

The specific gravity and refraction were much lower in the oil from the frozen plant. A most remarkable difference between the oils is noted in the rotation, the rotation of the oil from the frozen plants being but one-sixth that of the unfrozen plants. The oil from the latter doubtless contained much higher content of laevogyrate compounds, possibly carvone. The oil from the frozen plants was much more readily soluble in 80 per cent alcohol, dissolving in one-half volume of alcohol, showing no turbidity when alcohol was added in excess, indicating a possible lower content of terpenes and a higher content of alcohol-soluble compounds.

The ester and alcohol constituents of the oil from the frozen plants differed greatly from the unfrozen material. The much higher ester content is especially significant, indicating increased activity in the esterification process in the frozen plants. The higher alcohol content also points to the existence of favorable conditions, due to frost action, affecting the formation of alcohols in the oil.

CONCLUSIONS

The yield of oil in the spearmint plant is affected by seasonal conditions, being distinctly higher in some seasons than in others. The maximum content of oil appears to be present during the flowering period, the tops containing the highest percentage of oil. Drying of the plants or plant parts results in a lower yield of oil and causes changes producing increased ester and alcohol content. Esterification and alcohol formation tend to increase as the plant matures. Freezing of the plant produces a marked increase in the formation of the odor-bearing esters and alcohols.

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CARBONATION STUDIES

II—THE CARBONATION OF DISTILLED WATER

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Water is the principal solvent in carbonated beverages such as wines, pops, malt liquors, etc., consequently a knowledge of its solvent and holding power for carbon dioxide gas is of basic importance. Data are extant for the solubility of carbon dioxide in water up to moderate pressures.¹ But very little work, if any, has been done at higher pressures, especially upon the rate of evolution of carbon dioxide from its aqueous solutions, the so-called "holding power" of the solution. The data here presented were secured on distilled water in order to give fundamental characteristics which were needed in connection with our further studies on carbonation.

METHOD AND APPARATUS

770 cc. of distilled water from our regular laboratory supply were placed in a quart champagne bottle,²

¹ Findlay and Creighton, *J. Chem. Soc.*, **97** (1910), 536; Findlay and Shen, *Ibid.*, **99** (1911), 1313; **101** (1912), 1459; Findlay and Williams, *Ibid.*, **103** (1913), 636; Findlay and King, *Ibid.*, **103** (1913), 1170.

² This quantity of liquid used in a quart bottle gives a suitable gas cushion, 18 to 25 cc. above the liquid, and approximates trade conditions of bottling.

and iced until the liquid was at the freezing temperature. An impregnating apparatus, previously described¹ and consisting essentially of a rotating stirrer fitting into the bottle, with means for admitting gas while stirring, and of measuring the pressure of the gas, was connected with a cylinder of carbon dioxide, and the water impregnated under the conditions of pressure and stirring given below. The finished product was then examined as to its holding power for the gas.

Portions of the gas withdrawn from the bottle were measured and analyzed in the apparatus shown in Fig. I. This consists of a relatively large gas burette, *G*, to hold the large quantity of gas which rushes out of the carbonated water on opening the valve of the stirring head; and a graduated gas burette, *B*, serving to measure portions of the gas from *G*, before and after

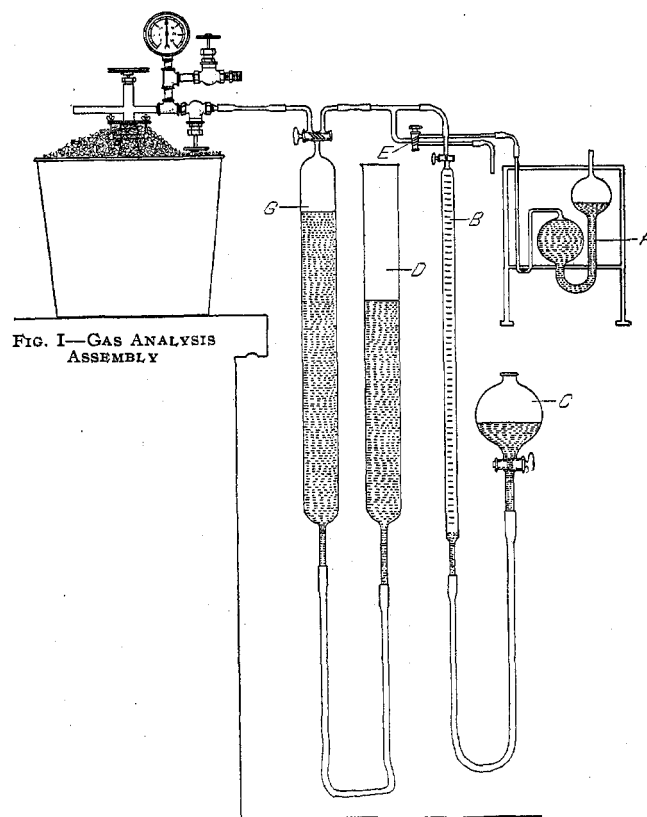


FIG. I—GAS ANALYSIS ASSEMBLY

absorption in sodium hydroxide solution in bulb *A*. Levelling tubes *C* and *D* enable one to transfer gas at will through the proper connections as shown in Fig. I. The two-way stopcock *E* and exit tube permit gas to be ejected from the system, after measurement and analysis. The apparatus is filled with a saturated brine solution which does not absorb enough carbon dioxide during the short interval of contact of gas and solution to affect the measurements of gas volume.

Recovery of pressure in the bottle after the gas cushion has been allowed to come to atmospheric pressure² is indicated on the pressure gauge when the valve is again closed. The rate of pressure recovery

¹ "Carbonation Studies—I. A Mechanical Stirrer for Impregnating Liquids with Gases," *THIS JOURNAL*, **9** (1917), 787.

² Accomplished by opening the stirring head valve for an instant and allowing gas to escape into tube *G*, Fig. I.

TABLE I—PRESSURE RECOVERY AND ANALYTICAL DATA. DISTILLED WATER. CARBONATION No. 1, SLOW SPEED STIRRING

| OPENING: First Temperature of Bottle: 0° Opening Pressure: 65 Lbs. | SECOND | | THIRD | | FOURTH | | FIFTH | | SIXTH | | SEVENTH | | EIGHTH | | NINTH | |
|--|---------------------|-----------------|-----------------|-------------|-----------------|-------------|-----------------|-------------|-----------------|-------------|-----------------|-------------|-----------------|-------------|-----------------|-------------|
| | 0° | | 0° | | 0° | | 0° | | 0° | | 0° | | 0° | | 0° | |
| | 30.5 lbs. | | 31.1 lbs. | | 30.0 lbs. | | 30.1 lbs. | | 27.0 lbs. | | 29.0 lbs. | | 27.5 lbs. | | 27.2 lbs. | |
| | PERIOD (a) M. S. | PR. (b) Lbs. | PERIOD M. S. | PR. Lbs. | PERIOD M. S. | PR. Lbs. | PERIOD M. S. | PR. Lbs. | PERIOD M. S. | PR. Lbs. | PERIOD M. S. | PR. Lbs. | PERIOD M. S. | PR. Lbs. | PERIOD M. S. | PR. Lbs. |
| RATE OF PRESSURE RECOVERY | 0 0 | 0.0 | 0 0 | 0.0 | 0 0 | 0.0 | 0 0 | 0.0 | 0 0 | 0.0 | 0 0 | 0.0 | 0 0 | 0.0 | 0 0 | 0.0 |
| | 0 5 | 1.0 | 0 1 | 3.0 | 0 1 | 2.0 | 0 1 | 4.0 | 0 1 | 3.0 | 0 1 | 6.0 | 0 1 | 3.0 | 0 1 | 2.0 |
| | 1 10 | 2.0 | 0 10 | 8.0 | 0 2 | 3.0 | 0 4 | 6.0 | 0 2 | 5.0 | 0 3 | 7.0 | 0 2 | 6.0 | 0 3 | 5.0 |
| | 2 08 | 3.0 | 0 19 | 10.0 | 0 5 | 4.0 | 0 5 | 7.0 | 0 3 | 6.0 | 0 5 | 8.0 | 0 4 | 7.0 | 0 5 | 7.0 |
| | 3 20 | 5.0 | 0 24 | 11.0 | 0 7 | 5.0 | 0 8 | 8.0 | 0 5 | 7.0 | 0 7 | 9.0 | 0 6 | 8.0 | 0 9 | 8.0 |
| | 3 45 | 6.0 | 0 34 | 12.0 | 0 9 | 6.0 | 0 10 | 9.0 | 0 11 | 8.0 | 0 13 | 11.0 | 0 10 | 9.0 | 0 11 | 9.0 |
| | 4 13 | 7.0 | 0 43 | 13.0 | 0 10 | 7.0 | 0 12 | 10.0 | 0 13 | 9.0 | 0 15 | 12.0 | 0 13 | 10.0 | 0 13 | 10.0 |
| | 4 35 | 8.0 | 0 55 | 14.0 | 0 14 | 8.0 | 0 15 | 11.0 | 0 15 | 10.0 | 0 18 | 13.0 | 0 16 | 11.0 | 0 17 | 11.0 |
| | 4 55 | 9.0 | 1 15 | 15.0 | 0 17 | 9.0 | 0 21 | 12.0 | 0 21 | 11.0 | 0 21 | 14.0 | 0 23 | 12.0 | 0 24 | 12.5 |
| | 5 45 | 11.0 | 1 32 | 16.0 | 0 24 | 10.0 | 0 28 | 13.0 | 0 26 | 12.0 | 0 26 | 15.0 | 0 29 | 13.0 | 0 30 | 13.0 |
| | 6 20 | 12.0 | 2 10 | 17.0 | 0 29 | 11.0 | 0 38 | 14.0 | 0 32 | 13.0 | 0 36 | 16.0 | 0 39 | 14.0 | 0 39 | 14.0 |
| | 7 50 | 14.0 | 2 50 | 18.0 | 0 42 | 12.0 | 1 03 | 16.0 | 0 44 | 14.0 | 0 48 | 17.0 | 0 50 | 15.0 | 0 53 | 15.0 |
| | 8 45 | 15.0 | 4 00 | 19.0 | 0 52 | 13.0 | 1 18 | 17.0 | 0 55 | 15.0 | 1 05 | 18.0 | 1 07 | 16.0 | 1 09 | 16.0 |
| | 10 00 | 16.0 | 5 35 | 20.0 | 1 09 | 14.0 | 1 45 | 18.0 | 1 11 | 16.0 | 1 23 | 19.0 | 1 29 | 17.0 | 1 27 | 17.0 |
| | 11 30 | 17.0 | 7 45 | 21.0 | 2 15 | 15.0 | 2 15 | 19.0 | 2 19 | 18.5 | 3 08 | 19.0 | 3 55 | 22.5 | 2 05 | 18.0 |
| | 19 20 | 18.5 | 12 30 | 23.0 | 3 05 | 18.0 | 3 07 | 20.0 | 3 24 | 20.0 | 5 48 | 21.0 | 15 25 | 24.0 | 3 07 | 19.0 |
| | 26 30 | 19.0 | 16 25 | 24.0 | 4 05 | 19.0 | 4 20 | 21.0 | 8 39 | 23.0 | 9 58 | 23.0 | 31 .. | 25.5 | 6 32 | 21.0 |
| | 33 05 | 20.0 | 23 10 | 25.0 | 5 30 | 20.0 | 5 35 | 22.0 | 19 49 | 25.0 | 13 33 | 24.0 | 43 .. | 26.2 | 8 52 | 22.0 |
| | 86 .. | 21.0 | 34 00 | 26.0 | 7 15 | 21.0 | 7 45 | 23.0 | 30 .. | 26.0 | 23 38 | 25.0 | 58 .. | 27.0 | 17 02 | 24.0 |
| | 1140 .. | 30.5 | 46 .. | 27.0 | 9 15 | 22.0 | 15 05 | 25.0 | 45 .. | 27.0 | 50 .. | 26.5 | 73 .. | 27.5 | 37 .. | 25.2 |
| | | | 76 .. | 28.5 | 12 03 | 23.0 | 32 15 | 27.0 | | | 64 .. | 27.0 | | | 61 .. | 26.1 |
| | | | 129 .. | 29.8 | 15 05 | 24.0 | 41 .. | 27.5 | | | 1020 .. | 29.0 | | | 92 .. | 27.2 |
| | | | 253 .. | 31.1 | 22 45 | 25.0 | 68 .. | 29.0 | | | | | | | | |
| | | | | | 35 30 | 26.0 | 138 .. | 29.8 | | | | | | | | |
| | | | | | 50 .. | 27.0 | 175 .. | 30.1 | | | | | | | | |
| | | | | | 1140 .. | 30.0 | | | | | | | | | | |
| Cc. Gas: | | | | | | | | | | | | | | | | |
| Withdrawn (c) 166.0 | | | | | | | | | | | | | | | | |
| Residual 5.8 | | | | | | | | | | | | | | | | |
| Per cent CO ₂ 96.5 | | | | | | | | | | | | | | | | |

(a) Period of Pressure Recovery is given in Minutes and Seconds, abbreviated M. and S.

(b) All gauge readings in this and the other tables are in lbs. per sq. in. where zero on the gauge equals 14.7 lbs. per sq. in. (atmospheric pressure).

(c) All gas volumes given are for standard conditions (0° C. and 760 mm. pressure) calculated from measurements at room temperature and pressure, allowance being made for the vapor pressure of the saturated sodium chloride solution over which the gas was collected, as taken from the table in the footnote on page 281.

was secured by using a stop-watch started as soon as the valve was closed, and taking simultaneous readings of time and pressure as long as the pressure continued to rise. After a sufficient number of pressure recovery curves to give the characteristic rates for the bottle had been taken, the remainder of the gas was withdrawn in convenient portions into the analysis apparatus, measured and analyzed. When practically all of the gas that would come off at ice temperature and atmospheric pressure was removed, the bottle was raised to room temperature. Further portions of gas were withdrawn, and the bottle was then placed in a steam bath and the remainder of the gas removed by boiling.

EXPERIMENTAL DATA AND DISCUSSION

CARBONATION No. 1. SLOW SPEED STIRRING

The conditions maintained during carbonation were as follows:

| | |
|--|----------------------------|
| Volume of distilled water used..... | 770 cc. |
| Volume of gas space ("gas cushion") over free surface of water in bottle..... | 18 cc. |
| Speed of stirrer..... | 400 revolutions per minute |
| Temperature of liquid..... | 0° C. (melting ice) |
| Carbonating pressure ¹ | 65 lbs. per sq. in. |

¹ All gas pressures are given in pounds per square inch above atmospheric (14.7 lbs. per sq. in.) as read by a standardized pressure gauge.

TIME SCHEDULE—Stirred under 65 lbs. pressure for 10 min., shut off carbon dioxide supply and stopped stirrer, and then opened the exit valve for an instant, thus "blowing off" the foreign gas accumulated in the gas cushion. Turned on gas, stirred at 65 lbs. pressure for 23 min., and again removed surface gas from bottle. Stirred again under the same pressure for 2 hrs. 5 min., and placed bottle in cold storage over night. Carbonation was resumed at 65 lbs. pressure, and continued for 7 hrs. 10 min. The bottle was then placed in cold storage over two nights and a day. It then showed a pressure of 20 lbs., indicating that equilibrium corresponding to the carbonating pressure had not been reached. Carbonation was continued for 3 hrs. 50 min. When the stirrer was stopped, and the gas supply shut off, the pressure in the bottle stood at 65 lbs. Total

time of stirring—13 hrs. 40 min. (round). Total period of carbonation—71 hrs.

The tests on the bottle of carbonated water were commenced immediately after the completion of the carbonation described above. The data for 17 recovery curves, together with the volume and composition of the gas evolved, are assembled in Table I, whose headings are self-explanatory.

Typical rate of pressure recovery curves, plotted from the data in Table I, using time intervals in minutes as abscissas and pressure in pounds per square inch above atmospheric as ordinates are shown in Fig. II.

PRESSURE RECOVERY CURVES—The curves plotted for Carbonation No. 1 in Fig. II were selected from the data with a view to securing uniformity in the length of time during which the pressure was allowed to rise, before the opening, and thus eliminating one of the variable factors. This factor of length of time between openings has a marked effect on the ensuing rate of pressure recovery curve as will be shown in subsequent data. In Carbonation No. 1, this effect is obscured by other factors, *e. g.*, the withdrawal of an excessive portion of gas at the first opening.

In view of the impression which prevails in the trade, that an artificially carbonated liquid loses its gas with extreme rapidity as compared with a liquid naturally carbonated (bottle fermented), the regularity of the pressure recovery curves (which of course register rate of gas evolution) is striking. One would rather expect a sudden rise of the curve and then a rather sharp cessation of pressure increase. With the exception of Curve 1, all of the curves given for Carbonation No. 1 show this regularity, being in general of logarithmic type.

Curve 1 shows a retardation in evolution of carbon dioxide in the initial portion of the curve, due to the

TABLE I (Concluded)

| TENTH 0° | ELEVENTH 0° | TWELFTH 0° | THIRTEENTH 0° | FOURTEENTH 0° | FIFTEENTH 0° | SIXTEENTH 0° | SEVENTEENTH 0° | 0° | 23° | 100° C. |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|--------|-------|---------|
| 27.5 Lbs. PERIOD M. S. Lbs. | 27.2 Lbs. PERIOD M. S. Lbs. | 26.5 Lbs. PERIOD M. S. Lbs. | 26.0 Lbs. PERIOD M. S. Lbs. | 25.6 Lbs. PERIOD M. S. Lbs. | 24.5 Lbs. PERIOD M. S. Lbs. | 25.8 Lbs. PERIOD M. S. Lbs. | 26.1 Lbs. PERIOD M. S. Lbs. | | ... | ... |
| 0 0 0.0 | 0 0 0.0 | 0 0 0.0 | 0 0 0.0 | 0 0 0.0 | 0 0 0.0 | 0 0 0.0 | 0 0 0.0 | ... | ... | ... |
| 0 1 4.0 | 0 1 5.0 | 0 1 3.0 | 0 1 3.0 | 0 1 2.0 | 0 1 2.0 | 0 2 4.0 | 0 1 2.0 | ... | ... | ... |
| 0 3 6.0 | 0 2 6.0 | 0 2 4.0 | 0 2 5.0 | 0 2 4.0 | 0 4 4.0 | 0 5 6.0 | 0 3 4.0 | ... | ... | ... |
| 0 6 7.0 | 0 4 7.0 | 0 4 5.0 | 0 5 7.0 | 0 4 5.0 | 0 6 5.0 | 0 7 7.0 | 0 4 5.0 | ... | ... | ... |
| 0 8 8.0 | 0 7 8.0 | 0 6 6.0 | 0 11 8.0 | 0 7 6.0 | 0 7 6.0 | 0 13 8.0 | 0 5 6.0 | ... | ... | ... |
| 0 12 9.0 | 0 11 9.0 | 0 9 7.0 | 0 15 9.0 | 0 9 7.0 | 0 11 7.0 | 0 23 9.0 | 0 7 7.0 | ... | ... | ... |
| 0 16 10.0 | 0 14 10.0 | 0 12 8.0 | 0 21 10.0 | 0 13 8.0 | 0 16 8.0 | 0 33 10.0 | 0 10 8.0 | ... | ... | ... |
| 0 20 11.0 | 0 20 11.0 | 0 16 9.0 | 0 27 11.0 | 0 17 9.0 | 0 21 9.0 | 0 49 12.0 | 0 13 9.0 | ... | ... | ... |
| 0 27 12.0 | 0 28 12.0 | 0 22 10.0 | 0 38 12.0 | 0 24 10.0 | 0 28 10.0 | 1 04 13.0 | 0 18 10.0 | ... | ... | ... |
| 0 39 13.0 | 0 39 13.0 | 0 30 11.0 | 0 52 13.0 | 0 31 11.0 | 0 36 11.0 | 1 22 14.0 | 0 25 11.0 | ... | ... | ... |
| 0 49 14.0 | 0 53 14.0 | 0 39 12.0 | 1 07 14.0 | 0 40 12.0 | 0 51 12.0 | 1 59 15.0 | 0 36 12.0 | ... | ... | ... |
| 1 06 15.0 | 1 11 15.0 | 0 51 13.0 | 1 37 15.0 | 0 55 13.0 | 1 07 13.0 | 2 44 16.0 | 0 50 13.0 | ... | ... | ... |
| 1 26 16.0 | 1 41 16.0 | 1 08 14.0 | 2 12 16.0 | 1 14 14.0 | 1 29 14.0 | 3 59 17.0 | 1 05 14.0 | ... | ... | ... |
| 1 56 17.0 | 2 19 17.0 | 1 33 15.0 | 3 14 17.0 | 1 41 15.0 | 2 04 15.0 | 5 29 18.0 | 1 32 15.0 | ... | ... | ... |
| 2 36 18.0 | 4 14 19.0 | 2 08 16.0 | 4 34 18.0 | 2 21 16.0 | 2 54 16.0 | 8 24 19.0 | 2 05 16.0 | ... | ... | ... |
| 3 41 19.0 | 10 39 21.5 | 2 56 17.0 | 6 54 19.0 | 3 11 17.0 | 4 00 17.0 | 10 40 20.0 | 2 50 17.0 | ... | ... | ... |
| 5 03 20.0 | 18 49 22.0 | 3 56 18.0 | 15 29 21.5 | 4 21 18.0 | 5 34 18.0 | 15 40 21.0 | 4 10 18.0 | ... | ... | ... |
| 13 36 23.0 | 18 49 23.0 | 5 06 19.0 | 19 34 22.0 | 6 41 19.0 | 8 04 19.0 | 25 40 22.0 | 6 50 19.0 | ... | ... | ... |
| 25 16 24.5 | 26 19 24.0 | 7 46 20.0 | 32 .. 23.0 | 9 31 20.0 | 11 54 20.0 | 47 .. 23.0 | 9 25 20.0 | ... | ... | ... |
| 31 16 25.0 | 42 .. 24.5 | 12 16 21.0 | 49 .. 24.0 | 15 21 21.0 | 20 14 21.0 | 96 .. 24.0 | 25 10 22.0 | ... | ... | ... |
| 54 .. 26.0 | 151 .. 26.5 | 16 46 22.0 | 90 .. 25.3 | 23 21 22.0 | 36 .. 22.2 | 126 .. 24.5 | | ... | ... | ... |
| 82 .. 26.8 | | 23 06 23.0 | 164 .. 25.6 | 58 .. 23.5 | 2400 .. 25.8 | 202 .. 25.5 | | ... | ... | ... |
| 147 .. 27.2 | | 40 .. 24.0 | | 94 .. 24.5 | | 250 .. 26.1 | | ... | ... | ... |
| 55.7 | 45.8 | 41.0 | 51.3 | 45.7 | 44.3 | 53.0 | 49.7 | 1615.5 | 766.5 | 983.7 |
| 1.2 | 0.8 | 0.7 | 1.2 | 0.4 | 0.5 | 1.5 | 0.8 | 15.5 | 3.8 | 2.0 |
| 97.8 | 98.3 | 98.3 | 97.7 | 99.1 | 98.9 | 97.2 | 98.4 | 99.0 | 99.5 | 99.8 |

GAS WITHDRAWN: At 0° C. 2575.8 cc.
 23° C. 766.5 cc.
 100° C. 983.7 cc.

Total Gas in Bottle 4326.0 cc.

Total Residual Gas from NaOH Absorption... 43.2 cc.
 Foreign Gases Present 1.0 per cent
 Gas Cushion 18 cc.
 Volume of Liquid 770 cc.

removal of an excessive amount of gas in the first opening and a consequent depletion of the gas content of the upper layers of the liquid; but the subsequent trend of this curve likewise becomes logarithmic. In succeeding openings of the bottle the valve was closed the instant that the gauge indicator stopped falling, so that only the gas was withdrawn that had been in excess of atmospheric pressure in the gas cushion and any retardation of the recovery curve, due to excessive gas removal, was eliminated.

As portions of gas are withdrawn from the bottle the amount of gas in the liquid, which is the driving force behind the pressure recovery, is gradually decreased. Hence the normal recovery curves, taken after like periods of standing, will naturally take the same form and fall slightly below each other according to their order of taking. Curve 1, due to the excessive gas withdrawal, falls much below its normal position, and as the upper layers have not yet regained their full share of gas, this effect persists in Curve 2 to a lesser extent, bringing it below its normal position. The curves beyond No. 4 are for practically normal conditions.

ACCORDANCE WITH HENRY'S LAW—To one who has not followed the carbonation industry, some of the data presented and some of the considerations discussed would appear almost axiomatic; but in looking over the field, it appears necessary to include these. For example, the solubility of these gases can be very closely calculated for various temperatures and pressures from existing data according to Henry's law. In the practical operation of carbonating machinery, however, it would appear that saturation in respect to carbon dioxide or other gas does not attain to the value that would be expected.¹

One of the contributory causes to this incomplete saturation is the presence of foreign gases which lower

¹ Henry's law is not expected, of course, to hold absolutely rigid with any gas such as carbon dioxide, which combines with the solvent or which undergoes polymerization when in solution.

the partial pressure of the carbon dioxide gas. This means that the effective pressure of the carbonation is the partial pressure of carbon dioxide, and not the total pressure of gases in the gas cushion as shown by the gauge.

The total volume of gas forced into the system was 4326 cc. calculated to 0° C. and 760 mm. pressure, allowing for the vapor tension¹ of the brine solution over which the gas was collected. Using the solubility of carbon dioxide in water at 0° C. and 760 mm. as 1.713 volumes² carbon dioxide per unit volume of water, at the indicated carbonating pressure, 65 lbs. per sq. in., there would be according to Henry's law 7150 cc. of gas dissolved in the 770 cc. of water in the bottle.

It might then be inferred that at this high pressure Henry's law does not hold; but in this case we are not dealing with equilibrium conditions. The initial pressure, 65 lbs., simply represents the carbonation pressure from the source of carbon dioxide gas plus the partial pressures of any foreign gases³ left in the gas cushion.

The partial pressure⁴ of carbon dioxide in the gas

¹ From the data obtained by Emden, and given in Landolt-Bornstein, "Physikalisch-Chemische Tabellen," 4th Ed., 1912, p. 410, Table 119, the vapor tension of a solution of NaCl saturated at 20° C. was calculated for various temperatures by graphical extrapolation. These calculated data are given here for convenient reference in the following table:

VAPOR TENSION OF SODIUM CHLORIDE SOLUTION
 (36 g. NaCl per 100 g. H₂O = saturation point at 20° C.)

| Temp. 15° C. | Pressure mm. of Hg | Temp. 22° C. | Pressure mm. of Hg | Temp. 29° C. | Pressure mm. of Hg |
|-----------------|-----------------------|-----------------|-----------------------|-----------------|-----------------------|
| 15 | 9.6 | 22 | 15.0 | 30 | 22.1 |
| 16 | 10.2 | 23 | 15.9 | 31 | 23.3 |
| 17 | 10.9 | 24 | 16.8 | 32 | 24.7 |
| 18 | 11.6 | 25 | 17.7 | 33 | 26.2 |
| 19 | 12.4 | 26 | 18.7 | 34 | 27.8 |
| 20 | 13.2 | 27 | 19.8 | 35 | 29.4 |
| 21 | 14.1 | 28 | 20.9 | | 31.0 |

² Van Nostrand's "Chemical Annual," Olsen, 3rd Ed., 1913, p. 736, Table XXV. Data by Bohr and Bock.

³ The foreign gases present come from three sources: air originally dissolved in the water used, air in gas cushion above the liquid, and the small amount of nitrogen in the carbon dioxide gas used. See paragraph on gas analysis and composition for the quantities of foreign gas present.

⁴ The value of the partial pressure of CO₂ in the gas cushion is found as follows: Since the opening pressure in the gas cushion was 65 lbs. above atmospheric, or 5.42 atmospheres, and the volume of foreign gas withdrawn

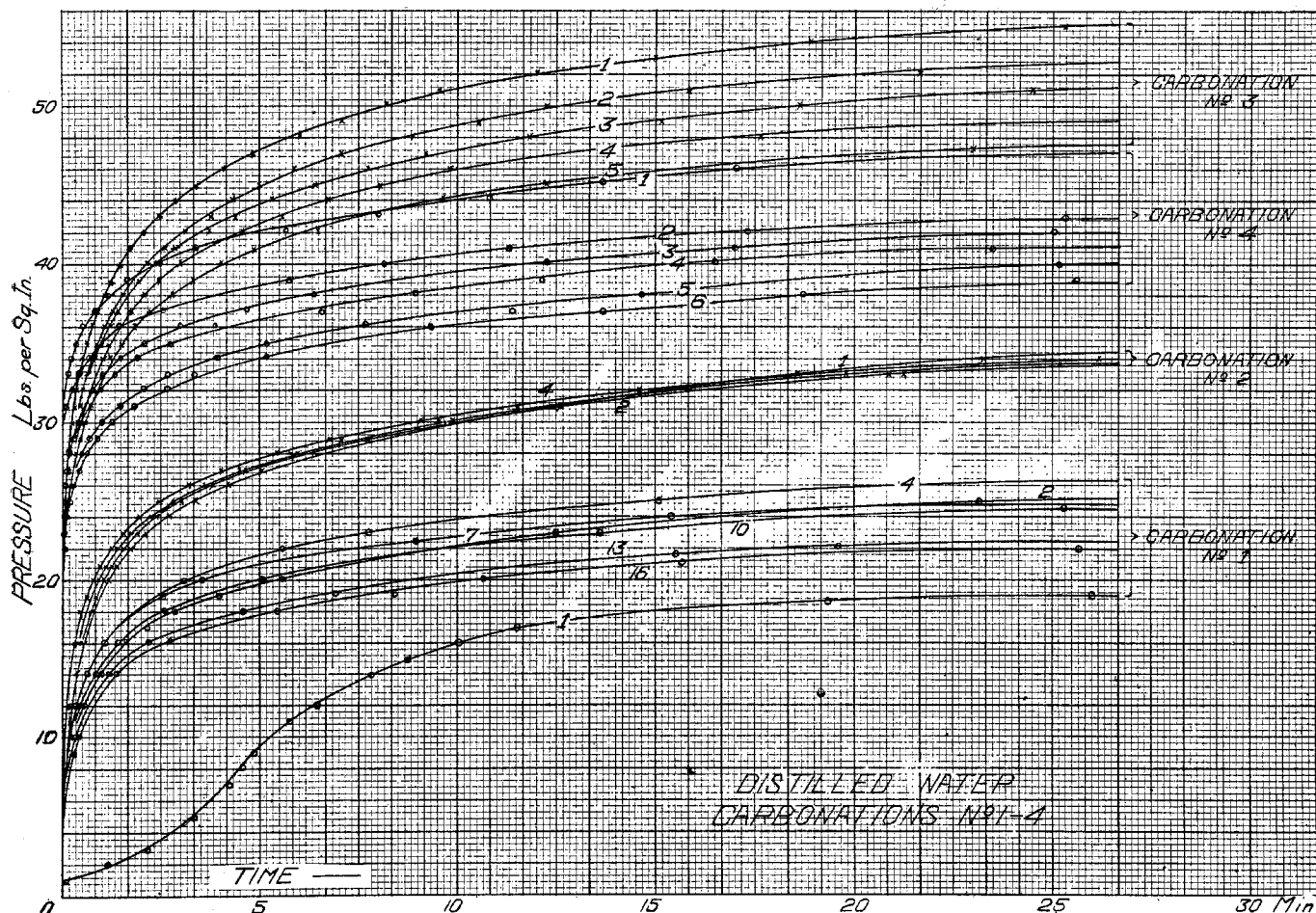


FIG. II—PRESSURE RECOVERY CURVES

cushion of the bottle at this stage is 5.03 atmospheres or 59.2 lbs. above atmospheric pressure, and the volume of CO_2 in the liquid, if complete saturation had been reached, would be 6635 cc. Actually there were 4190 cc. of carbon dioxide in the liquid. This simply shows that saturation was not complete, and that even after this extremely long period of stirring complete equilibrium between the gas dissolved in the liquid and the gas in the gas cushion under the carbonating pressure was not reached.

When, however, the recovered pressure, 30.5 lbs., 19 hrs. after the first opening of the bottle (Table I) is reached, a comparison of the total carbon dioxide contained in the liquid at that point, 4070 cc.,¹ with the theoretical volume calculated from solubility data and at the first opening by reducing the pressure to atmospheric was 5.8 cc., there must have been $(5.8 \times 5.42) + 4.42 = 7.1$ cc. of foreign gas in the gas cushion before opening. With the volume of gas cushion 18 cc. the partial pressure of foreign gas is $7.1 \div 18 = 0.39$ atmospheres. The partial pressure of carbon dioxide in the gas cushion is then $5.42 - 0.39 = 5.03$ atmospheres or 59.2 lbs. above atmospheric.

¹ The total gas in the bottle at this point is 4160 cc. (4326 cc. — 166 cc. withdrawn at the first opening). Of this volume, a portion $(18 \times 30.5 + 14.7/14.7 = 55.3 \text{ cc.})$ is in the gas cushion above the liquid, and the remainder, 4105 cc. (reading to the nearest unit), is dissolved in the liquid. The foreign gas withdrawn at the second opening is 1.5 cc.; foreign gas in gas cushion before withdrawal $= (1.5 \times 3.07) + 2.07 = 2.2 \text{ cc.}$ This volume subtracted from the total volume of foreign gas in the bottle, 37.4 cc., leaves 35.2 cc. foreign gas in the liquid. The actual volume of CO_2 in the liquid then at the time of 2nd opening was $4105 - 35 = 4070 \text{ cc.}$ The partial pressure of foreign gas was $2.2/18 = 0.12$ atmospheres or 1.8 lbs. The partial pressure of carbon dioxide then equals $30.5 - 1.8 = 28.7$ lbs. above atmospheric. The calculated volume of CO_2 in the liquid corresponding to this pressure according to Henry's law is $(28.7 + 14.7) \div 14.7 \times 0.770 \times 1.713 = 3890 \text{ cc.}$

Henry's law, 3890 cc., shows a slight degree of supersaturation. Our observation has been that complete equilibrium in the bottle between the gas in the liquid and in the gas cushion is not quite reached at the end of 19 hrs., but is approximately so after a 40-hr. period, as will be shown by subsequent data. These results, then, show that at high pressures of CO_2 we have a close agreement with Henry's law.

Applying now these considerations to the case of carbonated beverages as put out in the trade, it will be seen how and why a poorly carbonated product (with large percentage of foreign gas present or insufficient period of carbonation) may have a high initial pressure in the gas cushion, without having a correspondingly great quantity of gas held in the liquid. The result of this is that, when the pressure drops to atmospheric upon opening of the bottle, the liquid may remain almost non-effervescent.

COMPOSITION OF THE GAS—The total residual gas after absorption over sodium hydroxide was 43.2 cc. or 1.0 per cent of the total gas.¹ Analysis shows that a large portion of the residual foreign gas in the gas cushion is withdrawn at the first opening. Thus of the total residual gas in the bottle 5.8 cc., or approximately 13 per cent, was withdrawn at the first opening. In the next two openings also comparatively large

¹ The carbon dioxide gas used in these carbonations showed an average analysis of 99.7 per cent CO_2 . The foreign gas contained no oxygen or carbon monoxide, and consisted of nitrogen, with perhaps a trace of the rare gases.

TABLE IIA—CARBONATING CONDITIONS: CARBONATION No. 2

| Distilled Water Used 770 cc. | | Temperature of Water during Carbonation 0° C. | | Speed of Stirrer 400 r. p. m. | Carbonating Pressure 70 lbs. per sq. in. | Gas Cushion 25 cc. | |
|------------------------------------|---------------|---|--------------------------------|-------------------------------------|--|---------------------------|---|
| PERIOD OF STIRRING | | | PRESSURE AT END OF STIRRING | | SUBSEQUENT TREATMENT | PERIOD OF RISE Sec. | PRESSURE RECOVERED Lbs. per sq. in. |
| Started at | Stopped at | Interval Hrs. | Min. | Lbs. per sq. in. | | | |
| 3: 43 | 3: 53 | 0 | 10 | 70 | Opened valve, letting off gas to zero pressure. Closed valve, { noting pressure recovery in each case. Let bottle stand over night. Pressure dropped to zero. Let bottle stand over night. Pressure dropped to 34.5 lbs. Gas supply shut off. Gas supply turned on. | 240 | 0 |
| 3: 57 | 4: 20 | 0 | 23 | 56 | | 10 | 6 |
| 4: 24 | 4: 30 | 0 | 6 | 41 | | | |
| 11: 35 | 4: 31 | 4 | 56 | 70 | | | |
| 11: 05 | 12: 40 | 1 | 35 | 70 | Let bottle stand over Sunday, pressure fell to 60 lbs. Connected to analysis apparatus and began test (See Table IIB). TOTAL PERIOD OF CARBONATION—48 hrs. 40 min. (round). | | |
| 12: 40 | 1: 40 | 1 | 0 | 48.5 | | | |
| 1: 40 | 4: 25 | 2 | 45 | 70 | | | |
| Total Stirring..... | | 10 | 55 | | | | |

TABLE IIB—PRESSURE RECOVERY AND ANALYTICAL DATA: CARBONATION No. 2. SLOW SPEED STIRRING

| First Opening 0° | | Second Opening 0° | | Third Opening 0° | | Fourth Opening 0° | | 0° | 24° | 100° C. |
|---|---------------------|----------------------|---------------------|---------------------|---------------------|----------------------|---------------------|------------------|--------------|---------|
| Temperature of Bottle Opening Pressure | Period Min. Sec. | Pressure Lbs. | Period Min. Sec. | Pressure Lbs. | Period Min. Sec. | Pressure Lbs. | Period Min. Sec. | Pressure Lbs. | | |
| 60.0 lbs. | 0 0 | 0.0 | 0 0 | 0.0 | 0 0 | 0.0 | 0 0 | 0.0 | | |
| | 0 2 | 3.0 | 0 1 | 5.0 | 0 1 | 4.0 | 0 3 | 8.0 | | |
| | 0 5 | 6.0 | 0 8 | 10.0 | 0 3 | 8.0 | 0 6 | 10.0 | | |
| | 0 11 | 10.0 | 0 10 | 11.0 | 0 5 | 10.0 | 0 9 | 12.0 | | |
| | 0 15 | 12.0 | 0 19 | 14.0 | 0 12 | 14.0 | 0 14 | 14.0 | | |
| | 0 23 | 14.0 | 0 28 | 16.0 | 0 18 | 16.0 | 0 20 | 16.0 | | |
| | 0 31 | 16.0 | 0 42 | 18.0 | 0 28 | 18.0 | 0 30 | 18.0 | | |
| | 0 45 | 18.0 | 1 05 | 20.0 | 0 37 | 19.0 | 0 44 | 20.0 | | |
| | 1 01 | 20.0 | 1 23 | 21.0 | 0 48 | 20.0 | 0 56 | 21.0 | | |
| | 1 15 | 21.0 | 1 43 | 22.0 | 1 02 | 21.0 | 1 11 | 22.0 | | |
| | 1 31 | 22.0 | 2 10 | 23.0 | 1 23 | 22.0 | 1 32 | 23.0 | | |
| | 1 56 | 23.0 | 2 41 | 24.0 | 1 44 | 23.0 | 1 52 | 24.0 | | |
| | 2 22 | 24.0 | 3 25 | 25.0 | 2 12 | 24.0 | 2 28 | 25.0 | | |
| | 3 02 | 25.0 | 4 11 | 26.0 | 2 53 | 25.0 | 3 10 | 26.0 | | |
| | 3 51 | 26.0 | 5 08 | 27.0 | 3 38 | 26.0 | 4 03 | 27.0 | | |
| | 4 43 | 27.0 | 6 22 | 28.0 | 4 40 | 27.0 | 5 25 | 28.0 | | |
| | 5 59 | 28.0 | 7 42 | 29.0 | 5 55 | 28.0 | 6 45 | 29.0 | | |
| | 7 12 | 29.0 | 9 50 | 30.0 | 7 10 | 29.0 | 9 05 | 30.0 | | |
| | 9 03 | 30.0 | 12 30 | 31.0 | 9 30 | 30.0 | 12 25 | 31.0 | | |
| | 11 33 | 31.0 | 15 50 | 32.0 | 12 35 | 31.0 | 15 35 | 32.0 | | |
| | 14 35 | 32.0 | 21 15 | 33.0 | 15 50 | 32.0 | 27 00 | 34.0 | | |
| | 18 34 | 33.0 | 27 45 | 34.0 | 20 50 | 33.0 | 35 .. | 35.0 | | |
| | 24 05 | 34.0 | 35 .. | 35.0 | 26 10 | 34.0 | 45 .. | 36.0 | | |
| | 37 .. | 35.5 | 46 .. | 36.0 | 32 40 | 35.0 | 60 .. | 37.0 | | |
| | 43 .. | 36.0 | 65 .. | 37.0 | 44 .. | 36.0 | 1000 .. | 40.3 | | |
| | 59 .. | 37.0 | 91 .. | 38.0 | 61 .. | 37.0 | | | | |
| | 70 .. | 38.0 | 107 .. | 38.5 | 100 .. | 38.0 | | | | |
| | 96 .. | 39.0 | 2900 .. | 43.5 | 160 .. | 39.0 | | | | |
| | 125 .. | 40.0 | | | | | | | | |
| | 1140 .. | 43.5 | | | | | | | | |
| Cc. Gas: Withdrawn | 63.6 | | 89.0 | | 91.1 | | 72.0 | | 2825.4 | 947.4 |
| Residual | 10.4 | | 6.0 | | 5.1 | | 1.6 | | 17.7 | 9.0 |
| Per cent CO ₂ | 83.6 | | 93.3 | | 94.4 | | 97.8 | | 99.4 | 99.1 |
| GAS WITHDRAWN: At 0° C..... | | 3141.1 cc. | | | | | | | 51.6 cc. | |
| 24° C..... | | 947.4 cc. | | | | | | | 1.0 per cent | |
| 100° C..... | | 1041.0 cc. | | | | | | | 25 cc. | |
| Total Gas in Bottle..... | | 5129.5 cc. | | | | | | | 770 cc. | |

portions of residual gas were found. After this period, the volumes of residual gas in the portions withdrawn at the various openings were much smaller and fairly constant, except that upon standing for long periods (over night) more of the foreign gas collected in the gas cushion, giving a lower per cent of carbon dioxide in the gas withdrawn at the succeeding opening.

EFFECT OF GAS CUSHION—The volume of the gas cushion was determined, as necessary to the determination of the partial pressures of the gases in it, and since the rate of rise of pressure obviously is influenced somewhat by the size of the space that the gas liberated at the surface of the liquid has to fill.

CARBONATION No. 2. SLOW SPEED STIRRING

A second bottle of distilled water was carbonated with the stirrer rotating at the same rate and the data of the first carbonation were practically duplicated.

The conditions of carbonation are given in Table IIA. In Table IIB is presented the rate of pressure recovery data for Carbonation No. 2, and the corresponding curves are plotted in Fig. II.

DISCUSSION OF DATA—The carbonating pressure from the cylinder was a little higher in this case than in the first carbonation (70 lbs. compared with 65 lbs.) and consequently a somewhat greater volume of gas was forced into the liquid in a slightly shorter time than in the first carbonation. The data, however, coincide

with those of Carbonation No. 1 in general. It is again shown that at this slow speed stirring (400 r. p. m.) a very long period of stirring (11 to 13 hrs.) is necessary to obtain a fair degree of carbonation, and even after this long period the saturation point is not reached. To illustrate, the partial pressure of carbon dioxide gas at the first opening is 4.56 atmospheres¹ or 52.3 lbs. above atmospheric pressure, and the corresponding volume of carbon dioxide that should be dissolved in the liquid according to Henry's law, is 6015 cc. The actual volume of CO₂ in the liquid at this point is only 4965 cc.

At the third opening, after the bottle had stood for over 40 hrs. and equilibrium between the carbon dioxide in the gas cushion and in the liquid had practically been reached, we find a very close agreement with Henry's law and solubility data. The actual volume of carbon dioxide in the liquid at this point is 4850 cc. The partial pressure of carbon dioxide is 3.69 atmospheres or 39.6 lbs. per sq. in. above atmospheric pressure, and the corresponding volume of gas in the liquid should be: $770 \times 1.713 \times 3.69 = 4865$ cc.

¹ The partial pressure of CO₂ is determined in a manner similar to that in Carbonation No. 1, i. e., calculating the volume of foreign gas in the gas cushion from the volume of foreign gas withdrawn at the first opening, from that the partial pressure of foreign gas, and subtracting the latter from the total initial pressure to obtain the partial pressure of CO₂. The volume of CO₂ actually in the liquid is the total gas volume minus the volume of gas in gas cushion, minus the volume of foreign gas in the liquid.

The agreement is as close as could possibly be obtained within the limits of accuracy afforded by the methods used.

RATE OF PRESSURE RECOVERY—By glancing at the pressure recovery curves shown in Carbonation No. 2, Fig. II, it will be seen that the general form is of the same logarithmic type as for the curves in Carbonation No. 1. The curves lie very close together, over-running one another, much as did the first four curves in Carbonation No. 1. If a continued set of curves had been taken in this case down to a low pressure recovery, the curves would have gradually fallen below those preceding in a similar manner to the curves in Carbonation No. 1.

There are three important factors that affect the rate of pressure recovery from the same solution at various stages. One which has been mentioned before is the quantity of gas removed at the opening. The removal of an excessively large amount of gas (by not closing gauge as soon as indicator ceases to fall) strips the gas from the top layers of solution, and retards the rate of pressure recovery.

A second factor is the formation of bubbles on the container surface. When gas escapes from the liquid in a container, small bubbles form on the sides of the container serving as nuclei for the liberation of gas from solution. The pressure recovery curve taken after the bottle has been standing over night shows a slowing down due to the resolution of the bubbles that had formed on the inner surface of the bottle. As soon as the bottle is opened we again have the bubbles formed, and if a second recovery curve is taken on the same day the rate will be speeded up. The shorter the period between openings the more will this speeding up be in evidence.

A third factor affecting the rate of pressure recovery is the relation between the concentrations of gas in the various layers of liquid and in the gas cushion at the time of opening the bottle. When the bottle is opened and the gas in excess of atmospheric pressure is withdrawn from the gas cushion, the gas in the upper layers of liquid rushes into the gas cushion while that in the lower layers passes more gradually into both gas cushion and stripped upper layers, until finally when equilibrium is reached the concentration throughout the liquid layers is practically uniform. However, when the bottle is opened before equilibrium has been reached, the upper liquid layers are not at their full concentration, and hence the rate of pressure recovery is slowed down. The amount of this slowing down will depend on the interval between the successive openings: the shorter the interval the greater the tendency to slow down the pressure recovery rate, due to this effect.

We have, then, two counterbalancing factors, formation of bubbles and relative gas concentrations in the different liquid layers, both of which are dependent upon the period between successive openings. The shorter the period the more will the rate curve tend to be speeded up, due to bubble formation, but at the same time the more will it tend to slow down, due to low concentration of gas in the upper layers. The exact length of the period, the nature of the solution,

the total pressure in the bottle, the roughness of the inner bottle surface (serving to accentuate bubble formation) all go to determine which of these counterbalancing factors will predominate. Often then the curve will rise excessively during the first few minutes owing to the presence of bubbles, and then recross the preceding curve and fall below it, due to the low concentration of the upper layers of solution at the time of opening. The action of these factors may be seen in the curves in Carbonation No. 2, Fig. II, but are brought out more distinctly in Carbonations Nos. 3 and 4.

COMPOSITION OF THE GAS—While the amount of foreign gas in the bottle was slightly greater than in Carbonation No. 1, the percentage of foreign gas based on the total gas content was identical in the two cases, being 1.0 per cent. Of the total foreign gas present (51.6 cc.) 10.4 cc., or about 20 per cent, was withdrawn at the first opening. It will be noticed here again that the foreign gas does not come out of the liquid as rapidly as the carbon dioxide does, so that the volume of foreign gas in the portions withdrawn is smaller than normal, except where the bottle has been allowed to stand over night before opening.

EFFECT OF GAS CUSHION—The volume of gas cushion, 25 cc., is 7 cc. greater than that in Carbonation No. 1. The smaller gas cushion would tend to favor a somewhat more rapid rise of pressure due to liberated gas, but this is partly compensated, in case of the larger gas cushion, by the increased area of the free surface of liquid in the bottle, produced by the flaring of the neck. This increased area permits the more rapid evolution of gas. It was shown by measurement and graphical calculations that, at the point on a standard champagne bottle where the neck begins to flare, the increase in volume of the gas cushion bears a linear relation to the increase in free surface of the liquid in the bottle. Bottles of such size as to furnish a 25 cc. gas cushion were also used in Carbonations Nos. 3 and 4.

CARBONATION NO. 3. HIGH SPEED STIRRING

The remarkable slowness with which the carbon dioxide was absorbed in Carbonation No. 1, suggested that increased rate of stirring be tried. Consequently the speed of the stirrer was increased from 400 revolutions per minute to 2500.

The conditions of carbonation for this bottle are given in Table IIIA.

The rate of pressure recovery data are presented in Table IIIB, under appropriate headings, and the rate curves plotted therefrom are shown in Carbonation No. 3, Fig. II.

One is immediately struck by the tremendous increase in efficiency of carbonation produced by a simple increase in speed of stirring. The total gas forced into the system was 6263 cc. stirring at 2500 r. p. m. compared with 5130 cc. at 400 r. p. m. (Carbonation No. 2), the carbonation pressure, volume of liquid, volume of gas cushion, and number of blow-offs being the same. The period of stirring was only 6 minutes with the high speed stirring compared with approximately 11 hours for Carbonation No. 2. This means that by increasing the rate of stirring about six times

TABLE IIIA—CARBONATING CONDITIONS: CARBONATION No. 3

| Distilled Water Used 770 cc. | | | Temperature of Water during Carbonation 0° C. | | Speed of Stirrer 2500 r. p. m. | | Carbonating Pressure 70 lbs. per sq. in. | | Gas Cushion 25 cc. | | |
|------------------------------------|---------------|------------------|---|--|--------------------------------------|--|--|--|---|----|--|
| PERIOD OF STIRRING | | | PRESSURE AT END OF STIRRING | | SUBSEQUENT TREATMENT | | PERIOD OF RISE Sec. | | PRESSURE RECOVERED Lbs. per sq. in. | | |
| Started at | Stopped at | Interval Min. | Lbs. per sq. in. | | | | | | | | |
| 2 : 40 | 2 : 41 | 1 | 43 | } Opened valve, letting off gas to zero pressure. Closed valve, { noting pressure recovery in each case. Connected bottle to analysis apparatus and began test (See Table IIIB). TOTAL PERIOD OF CARBONATION—9 minutes. | | | | | 15 | 42 | |
| 2 : 42 | 2 : 44 | 2 | 62 | | | | | | | | |
| 2 : 46 | 2 : 49 | 3 | 70 | | | | | | | | |
| Total Stirring..... | | | 6 | | | | | | | | |

TABLE IIIB—PRESSURE RECOVERY AND ANALYTICAL DATA: CARBONATION No. 3. HIGH SPEED STIRRING

| First Opening | | Second Opening | | Third Opening | | Fourth Opening | | Fifth Opening | | 0° | | 26° | | 100° C. | |
|--|------|----------------|------|---------------|------|--|------|---------------|------|-------------|------|-------------|------|-------------|------|
| Temperature of Bottle Opening Pressure | | 0° | | 0° | | 0° | | 0° | | 0° | | 0° | | 26° | |
| 70.0 lbs. | | 60.0 lbs. | | 56.7 lbs. | | 54.0 lbs. | | 53.0 lbs. | | | | | | | |
| PERIOD Min. | Sec. | PERIOD Min. | Sec. | PERIOD Min. | Sec. | PERIOD Min. | Sec. | PERIOD Min. | Sec. | PERIOD Min. | Sec. | PERIOD Min. | Sec. | PERIOD Min. | Sec. |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 |
| 0 | 2 | 0 | 2 | 0 | 2 | 0 | 2 | 0 | 2 | 0 | 2 | 0 | 2 | 0 | 2 |
| 0 | 3 | 0 | 3 | 0 | 3 | 0 | 3 | 0 | 3 | 0 | 3 | 0 | 3 | 0 | 3 |
| 0 | 5 | 0 | 5 | 0 | 4 | 0 | 4 | 0 | 5 | 0 | 5 | 0 | 5 | 0 | 5 |
| 0 | 15 | 0 | 22 | 0 | 7 | 0 | 13 | 0 | 8 | 0 | 8 | 0 | 8 | 0 | 8 |
| 0 | 19 | 0 | 28 | 0 | 14 | 0 | 16 | 0 | 11 | 0 | 11 | 0 | 11 | 0 | 11 |
| 0 | 22 | 0 | 33 | 0 | 23 | 0 | 22 | 0 | 13 | 0 | 13 | 0 | 13 | 0 | 13 |
| 0 | 25 | 0 | 40 | 0 | 29 | 0 | 30 | 0 | 17 | 0 | 17 | 0 | 17 | 0 | 17 |
| 0 | 31 | 0 | 47 | 0 | 34 | 0 | 38 | 0 | 22 | 0 | 22 | 0 | 22 | 0 | 22 |
| 0 | 37 | 0 | 52 | 0 | 41 | 0 | 47 | 0 | 27 | 0 | 27 | 0 | 27 | 0 | 27 |
| 0 | 45 | 0 | 63 | 0 | 50 | 0 | 58 | 0 | 34 | 0 | 34 | 0 | 34 | 0 | 34 |
| 0 | 55 | 1 | 19 | 0 | 58 | 1 | 10 | 0 | 43 | 0 | 43 | 0 | 43 | 0 | 43 |
| 1 | 03 | 1 | 34 | 1 | 10 | 1 | 26 | 0 | 52 | 0 | 52 | 0 | 52 | 0 | 52 |
| 1 | 14 | 1 | 54 | 1 | 27 | 1 | 46 | 0 | 63 | 0 | 63 | 0 | 63 | 0 | 63 |
| 1 | 25 | 2 | 10 | 1 | 44 | 2 | 08 | 0 | 74 | 0 | 74 | 0 | 74 | 0 | 74 |
| 1 | 42 | 2 | 37 | 2 | 04 | 2 | 30 | 0 | 85 | 0 | 85 | 0 | 85 | 0 | 85 |
| 2 | 03 | 3 | 10 | 2 | 27 | 3 | 01 | 0 | 96 | 0 | 96 | 0 | 96 | 0 | 96 |
| 2 | 31 | 3 | 47 | 2 | 53 | 3 | 25 | 0 | 107 | 0 | 107 | 0 | 107 | 0 | 107 |
| 2 | 55 | 4 | 20 | 3 | 43 | 4 | 36 | 0 | 118 | 0 | 118 | 0 | 118 | 0 | 118 |
| 3 | 25 | 5 | 01 | 4 | 25 | 5 | 37 | 0 | 129 | 0 | 129 | 0 | 129 | 0 | 129 |
| 4 | 02 | 5 | 52 | 5 | 23 | 6 | 44 | 0 | 140 | 0 | 140 | 0 | 140 | 0 | 140 |
| 4 | 50 | 7 | 05 | 6 | 25 | 8 | 01 | 0 | 151 | 0 | 151 | 0 | 151 | 0 | 151 |
| 6 | 00 | 8 | 52 | 7 | 43 | 9 | 49 | 0 | 162 | 0 | 162 | 0 | 162 | 0 | 162 |
| 7 | 05 | 10 | 35 | 9 | 14 | 17 | 40 | 0 | 173 | 0 | 173 | 0 | 173 | 0 | 173 |
| 8 | 15 | 12 | 15 | 11 | 51 | 35 | .. | 0 | 184 | 0 | 184 | 0 | 184 | 0 | 184 |
| 9 | 35 | 15 | 52 | 15 | 09 | 54 | .. | 0 | 195 | 0 | 195 | 0 | 195 | 0 | 195 |
| 12 | 05 | 21 | 40 | 18 | 35 | 110 | .. | 0 | 206 | 0 | 206 | 0 | 206 | 0 | 206 |
| 15 | 00 | 27 | 40 | 24 | 30 | 200 | .. | 0 | 217 | 0 | 217 | 0 | 217 | 0 | 217 |
| 18 | 50 | 40 | .. | 36 | .. | .. | .. | 0 | 228 | 0 | 228 | 0 | 228 | 0 | 228 |
| 25 | 20 | 68 | .. | .. | .. | .. | .. | 0 | 239 | 0 | 239 | 0 | 239 | 0 | 239 |
| 32 | 50 | 125 | .. | .. | .. | .. | .. | 0 | 250 | 0 | 250 | 0 | 250 | 0 | 250 |
| 66 | .. | .. | .. | .. | .. | .. | .. | 0 | 261 | 0 | 261 | 0 | 261 | 0 | 261 |
| 1260 | .. | .. | .. | .. | .. | .. | .. | 0 | 272 | 0 | 272 | 0 | 272 | 0 | 272 |
| Cc. Gas: | | | | | | | | | | | | | | | |
| Withdrawn 133.0 | | 114.7 | | 111.2 | | 121.0 | | 103.0 | | 3965.6 | | 856.4 | | 858.6 | |
| Residual 10.9 | | 5.9 | | 2.7 | | 3.9 | | 1.2 | | 13.3 | | 5.6 | | 0.2 | |
| Per cent CO ₂ 91.2 | | 94.9 | | 97.6 | | 96.8 | | 98.8 | | 99.7 | | 99.3 | | 99.9 | |
| GAS WITHDRAWN: AT 0° C..... | | 4548.5 cc. | | 4548.5 cc. | | Total Residual Gas from NaOH Absorption... | | 44.4 cc. | | | | | | | |
| 26° C..... | | 856.4 cc. | | 856.4 cc. | | Foreign Gases Present..... | | 0.7 per cent | | | | | | | |
| 100° C..... | | 858.2 cc. | | 858.2 cc. | | Gas Cushion..... | | 25 cc. | | | | | | | |
| Total Gas in Bottle..... | | 6263.1 cc. | | 6263.1 cc. | | Volume of Liquid..... | | 770 cc. | | | | | | | |

we have increased the speed of carbonation over 100 times.

We have a nearer approach to saturation of the liquid at the end of this short period of high speed stirring than with the extremely long period using slow speed. The actual volume of carbon dioxide in the liquid before the bottle is opened is 6090 cc., whereas the volume corresponding to the partial pressure of CO₂ over the liquid (5.25 atmospheres) calculated from solubility data and Henry's law is 6925 cc. After withdrawing portions of gas, and letting the bottle stand while the gas comes out of the liquid until equilibrium is practically established, we have, as in the two previous carbonations, a fairly close agreement with Henry's law.

PRESSURE RECOVERY CURVES—In considering the rate of pressure recovery curves for Carbonation No. 3, it will be noted that Curve 1, taken shortly after carbonating, is somewhat high since the bubbles on the container surface have not had time to be suppressed. Curve 2, taken after standing over night, gives the normal¹ pressure recovery. Curve 3, taken on the same day as No. 2, starts up fairly rapidly

¹ We will consider as normal the pressure recovery from the quiescent state of the liquid, after equilibrium is practically reached.

because of bubble formation, but falls quite a bit below it due to the subnormal concentration of the gas in the upper layers. After standing over night Curve 4 again gives a normal pressure recovery, the difference between the two normal curves, Nos. 2 and 4, being due to the lowering of the total gas content of the liquid by the volume of gas removed from the bottle between the two openings. Curve 5 again shows a depression due to low concentration of gas in the upper layers of liquid. The regular logarithmic form of pressure recovery curve is obtained here as in the other carbonations.

COMPOSITION OF THE GAS—The residual volume from absorption over sodium hydroxide was 44.4 cc. or 0.7 per cent of the total gas. As in the previous carbonations a large portion of this foreign gas, 10.9 cc., nearly 25 per cent, was withdrawn at the first opening. Over 50 per cent of the foreign gas was withdrawn by the fourth opening, whereas less than 8 per cent of the total gas was withdrawn during the same time.

CARBONATION NO. 4

A second bottle of distilled water was carbonated at the same high rate of stirring, and in addition the effect of residual foreign gas in the gas cushion was

TABLE IVA—CARBONATING CONDITIONS: CARBONATION No. 4

| Distilled Water Used 770 cc. | Temperature of Water during Carbonation 0° C. | Speed of Stirrer 2500 r. p. m. | Carbonating Pressure 70 lbs. per sq. in. | Gas Cushion 25 cc. |
|---|---|---|--|---------------------------|
| PERIOD OF STIRRING— Started at Stopped at Interval | PERIOD AT END OF STIRRING Lbs. per sq. in. | SUBSEQUENT TREATMENT | | PERIOD OF RISE Sec. |
| 3 : 09 | 3 : 10 | Opened valve, letting off gas to zero pressure. Closed valve, noting pressure recovery in each case | | 10 |
| 3 : 11 | 3 : 12 | | | 10 |
| 3 : 13 | 3 : 14 | | | 10 |
| 3 : 15 | 3 : 16 | | | 10 |
| 3 : 17 | 3 : 18 | | | 10 |
| 3 : 20 | 3 : 21 | | | 10 |
| 3 : 23 | 3 : 24 | Connected bottle to analysis apparatus and began test (See Table IVB) | | 10 |
| Total Stirring..... | 7 | TOTAL PERIOD OF CARBONATION—15 min. | | |

TABLE IVB—PRESSURE RECOVERY AND ANALYTICAL DATA: CARBONATION No. 4—HIGH SPEED STIRRING

| First Opening Temperature of Bottle Opening | Second Opening | Third Opening | Fourth Opening | Fifth Opening | Sixth Opening | 0° | 20° | 100° C. |
|--|---------------------|---------------------|---------------------|--|---------------------|---------------------|---------------------|---------------------|
| Pressure 66.0 lbs. | 48.5 lbs. | 48.0 lbs. | 46.0 lbs. | 47.5 lbs. | 44.5 lbs. | | | |
| PERIOD Min. Sec. | PERIOD Min. Sec. | PERIOD Min. Sec. | PERIOD Min. Sec. | PERIOD Min. Sec. | PERIOD Min. Sec. | PERIOD Min. Sec. | PERIOD Min. Sec. | PERIOD Min. Sec. |
| 0 0 | 0 0 | 0 0 | 0 0 | 0 0 | 0 0 | 0 0 | 0 0 | 0 0 |
| 0 7 | 0 3 | 0 1 | 0 1 | 0 1 | 0 3 | 0 3 | 0 3 | 0 3 |
| 0 10 | 0 5 | 0 2 | 0 2 | 0 2 | 0 4 | 0 4 | 0 4 | 0 4 |
| 0 13 | 0 11 | 0 5 | 0 5 | 0 5 | 0 6 | 0 6 | 0 6 | 0 6 |
| 0 16 | 0 18 | 0 8 | 0 8 | 0 9 | 0 7 | 0 7 | 0 7 | 0 7 |
| 0 20 | 0 25 | 0 10 | 0 10 | 0 11 | 0 13 | 0 13 | 0 13 | 0 13 |
| 0 30 | 0 39 | 0 14 | 0 12 | 0 14 | 0 17 | 0 17 | 0 17 | 0 17 |
| 0 49 | 0 59 | 0 21 | 0 19 | 0 20 | 0 26 | 0 26 | 0 26 | 0 26 |
| 1 11 | 1 29 | 0 33 | 0 26 | 0 29 | 0 37 | 0 37 | 0 37 | 0 37 |
| 1 40 | 2 36 | 0 47 | 0 42 | 0 41 | 0 50 | 0 50 | 0 50 | 0 50 |
| 2 25 | 3 45 | 1 02 | 0 58 | 1 02 | 1 13 | 1 13 | 1 13 | 1 13 |
| 3 30 | 5 45 | 1 30 | 1 20 | 1 32 | 1 50 | 1 50 | 1 50 | 1 50 |
| 5 40 | 8 10 | 2 05 | 1 58 | 2 05 | 2 30 | 2 30 | 2 30 | 2 30 |
| 8 00 | 11 20 | 2 58 | 2 44 | 2 48 | 3 20 | 3 20 | 3 20 | 3 20 |
| 10 50 | 17 20 | 4 43 | 3 53 | 3 55 | 5 10 | 5 10 | 5 10 | 5 10 |
| 13 40 | 25 20 | 6 25 | 6 35 | 5 10 | 9 20 | 9 20 | 9 20 | 9 20 |
| 17 00 | 34 00 | 9 05 | 8 55 | 7 40 | 13 40 | 13 40 | 13 40 | 13 40 |
| 41 .. | 44 .. | 12 15 | 12 10 | 11 25 | 18 40 | 18 40 | 18 40 | 18 40 |
| 1320 .. | 70 .. | 17 00 | 16 30 | 14 40 | 25 30 | 25 30 | 25 30 | 25 30 |
| | 120 .. | 25 00 | 23 30 | 18 50 | 35 20 | 35 20 | 35 20 | 35 20 |
| | 165 .. | 41 .. | 37 .. | 25 10 | 57 .. | 57 .. | 57 .. | 57 .. |
| | | 58 .. | 56 .. | 34 45 | 86 .. | 86 .. | 86 .. | 86 .. |
| | | 75 .. | 76 .. | 52 .. | | | | |
| | | 100 .. | 1260 .. | 81 .. | | | | |
| | | | | 113 .. | | | | |
| | | | | 167 .. | | | | |
| Cc. Gas: | | | | | | | | |
| Withdrawn 120.8 | 134.1 | 100.6 | 102.7 | 108.9 | 97.9 | 3761.4 | 657.7 | 1177.9 |
| Residual 3.9 | 3.0 | 0.5 | 0.4 | 0.9 | 0.4 | 7.7 | 1.1 | 1.1 |
| Per cent CO ₂ 96.8 | 97.8 | 99.5 | 99.6 | 99.2 | 99.6 | 99.8 | 99.8 | 99.9 |
| GAS WITHDRAWN: AT 0° C..... | 4426.4 cc. | 657.7 cc. | | Total Residual Gas from NaOH Absorption... | 19.0 cc. | | | |
| 20° C..... | 1177.9 cc. | | | Foreign Gases Present..... | 0.3 per cent | | | |
| 100° C..... | | | | Gas Cushion..... | 25 cc. | | | |
| Total Gas in Bottle..... | 6262.0 cc. | | | Volume of Liquid..... | 770 cc. | | | |
| 19.0 cc. total residual gas from NaOH absorption | | | | | | | | |
| 0.3 per cent—foreign gases present | | | | | | | | |

more nearly eliminated by "blowing off" the surface gas several times. The conditions of carbonating are given in Table IVA.

Table IVB presents the data on rate of pressure recovery, and on the analysis of the gas. The rate of pressure recovery curves are plotted in Carbonation No. 4, Fig. II.

In Carbonation No. 4 the same volume of gas, 6262 cc., was forced into the system as in Carbonation No. 3. No. 4 was stirred for seven minutes and No. 3 for six minutes, but to offset this the carbonating pressure in No. 3 was slightly greater. Also No. 4 had the surface gas "blown off" six times as compared with twice in No. 3 and as this blowing off removes quite a little gas from the system, it would naturally take slightly longer to bring No. 4 to efficient carbonation. The degree of saturation in Carbonation No. 4 was almost exactly the same as in Carbonation No. 3, and somewhat higher than in the carbonations with slow speed stirring. The actual total carbon dioxide in the liquid was 6110 cc.,¹ whereas the calculated volume from the observed partial pressure (5.30 atmospheres or 63.3 lbs. per sq. in. above atmos-

pheric) was 6990 cc. Comparison of the observed and calculated volumes of gas in the liquid at later openings upon the attaining of equilibrium after the bottle had stood over night, showed a close agreement with Henry's law and solubility data.

RATE OF PRESSURE RECOVERY—In considering the rate of pressure recovery curves for Carbonation No. 4, it will be noticed that Curve 1, taken immediately following the first opening of the bottle, shows a very rapid rise due to presence of bubbles on the inner surface of the container. Where the bottle stands over night, pressure recovery Curve 2 shows a slowing down due to re-solution of the bubbles. The curve taken at this stage, when there is approximate equilibrium between the gas in the various layers of liquid and in the gas cushion, is in reality the normal form of curve. Curves 3 and 4, taken the same day as No. 2, are speeded up due to lack of time for re-solution of the bubbles, formed at the opening of the bottle, and lie fairly close to No. 2. Here the time elapsing between curves is such that the speeding-up effect due to the bubbles predominates over the slowing-down effect caused by low concentration of gas in the upper layers. Curve 5, taken after standing over night, is another normal curve. No. 6, taken on the same day, again shows the speeding-up characteristic.

¹ The method of determining the actual volume of CO₂ in the liquid and the partial pressure of CO₂ in the gas cushion is detailed in footnote 4, col. 2, page 281, and footnote 1, col. 1, page 282.

COMPOSITION OF THE GAS—The repeated "blow-offs" during carbonation (six in number) have the effect of giving a very pure carbon dioxide in the system. After the first two openings of the bottle (Table IVB), the gas portions withdrawn contained 99.5 per cent of carbon dioxide, and the major portion of the gas showed from 99.8 to 99.9 per cent carbon dioxide. The total residual volume, or foreign gas, was only 19.0 cc., 0.3 per cent of the total, and about one-third as much as in the other carbonations with only two blow-offs.

RELATION OF INITIAL PRESSURE TO GAS CONTENT—From the data and discussion that have preceded it can readily be seen why the initial pressure (the pressure of the gas cushion indicated on a gauge connected to a bottle of carbonated liquid before opening the bottle and removing any of the gas) of a bottle of carbonated liquid is no indication of the gas content of

indication of the amount of carbon dioxide in the liquid. Fig. III shows graphically how far the initial partial pressures of CO_2 in the four experimental carbonations depart from the saturation curve between gas content and corresponding partial pressure of carbon dioxide. This departure of the initial pressure from the saturation curve is greater in the slow speed stirring tests, Nos. 1 and 2, where the liquid was not brought to as high a degree of saturation as in the high speed carbonations, Nos. 3 and 4.

If the excess gas in the gas cushion of the bottle is withdrawn, and the bottle is not kept at 0°C . but is allowed to warm up, an excess of gas passes into the gas cushion, all of which will not go back into solution when the bottle is again brought to ice temperature. Hence the partial pressure of carbon dioxide at that point will bear no direct relationship to the gas

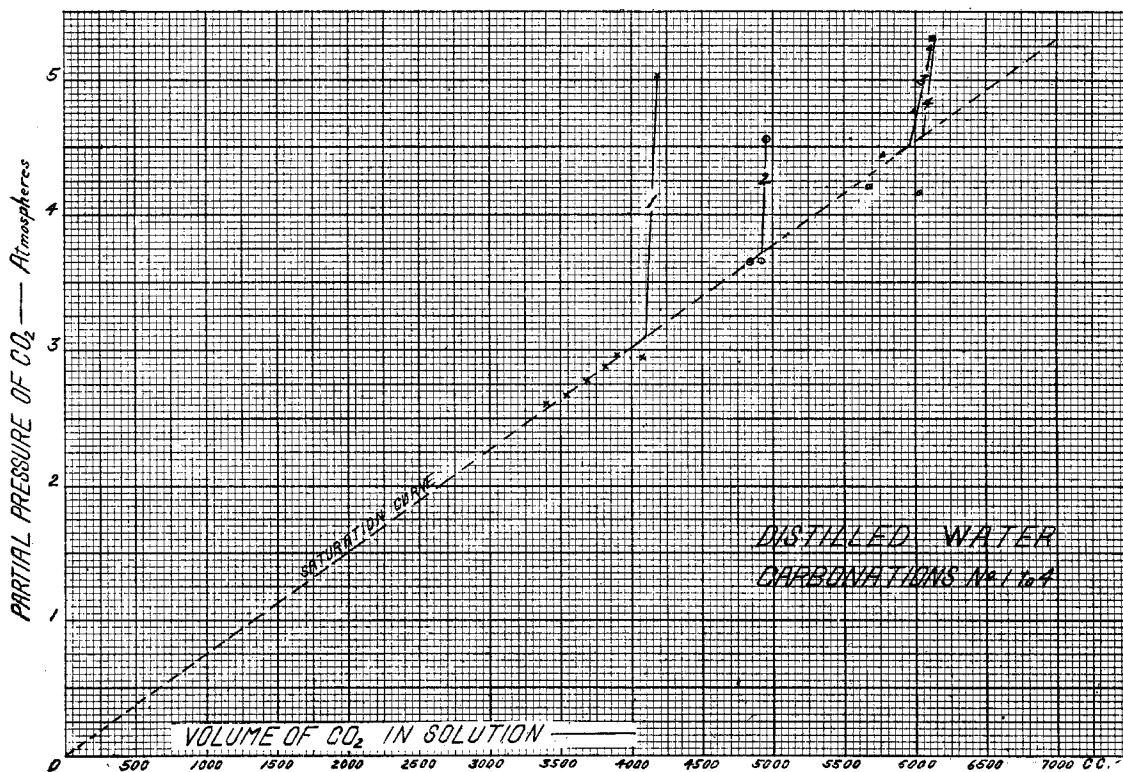


FIG. III.—DEPARTURE OF INITIAL PARTIAL PRESSURES OF CO_2 FROM THE SATURATION CURVE

that liquid. If the bottle is taken directly from the carbonating machine and kept iced until the initial pressure is read, that initial pressure will simply be the pressure of carbon dioxide under which the liquid was carbonated and the bottle was sealed, plus the partial pressure due to any residual foreign gas in the gas cushion.

However, if the excess gas in the gas cushion is drawn off and the bottle kept closed and iced until the pressure recorded on the gauge has reached a maximum (point of equilibrium between gas in liquid and in gas cushion), the partial pressure of the carbon dioxide¹ in the gas cushion at that time will be a true

¹ The method of determining the partial pressure of CO_2 is to record the total pressure, withdraw the excess gas in the gas cushion, measure the volume of foreign gas withdrawn, from that calculate the volume of foreign gas in the gas cushion before withdrawal, then from the volume of the gas cushion and volume of foreign gas calculate the partial pressure of foreign gas, subtract this from the total pressure to give the partial pressure of CO_2 .

content of the liquid. The reason that the gas after once coming out from the liquid does not readily re-enter is due to poor surface contact between the layers of gas and liquid not in equilibrium. Even with a stirrer rotating at 400 r. p. m., as has been shown in the data, equilibrium is not complete after 11 or 12 hrs. of stirring. Such a condition of warming up and recooling with consequent increase in the volume and pressure of gas in the gas cushion is the natural result of the ordinary commercial methods of handling artificial beverages.

SUMMARY

I—A method of study has been developed for systems under high pressure, which can be applied to the statics and dynamics of gas-liquid and of gas-liquid-solid systems.

II—Regular rate of pressure recovery curves nearly

reproducible and evidently logarithmic in form have been obtained.

III—A high degree of impregnation of water with carbon dioxide gas has been obtained using a rotary stirrer while maintaining the liquid under a steady pressure of gas.

IV—The effect of an increase in speed of stirring is to tremendously shorten the time of carbonation, and at the same time increase the degree of impregnation.

V—In an efficiently carbonated water the gas content, after the first opening of the bottle, closely approximates Henry's law.

VI—The degree of impregnation of a liquid with a gas is not directly indicated by the "initial pressure," that is, the pressure of the gas over the free surface of the liquid before the first opening of the bottle.

VII—The length of time that the carbonated water is allowed to stand before opening bears a marked relation to the maintenance of the supersaturated condition after the pressure in the gas cushion is released. This effect is evidently due to the gradual solution of fine gas bubbles retained on the inner surface of the container.

VIII—By "blowing off" of the foreign gases in the gas cushion, a higher degree of carbonation can be secured. This principle has been used by the practical men in the trade.

IX—A high degree of carbonation may be obtained using distilled water alone, as a solvent, and if this product is allowed to stand for a period before opening, the carbon dioxide gas is retained remarkably well.

BUREAU OF CHEMISTRY
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EXAMINATION OF AMERICAN-MADE ACETYSALICYLIC ACID

By PAUL NICHOLAS LERCH
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At the request of the Council on Pharmacy and Chemistry, the A. M. A. Chemical Laboratory has undertaken examinations of American-made synthetic drugs. The most extensively used synthetic is acetylsalicylic acid and hence an investigation of this product was deemed expedient.

For seventeen years acetylsalicylic acid was protected by a United States Patent (the proprietors were not given a patent in other countries) and sold under the name "Aspirin." In February 1917 the patent expired, and since then a number of firms have engaged in the manufacture of acetylsalicylic acid, selling it either as such or as aspirin, modified, of course, by a distinctive firm designation. During this period the former manufacturers (The Bayer Co., New York, in past years called Farbenfabriken of Elberfeld Co., New York) have been extensively advertising, both to physicians and the public, the alleged superior qualities of their product. The chemical examination, therefore, was concerned chiefly with tests of purity, and the comparison of the American brands with the formerly patented product.

In European countries, acetylsalicylic acid¹ is described in the various pharmacopoeias as a condensation product of acetic anhydride or acetyl chloride with salicylic acid (*o*-hydroxybenzoic acid). Generally the test of identification is hydrolysis of acetylsalicylic acid and qualitative tests for acetic acid and salicylic acid. For purposes of purity the requirements are essentially that the specimen should have a certain melting point, should show absence of salicylic acid by means of ferric chloride (the manipulations for the tests are variously described) and leave no appreciable ash. The two tests of purity most generally employed, however, are the melting point and the reaction with ferric chloride.

MELTING POINT

The melting point of acetylsalicylic acid has been given at various temperatures from 118° to 137° C.;² the *British Pharmacopoeia* describes the melting point at 133° to 135° C.; the *German Pharmacopoeia* "about 135° C.;" the *French Pharmacopoeia* at 135° C.; *New and Nonofficial Remedies*, 1917, 134–136° C. The Bayer Company, in the patent trial at Chicago a number of years ago, gave among the "four infallible tests" a melting point of "about 135° C." Several men have carefully determined the melting point in recent years. Emery and Wright³ in 1912 found that "Aspirin, Bayer" melted at 130.5–131° C. In France, François⁴ has determined the melting point of pure acetylsalicylic acid, which, according to his method, is 132° C. When various samples of acetylsalicylic acid were examined in this laboratory, it was found that the melting point of none was as high as that described in *New and Nonofficial Remedies* or the British, French, or German pharmacopoeias when taken according to the general method of the *U. S. Pharmacopoeia*, Vol. 9, p. 596. On critical observation, it may be seen that the melting point of acetylsalicylic acid is preceded and accompanied by decomposition. If the sample in the melting tube is heated from the original room temperature of the bath to 120° C., the temperature of melting will be lower than if the bath is first heated to 120° C. and the melting-point tube then placed in the bath.⁵ Thus the melting point of acetylsalicylic acid, like so many organic compounds which decompose and do not melt sharply, is unsatisfactory and cannot be taken as an "infallible test" of purity, especially when determined by different operators who do not give their method in detail. After making a large number of melting-point determinations of acetylsalicylic acid, alone and in parallel with other operators, it was decided to use the

¹ Unfortunately, the non-descriptive name "aspirin" has been used extensively in European literature, and has even gotten into European pharmacopoeias, instead of the scientific name "acetylsalicylic acid."

² For reference to older literature see Beilstein, II, 1496 (889).

³ "The Melting Temperature of Aspirin and Salicylic Acid Mixtures," *Proc. Assoc. Off. Agr. Chem.*, 1912; Bureau of Chemistry, Department of Agriculture, Bull. 162.

⁴ "Assay of Aspirin," *J. pharm. Chim.*, 15 (1917), No. 7, 213.

⁵ Similar observations were made by Emery and Wright, who state: "An accurate determination of the melting temperature in this way (the rate of heating was such as to give a rise in temperature of about 1° per minute) is rendered difficult by the fact that 'aspirin' decomposes on heating, as evidenced in the depression of the melting temperature of the pure substance of about 1° for every five minutes' heating just below its melting temperature."