horizontal lines so that each one would intersect the stable portion of its respective activity curve at the same mole fraction. The values of the mole fraction, $N_1$, thus obtained are 0.835 and 0.352. These values represent the compositions at which unmixing should occur. Inspection of these curves shows that only one pair of horizontal lines will satisfy the above conditions.

Experiments are now in progress applying these methods to other solid solutions. It is hoped that extending the temperature range, especially in the direction of lower temperatures, will yield a more thorough knowledge of the nature of these solutions. Certainly, we would expect to find that any tendency toward the formation of compounds would become intensified with a decrease in temperature.

## Summary

1. The technique of making precise potential measurements of galvanic cells containing solid electrolytes has been described.

2. The energy changes of solid silver chloride upon a dilution with sodium chloride have been determined at mole fractions of silver chloride varying from 1 to 0.160, between the temperatures of 150 and 230°.

3. The course of an activity curve for a supersaturated condition has been followed experimentally over its complete range of composition.

4. It is pointed out that Tammann's "limits of resistance" can be explained on the basis of this type of activity function.

5. The existence of a regular arrangement of sodium ions in the silver chloride–sodium chloride lattice is verified.

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE LABORATORIES OF THE COLUMBIA CHEMICAL DIVISION OF THE PITTSBURGH PLATE GLASS CO., AND OF NEW YORK UNIVERSITY]

# AQUEOUS SOLUBILITY OF SALTS AT HIGH TEMPERATURES. I. SOLUBILITY OF SODIUM CARBONATE FROM 50 TO 348°[1]

BY WILLIAM F. WALDECK, GEORGE LYNN AND ARTHUR E. HILL

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This investigation was carried out for the purpose of developing a satisfactory method for the determination of solubilities at high temperatures and pressures, and with its aid determining the solubility of sodium carbonate up to the critical temperature of water. From the solubility curve it was intended to ascertain the temperature of the transition of the monohydrate to the anhydrous form in contact with the solution under its own vapor pressure.

**Previous High-Temperature High-Pressure Solubility Methods.**—The

[1] Presented by W. F. Waldeck as thesis for the degree of Master of Science at New York University.

sealed tube or plethostatic method,[2] which consists in noting the temperature at which the last trace of solid in a synthetic mixture disappears, is the oldest and still the most common method. It apparently was first used by Guthrie[3] for potassium nitrate in water at high temperatures. It was later applied by Alexejew[4] to the determination of the mutual solubility of liquids. Wuite's[5] classical work on sodium sulfate up to the critical temperature of water was carried out with the sealed tube method, using tubes of quartz at the higher temperatures. The exhaustive work of Morey[6] on the ternary system $H_2O$–$K_2SiO_3$–$SiO_2$, going up to temperatures of 1000° and pressures of 560 atmospheres, was accomplished by a "hydrothermal quenching method," which was in effect a plethostatic one.

Direct solubility measurements by withdrawal or isolation of a sample of the saturated solution at high temperatures seem to have been first accomplished by Tilden and Shenstone,[7] who used a silver-plated steel tube divided into two compartments by a platinum gauze, equilibrium being attained in the one compartment and a sample filtered into the other by simply inverting the tube. Upon cooling, the total sample was analyzed. The values they obtained, together with those of Étard,[8] who used a similar apparatus of glass for a great many salts, have been shown to be of doubtful accuracy by more recent work.

Partridge,[9] Boyer-Guillon[10] and Hall, Robb and Coleman,[11] have measured the solubility of calcium sulfate in water at elevated temperatures by withdrawing large quantities of solution from directly heated autoclaves.

Seyer and Todd[12] have utilized a small solubility device made of pipe fittings so arranged that tilting the tube would cause part of the solution to flow into a weighed sidearm. On cooling, the contents of the sidearm were analyzed.

The best of these direct solubility devices was that used by Robson[13] for magnesium sulfate. This was a small gold-lined monel metal bomb with a valve to permit withdrawal of a sample into a weighed, water-cooled copper tube, the sample being filtered through an alundum disk. Failure of the gold gasket above 240° and crystallization in the valve limited the

[2] For the terminology of solubility methods see Hill, THIS JOURNAL, **45**, 1143 (1923).

[3] Guthrie, *Phil. Mag.*, **18**, 105 (1884).

[4] Alexejew, *Ann. Physik*, **28**, 305 (1886).

[5] Wuite, *Z. physik. Chem.*, **46**, 818 (1903).

[6] Morey, THIS JOURNAL, **39**, 1173 (1917).

[7] Tilden and Shenstone, *Phil. Trans. Roy. Soc.* (London), **175**, Pt. 1, 23 (1884).

[8] Étard, *Ann. chim. phys.*, [7] **2**, 503 (1894).

[9] Partridge, THIS JOURNAL, **51**, 360 (1929).

[10] Boyer-Guillon, *Ann. Conservatoire Arts et Metiers*, [3] **2**, 207 (1900).

[11] Hall, Robb and Coleman, THIS JOURNAL, **48**, 927 (1926).

[12] Seyer and Todd, *Trans. Roy. Soc. Can.*, [3] **23**, 67 (1929).

[13] Robson, THIS JOURNAL, **49**, 2772 (1927).

usefulness of the device and made a contemplated ternary investigation impossible.

The solubility of some sparingly soluble salts has been determined indirectly by conductance measurements in a Noyes and Coolidge[14] bomb by Melcher.[15]

Apparatus for the investigation of pressure on solubilities at room temperature has been developed by von Stackelberg,[16] by Cohen and Sinnige[17] and by others.

Though some notably accurate solubility work[18] has been done with the sealed tube method, the inability of glass or quartz tubes to withstand the high pressures, the severe etching on the glass, and the impossibility of securing direct pressure measurements all made a direct measurement in bombs seem desirable.

**Previous Solubility Values for Sodium Carbonates.**—The most careful measurements of the aqueous solubility of sodium carbonate are those of Wells and McAdam[19] from 27.84 to 43.94°. Above this temperature the determinations are surprisingly few, and are due only to Mulder,[20] to Epple and to Seyer and Todd, the latter being the only work above the normal boiling point of the saturated solution. The values of Mulder and of Epple agree well with each other and apparently are the basis of the "International Critical Table" values. Seyer and Todd give values much below those of Mulder and Epple, and find at 149° a break in the solubility curve which they attribute to the transition of the monohydrate to the anhydrous form.

Jänecke[21] has given 107° as the transition of the monohydrate to the anhydrous forms, having obtained this value by applying pressure to dry, solid monohydrate, increasing the temperature and noting the temperature at which the sudden drop in pressure indicated that there had formed anhydrous crystals, and solution which escaped through small holes into another compartment. Due to the fact that the pressure applied to the monohydrate was in the neighborhood of 455 atmospheres, the value of 107° is probably widely different from the value at the pressures of the saturated solution.

[14] Noyes and Coolidge, *Publ. Carnegie Inst., Washington*, **63**, 59 (1907).

[15] Melcher, THIS JOURNAL, **32**, 50 (1910).

[16] Von Stackelberg, *Z. physik. Chem.*, **20**, 337 (1896).

[17] Cohen and Sinnige, *Trans. Faraday Soc.*, **5**, 269 (1905).

[18] Kracek, *J. Phys. Chem.*, **35**, 417, 947 (1931); Kracek, THIS JOURNAL, **53**, 2620 (1931).

[19] Wells and McAdam, *ibid.*, **29**, 726 (1907).

[20] Mulder, "Scheikundige Verhandelingen en Onderzoekingen," Vol. 3, Pt. 2, "Bijdragen tot de Geschiedenis van Het Scherkungig Gebonden Water," Rotterdam, 1864, as quoted in Seidell, "Solubilities of Inorganic and Organic Compounds," 2d ed.; Epple, Dissertation, Heidelberg, 1899, as quoted in Landolt-Börnstein, "Tabellen."

[21] Jänecke, *Z. physik. Chem.*, **90**, 269 (1915).

## Experimental Work

**Apparatus and Method.**—Most of the solubility determinations were made in the Type I bomb shown in section in Fig. 1. It was made entirely of Allegheny Metal (18% Cr, 8% Ni steel) and was fitted with a sampler, a relief valve and a capillary tube leading to a pressure gage. A copper gasket was used on the main joint. Considerable difficulty was experienced in keeping the sampler-valve stem tight until the "oxygen-tank" type of valve, as shown, was tried. A rubber disk, stock no. 76-S Soft Superbo Bibb Washer, Woodward Wanger Company, served satisfactorily as a valve disk up to 350°. In this type of valve, both the internal pressure and the external spring force the shoulder on the valve stem against the valve disk, thus sealing the device. The valve disk must therefore be hard enough under conditions of high temperature and pressure to withstand being forced out of the valve by the high pressure, but must also be soft enough at low temperatures, with the sampler evacuated, to seal effectively with only the tension of the spring holding the shoulder against the disk.

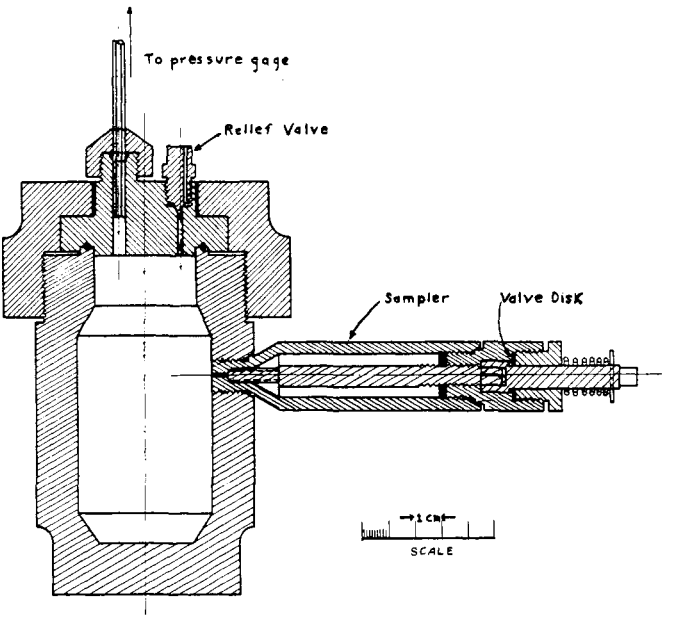


Fig. 1.—Type I solubility bomb.

The bomb was mounted in an oscillating cradle with the sampler valve-stem on the axis of oscillation and extending outside the electrically heated air-bath. This air-bath, of about 60 × 30 × 40 cm. dimensions, was made of asbestos cement board and insulated with 2.5 cm. of Sil-O-Cel. The heating coils were mounted in a box of asbestos board with both ends open, this forming a wind tunnel, supported inside the air-bath. A fan circulated the air through this wind tunnel and over the coils. Temperature regulation to about ±1° was obtained by use of a de Khotinsky bimetallic-strip thermoregulator specially soldered to withstand 400°. Temperatures were read from a calibrated thermometer with its bulb in the air stream. The bomb was oscillated fourteen times per minute through an arc of 115° from the vertical.

Due principally to heat losses through the sampler and cradle shaft, the temperature within the bomb was lower than that in the air-bath. This difference was compensated

for from a temperature correction curve prepared by inserting a thermo-element in a suitable non-volatile liquid in the bomb and taking simultaneous bomb and air-bath temperatures. The thermo-element was suitably calibrated, and sufficient time was allowed for the bomb to come to thermal equilibrium, two hours usually sufficing. This temperature correction varied from 2 at 100° to 23 at 400°.

In making a solubility determination, the sampler, which weighed about 450 g., was assembled, evacuated, weighed and screwed into the bomb. To the bomb were then added sufficient water, and reagent quality sodium carbonate in excess, to establish the liquid level well above the sampler orifice. Care was taken to allow sufficient space for thermal expansion so as not to fill the bomb completely and thus create enormous pressures. After the bomb was closed securely and placed in position in the cradle, the temperature of the air-bath was raised to about 25° above the desired temperature for an hour and then dropped back to the steady value for from four to eight hours. A series of solubility tests at 100° of varying duration showed saturation to be attained in less than four hours.

Oscillation was stopped and the bomb allowed to stand for thirty minutes in a vertical position before the sampler valve was opened. After one minute the valve was closed and the air-bath opened to cool. When cold, the sampler was unscrewed from the bomb, washed externally with water, dried and weighed to the nearest 10 mg., thus giving the weight of the sample (usually about 10 g.) to one part in a thousand. The sampler was then opened and the contents carefully washed into an Erlenmeyer flask with hot distilled water. The sodium carbonate was determined by titration with 1 *N* hydrochloric acid using methyl orange as indicator, and boiling out the carbon dioxide before the end-point was reached.

A check on the accuracy of the method was made by determining the solubility from 50 to 100° in a glass apparatus as used by Simmons and Waldeck[22] on lithium bromate. Here equilibrium was approached from both supersaturation and undersaturation. These values agreed well with those obtained with the bomb at 100°, the lowest temperature reached with the bomb. A further check was obtained at higher temperatures using an improved type of bomb with the sampler inside the bomb. In this case no temperature correction was made as the bomb was wholly within the air-bath. This new bomb will be described in a later paper.

**Corrosion.**—After the first few runs in the bombs, the inside surfaces became covered with a hard, black, adherent coating. This could not be removed by pickling, was taken off only with difficulty by emery, and was therefore left on. There was no noticeable contamination of the residual solution until temperatures of 200° and above were reached, when a slight yellow coloration was apparent. Above 300° the solution became strongly yellow colored, although curiously enough a solution that was heated to the critical temperature showed no coloration.

The most highly colored solution showed 0.0005% Fe, which was certainly as low as the original sodium carbonate, and negligible in any case. Treatment with dimethylglyoxime gave a barely visible cloudiness, and in view of the voluminous nature of this precipitate, this was taken as evidence of an extremely low nickel content. The color was undoubtedly due to chromium, since analysis showed 0.006% Cr. A solution of sodium chromate of the same chromium content showed an identical color.

[22] Simmons and Waldeck, THIS JOURNAL, **53**, 1725 (1931).

**Accuracy.**—The results, represented by Table I and the curve shown in Fig. 2, are believed to be accurate to within 0.1% sodium carbonate, from

TABLE I

SOLUBILITY OF SODIUM CARBONATE

| Temp., °C. | $Na_2CO_3$, % | Apparatus | Temp., °C. | $Na_2CO_3$, % | Apparatus |
|---|---|---|---|---|---|
| 50.0 | 32.0 | Glass | 139.0 | 28.1 | Bomb I |
| 60.0 | 31.6 | Glass | 145.0 | 27.7 | Bomb I |
| 75.5 | 31.0 | Glass | 152.0 | 27.7 | Bomb II |
| 83.6 | 30.8 | Glass | 159.0 | 26.8 | Bomb II |
| 99.5 | 30.6 | Bomb I | 170.0 | 26.1 | Bomb II |
| 100.0 | 30.8 | Glass | 174.0 | 25.5 | Bomb I |
| 100.0 | 30.9 | Bomb II | 176.0 | 25.5 | Bomb II |
| 100.5 | 30.8 | Glass | 180.0 | 25.0 | Bomb II |
| 100.5 | 30.8 | Glass | 200.0 | 23.3 | Bomb I |
| 103.0 | 30.8 | Bomb I | 225.0 | 20.7 | Bomb I |
| 106.0 | 30.7 | Bomb I | 239.0 | 18.7 | Bomb I |
| 112.5 | 30.8 | Bomb I | 275.0 | 13.2 | Bomb I |
| 113.0 | 30.8 | Bomb I | 300.0 | 8.4 | Bomb I |
| 116.0 | 30.3 | Bomb I | 301.0 | 8.4 | Bomb I |
| 121.5 | 29.8 | Bomb I | 321.0 | 4.8 | Bomb I |
| 125.0 | 29.5 | Bomb I | 326.0 | 4.4 | Bomb I |
| 131.5 | 28.8 | Bomb I | 348.0 | 0.0 | Bomb I |

50 to 150°, 0.2% from 150 to 250° and 0.3% above 250°. This uncertainty is due to the difference in temperature between the air-bath and the interior of the bomb, and to the fluctuation of the temperature of the

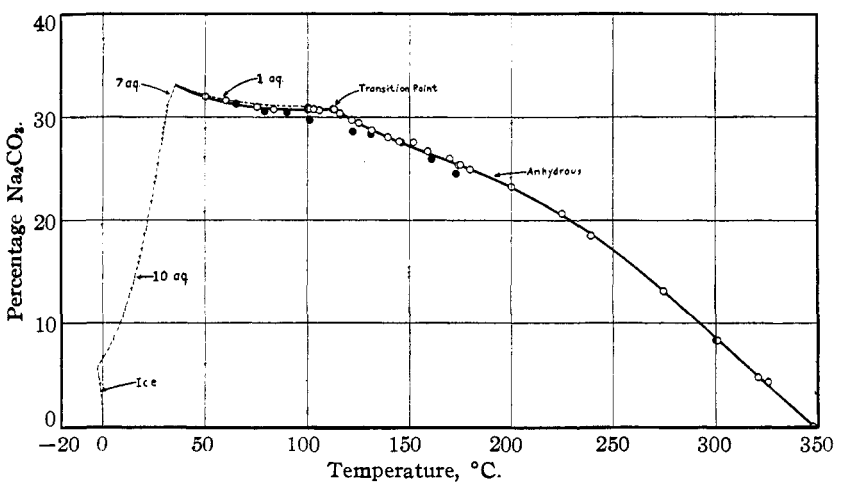


Fig. 2.—The solubility curve of sodium carbonate. – – – "International Critical Tables" values; ●, Seyer and Todd; ○, present work.

air-bath caused by slight sticking of the thermo-regulator contacts. While these rapid fluctuations did not affect the temperature of the bomb appreciably, it made the precise value of the temperature in doubt by about 1°.

**Transition Point.**—It is apparent from the discontinuity of the curve that the transition between the anhydrous and the monohydrated forms occurs at 112.5 ± 1°.

**Anhydrous Crystals.**—Anhydrous crystals were prepared at 140° and at 220° by heating in Bomb I solutions undersaturated at the temperatures in question until thermal equilibrium had been attained. The small valve at the top of the bomb was then opened slightly to permit a slow escape of steam. When no more steam issued from the valve, the bomb was opened while hot and the crystals examined immediately under a petrographic microscope.[23] The crystals tend toward flakes; biaxial, negative; $N_g$ = 1.544, $N_m$ 1.537, $N_p$ 1.410 (±0.001). The two optic axes are inclined in such a way that they are on the same side of the normal to the face of the flake, but one of them very nearly coincides with the normal; measurement with micrometer-eyepiece and Bertrand lens showed: $2E = 43 \pm 2°$, from which $2V = 28 \pm 2°$.

**Vapor Pressure of Saturated Solution.**—Pressure measurements were made by screwing into the socket at the end of the steel capillary, outside the bomb, ordinary Bourdon gages of the most favorable range for each particular measurement. The gages were flushed out with ether to remove oil, dried, and filled with water. They were calibrated on a dead-weight gage tester after each run. The two highest pressures, as recorded in Table II, were measured with a standard test gage. The results are plotted on a Dühring's rule basis[24] in Fig. 3.

TABLE II

THE VAPOR PRESSURE OF SATURATED SOLUTIONS OF SODIUM CARBONATE

| Temp., °C. | Pressure, atmospheres | Temp. at which water has the same pressure | Diff. in temp. between satd. soln. and water at the same pressure |
|---|---|---|---|
| 104.8 | 1.00 | 100.0 | 4.8 |
| 112.0 | 1.27 | 106.9 | 5.1 |
| 121.0 | 1.69 | 115.4 | 4.4 |
| 176.5 | 8.43 | 173.2 | 3.3 |
| 231.0 | 26.6 | 228.0 | 3.0 |
| 313.0 | 99.0 | 310.9 | 2.1 |
| 365.0 | 199 | 366.0 | −1.0 |

The negative value of this difference, at a temperature when the vapor pressure of the solution should be indistinguishable from that of pure water, was undoubtedly caused by the error of reading the gage, which could be read only to the nearest atmosphere, corresponding to 1°.

**Discussion.**—The discrepancy between the other solubility values and ours we do not find explicable. Epple and Mulder give higher values,

[23] The microscopic examination was conducted by Mr. B. K. Beecher.

[24] For a discussion of Dühring's rule see Monrad, *Ind. Eng. Chem.*, **21**, 139 (1929).

although our methods would tend to give high values, due to possible evaporation during sampling with the glass apparatus, or possible inclusion of suspended solid in the sample with the bombs. Epple's values, however, were also found to be high in the lower range of temperature by Wells and McAdam. On the other hand, Seyer and Todd were much more likely to get high values than we, and yet their values are much lower, with a totally different transition temperature.

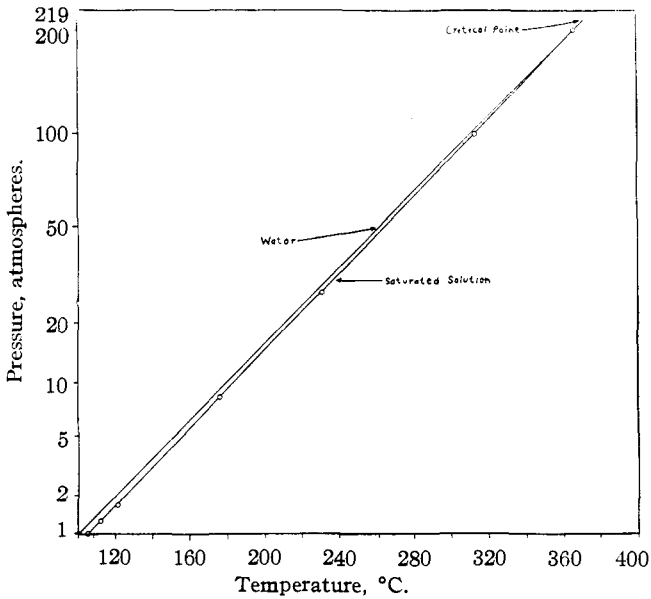


Fig. 3.—The vapor pressure of saturated solutions of sodium carbonate plotted by Dühring's method.

The transition temperature reported by Jänecke is obviously low because of the high pressure of approximately 450 atmospheres prevailing during the determination. Inspection of density values shows that the incongruent melting of monohydrate is attended by a shrinkage in volume, thus explaining the lowering of the transition temperature by pressure.

It is evident that this system is of the second type postulated by Smits,[25] in which the solubility curve intersects the binary critical curve. Since the solubility fell to zero at 348°, within the limits of error of the analysis, no investigations were carried on up to the critical temperature of water, 375°. It is probable that a definite, though undetectable, solubility exists at temperatures higher than 348°.

**Acknowledgment.**—The authors record with gratitude the active aid of the Research Laboratory of the Columbia Chemical Division, Pittsburgh

[25] Smits, *Z. physik. Chem.*, **51**, 194 (1905).

Plate Glass Company, the generosity of Mr. B. K. Beecher of that laboratory in making the petrographic examination, and the fine workmanship of Mr. William Latham, toolmaker of the Columbia plant, on the bombs, which contributed much to their success.

## Summary

1. Apparatus has been developed for the direct determination of solubilities and pressures at high temperatures and pressures.

2. The solubility of sodium carbonate in water has been determined from 50 to 350°.

3. The transition of the monohydrated into the anhydrous form in contact with solution under its own vapor pressure has been shown to occur at 112.5 ± 1° and 1.27 atmospheres pressure.

4. Crystals of anhydrous sodium carbonate have been grown at elevated temperatures and optical data on them are presented.

5. The vapor pressure of saturated solutions of sodium carbonate has been determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# A DOUBLE CAPILLARY METHOD FOR THE MEASUREMENT OF INTERFACIAL TENSION

BY G. L. MACK AND F. E. BARTELL

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In connection with some of our recent work we were confronted with the necessity of determining the interfacial tension of water against several different liquids which were expensive and which were difficult to obtain in large quantities in the pure state. It became highly desirable to develop a method which would require but a small amount of organic liquid for each measurement. The drop volume method of Harkins and the various capillary rise methods previously used, all required appreciable quantities of liquid. Sugden had solved a similar problem for surface tension determinations through the use of either a maximum bubble pressure method[1] or a double capillary method.[2] The first method did not, in its present form, appear to be applicable to the measurement of interfacial tensions. A modification of the second did seem promising.

Quite recently a method for the measurement of interfacial tensions of liquid–liquid systems based upon the principle of capillary rise had been developed, and had been quite generally used in this Laboratory.[3] With this apparatus from 10 to 20 cc. of organic liquid was required for

[1] Sugden, *J. Chem. Soc.*, **119**, 1483 (1921).

[2] Sugden, *ibid.*, **121**, 858 (1922); **125**, 27 (1924).

[3] Bartell and Miller, THIS JOURNAL, **50**, 1961 (1928).