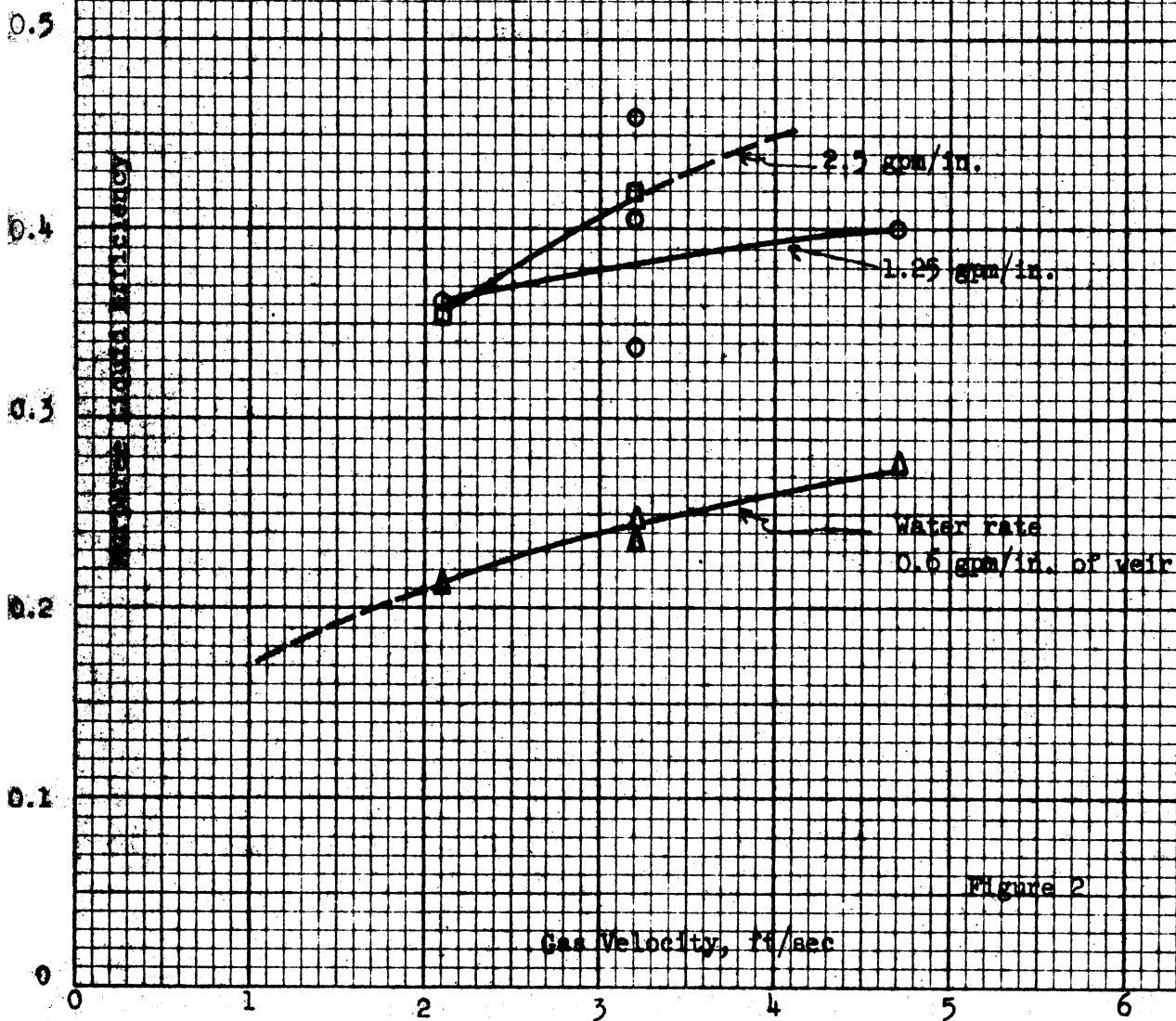between downcomer and splash baffle.

Figure 2

Absorption of Carbon Dioxide in Water
Murphree Tray Efficiency E_{ML}
vs.
F factor

F is based on gas velocity v in area of 0.606 sq ft
between downcomer and splash baffle.

2.5 gpm/in.

1.25 gpm/in.
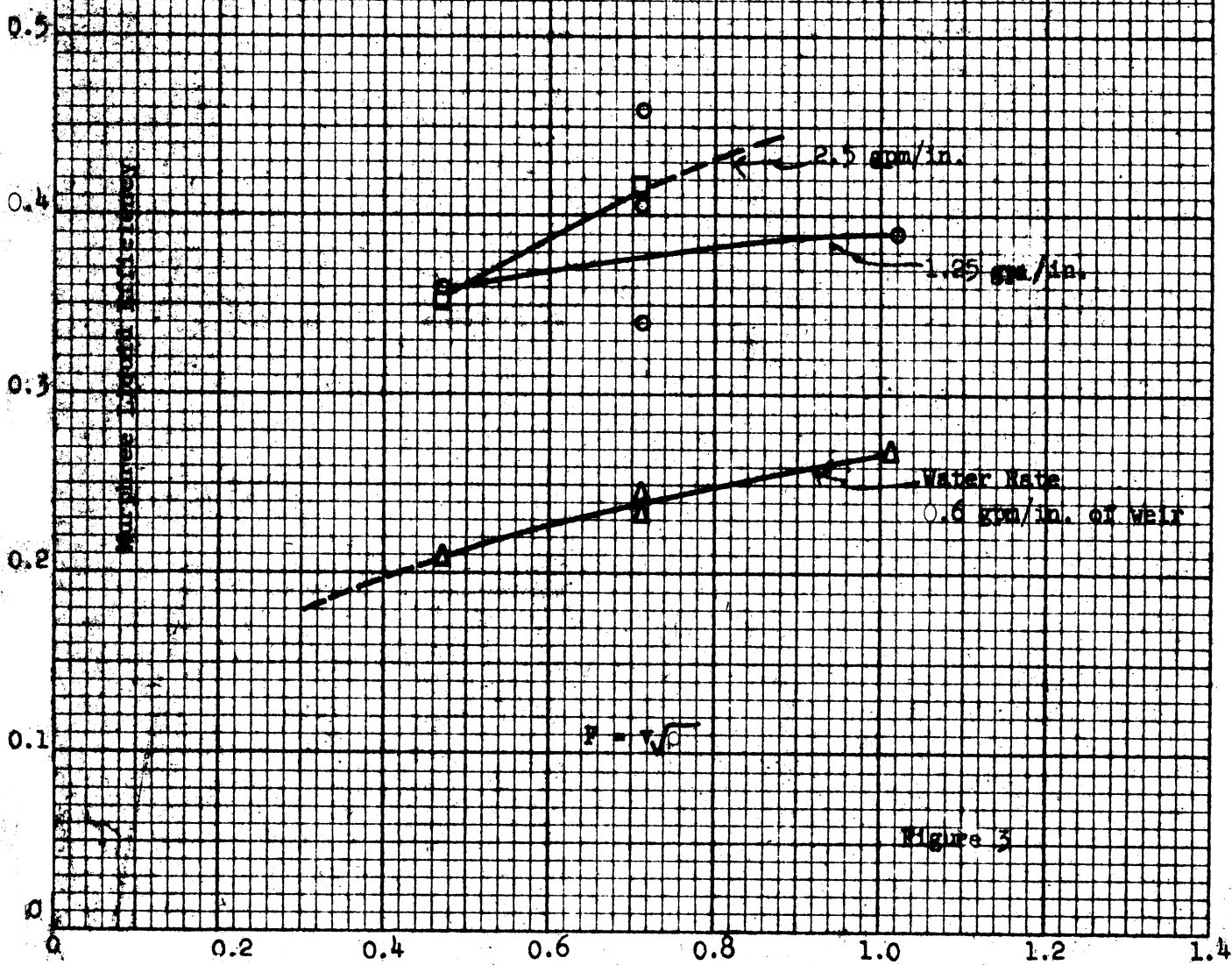
Water Rate
0.6 gpm/in. of weir

$F = v\sqrt{C}$

Figure 3

As the work progresses, many uncertainties and sources of difficulty are discovered. So many, in fact, that one wonders what information reported in the literature may be valid. It now appears that the proper action in the future on this project is to document sources of experimental error for future reference and to proceed without exhaustive study of these possible errors when relatively small. The objective of the study is the determination of the effect of fluid properties on efficiency, however expressed. It may be that only those sources should be eliminated which would cause errors in the relative effects of fluid properties. In other words, it may be too early for rigorous determination of absolute mass-transfer rates.

However, the major uncertainties in tower tests should be reported here. The first of these is sampling. The water at sampling point 1 (Fig. 1) contained carbon dioxide at flow rates of five gallons per minute and lower. This is a clear indication of back-mixing and shows that sampling point 3 will give erroneous results for computation of Murphree liquid tray efficiencies, although the data can be used for estimating mass transfer expressed in other ways.

To correct for this possible back-mixing, samples were taken of the liquid entering the downcomer on tray 4, at point 2, beginning with run 52. These data, if no back-mixing is assumed, show that as much as 40 percent of the transfer on a tray occurs in the downcomer at this liquid rate. The liquid flowing over the weir contains about one-half or more gas by volume. At the concentrations which exist in the two phases there is approximately the same weight of carbon dioxide in each phase. Considering the visible internal circulation in the downcomer at low liquid rates, a large amount of mass transfer in the downcomer is probable. This must be studied further.

As another means of estimating the effect of back-mixing on samples, visual observations were made of the movement of color across the tray as potassium permanganate solution was injected. It was introduced one-fourth inch from the outside edge of the last row of bubble caps, just above the tray floor. The observations are recorded in Table II.

Analytical Procedures

The largest source of error, and of annoyance, is the analytical procedure. As seen in Table I, the change in concentration across the test tray is about one-fourth of the total amount present. Therefore, errors are magnified by the process of subtraction. An error of 5% in one terminal concentration causes an error of about 20% in the difference and also in the tray efficiency.

The method most widely used[8] for carbon dioxide solution studies is, unfortunately, rather sensitive to traces of impurities. There are also difficulties if distilled water is used. The method involves neutralization

TABLE II

VISUAL OBSERVATIONS OF LIQUID MIXING ON TRAY

Water Rate, gal/min	Air Velocity, ft/sec	Comment
4.6	1.5	Color spread in about three seconds over entire plate, even under downcomer where liquid sample tap is located. A liquid sample drawn from tap at bottom of the downcomer was slightly colored. On the tray proper mixing was very good, but there was some gradation in color between the inlet and outlet end of the tray. (Darker at outlet end.)
4.6	2.4	Same as above except color spread a little faster and was distributed even more evenly. Outlet end darker than inlet and sample from downcomer at upstream end still slightly colored.
9	1.5 and 2.4	Color again spread over entire plate. However, color at outlet end of plate much darker than color near inlet end. No color was detectable by eye in liquid samples drawn from tap under inlet downcomer. Better mixing observed at the higher air rate.
13.5	1.5	Color spread over entire tray. Color much darker at outlet end of tray than inlet end.
13.5	2.4	Same as above only better mixing. Color did not appear under inlet downcomer around liquid sample tap.
18	2.4	Color spread over entire tray and liquid mixing was, perhaps, better at this flow rate than at 1.5 ft/sec air velocity because of increased height of liquid on tray and increased swirling.

of carbon dioxide in solutions by an excess of 0.02 N barium hydroxide and back titration with 0.01 to 0.02 N hydrochloric acid. Phenolphthalein is customarily used as an indicator. There are serious disadvantages of this method when tap water is used. They are:[6]

(1) indicators may not change color at the proper pH and in any case a color change rather than a precise pH is used, and

(2) dissolved solids have a buffering action and correction for their presence is uncertain.

To counter these objections, McKinney and Amorosi[6] proposed a method of:

(1) titrating the sample to a pH of 8.5,
(2) titrating with acid to a pH of 5.0,
(3) boiling of carbon dioxide and cooling,
(4) titrating with a base to a pH of 8.5.

The difference in molal equivalents required to titrate between pH of 5 and 8.5 before and after boiling is the amount of carbon dioxide originally present. This method is not directly usable here, but a modification has been suggested by Garber.[7]

The analytical method used here was the barium hydroxide neutralization but with a pH meter used instead of the phenolphthalein indicator in titrating. As an example of the possible error, gas samples are trapped in a bulb containing a barium hydroxide solution made with degassed, distilled water. The proper end point for titration is at 9.1 pH. The phenolphthalein end point is about 8.2-8.4 pH. Errors in carbon dioxide concentration were consistently 10-15 percent using the indicator. There are still difficulties in analyzing liquid samples even with the pH meter. For example, if the excess barium hydroxide is more than 5-6 ml of the 0.02 N solution per 100-ml sample results are apt to be erroneous. More important, it has been learned that with Ann Arbor water, at least, samples must be allowed to stand about four hours after addition of barium hydroxide before titrating. This has been verified by adding known quantities of the hydroxide to raw water and titrating after various periods of standing. An analysis of Ann Arbor water is given in Table III.

The result of analytical difficulties may be also seen in the work of Koch, et al.[5], as shown in Figs. 4 and 5. Koch and his coauthors report the absorption of carbon dioxide in packed columns. They ultimately changed from tap water to the use of circulating distilled water, but the data reported for mass-transfer rates show no large differences for tap-water as against distilled-water operation.

Solubility of Carbon Dioxide in Tap Water
at 66°F and 1 Atmospheric Pressure in the
Presence of Air

Data of Koch, Stutzman, Blum, and Hutchings
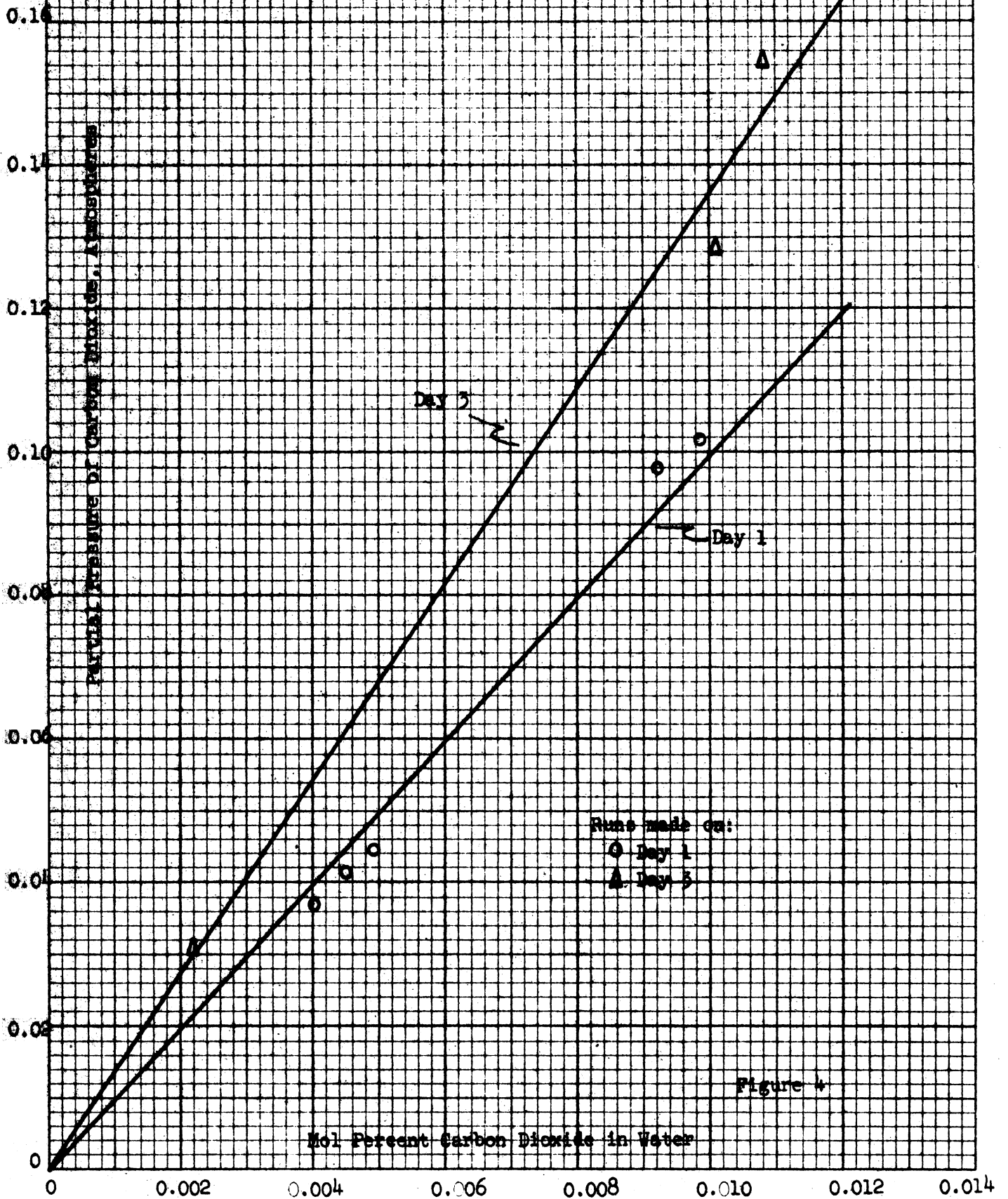(Chem. Eng. Progress 45, 677 (1949))

Figure 4

Solubility of Carbon Dioxide in Water
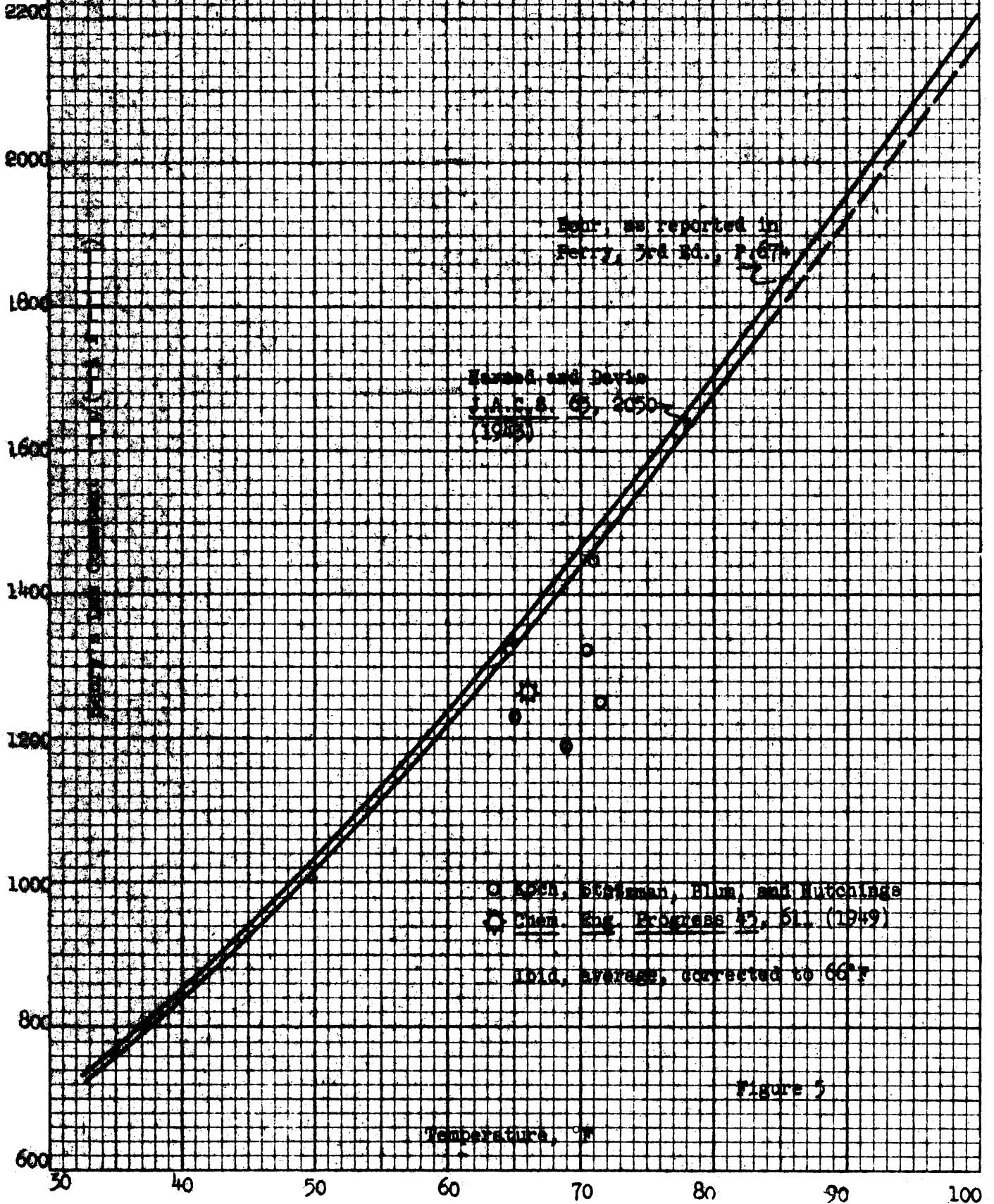Henry's Law Constant vs. Temperature

Bner, as reported in
Perry, 3rd Ed., p.674

Harned and Davis
J.A.C.S. 65, 2030
(1943)

o Koch, Stutzman, Blum, and Hutchings
Chem. Eng. Progress 42, 51, (1949)

ibid, average, corrected to 66°F

Figure 5

Temperature, °F

TABLE III

AVERAGE ANALYSIS OF ANN ARBOR WATER

Ions	Concentration parts/million
Calcium	18.8
Iron	nil
Magnesium	8.8
Sodium	30
Bicarbonate	4
Carbonate	10
Chloride	22
Sulfate	77
Acid insoluble	10
Total solids	190
Alkalinity	30 (as calcium carbonate)
Fluorine	1

Gas-Liquid Equilibrium Data

One of the results of analytical difficulties is that the impurities which cause trouble may also affect the equilibrium. The work of Harned and Davis[4], Fig. 6, showing the effect of salt on solubility of carbon dioxide, indicates that in water, dissolved solids, as such, will have a negligible effect. However, the alkaline solids will react with some of the carbon dioxide and this quantity of carbon dioxide will not contribute to the vapor pressure of the dissolved gas. It is this quantity which was mentioned earlier in the discussion of choice of tray for testing. Accordingly, the total amount of carbon dioxide in the liquid is corrected for the reacted carbon dioxide by blank analyses with distilled water.

The vapor-liquid equilibrium data used are shown in Fig. 5 as Henry's Law constants vs. temperature. The data of Bohr[1] as reported by Perry are the most widely used but are probably not as good as the data of Harned and Davis.[4] There is little difference between the two. Experimentally Bohr measured solubility by observing volume shrinkage of the gas phase. Harned and Davis analyzed the liquid phase. All used pure carbon dioxide in the gas phase at atmospheric pressure.

Koch, et al., however, measured solubilities for carbon dioxide-air-water systems. The partial pressures of carbon dioxide varied from

Solubility of Carbon Dioxide in Aqueous
Sodium Chloride Solution at 25°C

Figure 6
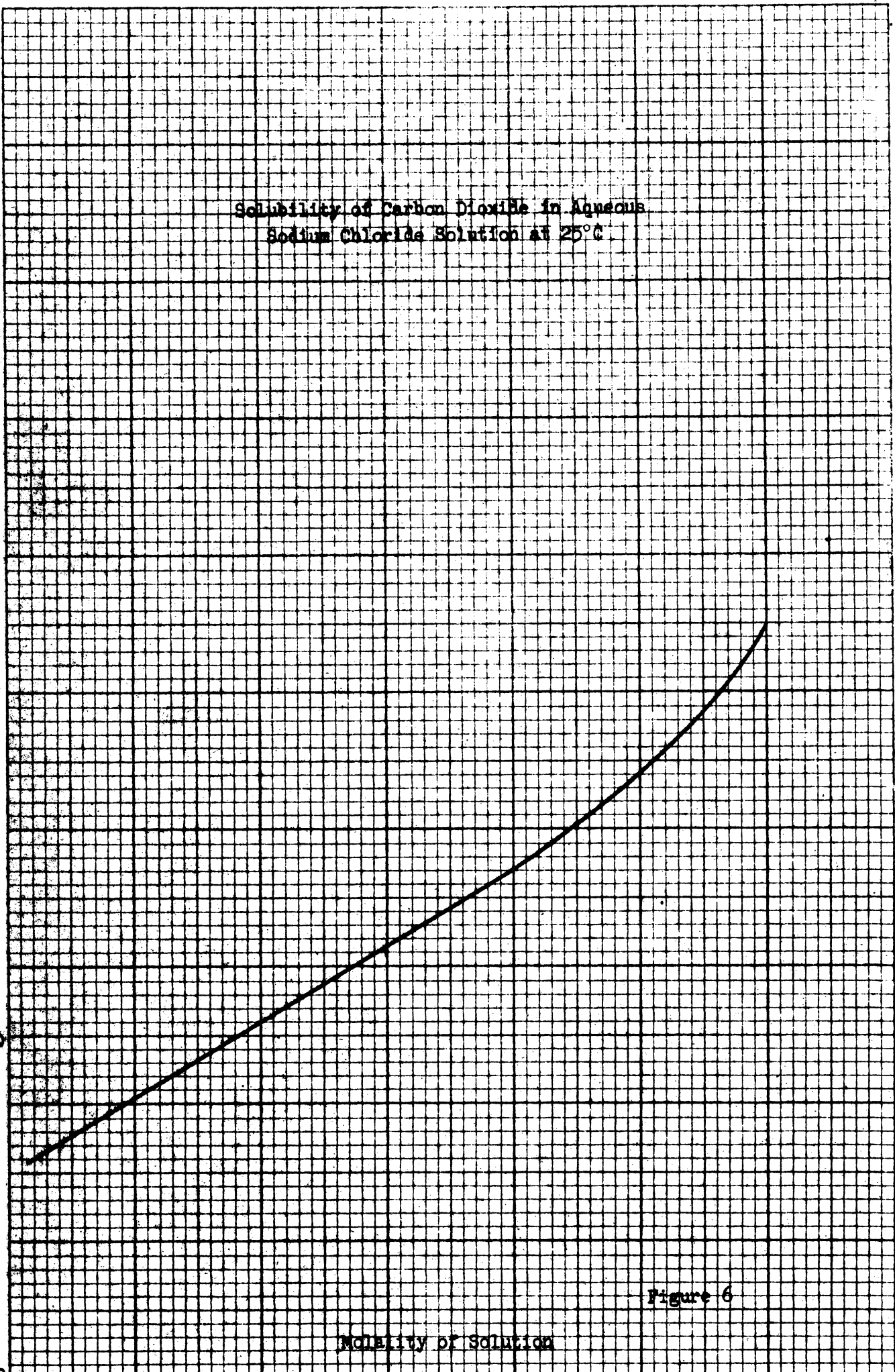
Molality of Solution

about 30 to 150 millimeters of mercury. The solubilities are lower than for a pure carbon dioxide gas phase. However, considering the scattering of the data and the method of analysis it seems best to use the Henry's Law constants of Bohr or of Harned and Davis. There are other solubility data also. Buch[2] reports solubilities of carbon dioxide in air mixtures at partial pressure of 15 millimeters of mercury down to almost zero. The data indicate a several-fold deviation from the solubility of pure gas, but the information may not be too reliable. A solubility apparatus has been constructed at Michigan for determining the validity of using Henry's Law constants measured for pure gas at atmospheric pressure for low partial pressures of carbon dioxide in air. The solubility and partial pressure of dissolved gas in Ann Arbor water will also be measured.

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