[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

The Solubility of Carbon Dioxide in Calcium Chloride–Water Solutions at 75, 100, 120° and High Pressures[1]

BY C. F. PRUTTON AND R. L. SAVAGE[2]

Introduction

The chemical reaction of hydrochloric acid on calcium carbonate, which takes place during the acid treatment of oil wells, results in the formation of carbon dioxide and calcium chloride solutions. In certain areas, as in California and the Gulf Coast, where high bottom hole pressures are encountered, the liberation of carbon dioxide gas bubbles by the reaction has been questioned.[3] It has been claimed that the high pressures would prevent this reaction or, if the reaction did take place, that the carbon dioxide would remain completely dissolved in the calcium chloride solution and, therefore, would be unavailable for agitation and dispersal of drilling mud sheaths or other insoluble particles.

Thermodynamic calculations reported by Chamberlain and Boyer[4] and by Stone and Kefley[5] indicate that a carbon dioxide pressure of approximately 10^8 atmospheres would be necessary to prevent the reaction of hydrochloric acid on calcium carbonate. If it is assumed that the reaction will take place at pressures of less than 10^8 atmospheres, then a measurement of the solubility of carbon dioxide in calcium chloride solutions under such pressures as may be encountered in oil wells would indicate whether or not the carbon dioxide gas would be evolved from the spent acid solution. The results of the present investigation indicate that the carbon dioxide gas would be evolved.

Previous investigations of the solubility of carbon dioxide in calcium chloride solutions have been carried out in this Laboratory but without covering fully a range of concentrations, pressures and temperatures.[6] The solubilities of carbon dioxide in water and water solutions of salts or other solutes have been reported but in only a few cases were these determined under pressure. MacKenzie[7] determined the solubility of carbon dioxide in solutions of calcium chloride at atmospheric pressure. Sander[8] used a static system to measure the solubility of carbon dioxide in water at several temperatures and at pressures up to 100 atm. The results are of only qualitative value since two sets of values vary by as much as 10%. The results obtained by Wiebe and Gaddy[9] include a pressure range up to 700 atm. for the solubility of carbon dioxide in water at 50, 75, and 100°. The values for the solubility of carbon dioxide in water at 100° were used to verify the results reported by Wiebe and Gaddy, who used a flow system.

Apparatus

A modification of the apparatus used by Frolich and co-workers[10] was used to determine the solubility of carbon dioxide in calcium chloride solutions. The 300-ml. capacity copper-plated reaction vessel, A (Fig. 1), was supported in a heater which could be rocked through 60° to provide agitation of the equilibrium solution. High pressure tubing connected the top of the autoclave to an exhaust valve, F, and to the two high pressure gages. A high pressure needle valve, B, at the bottom of the autoclave controlled the flow of saturated solution into the glass trap where the gas was evolved to be measured in a buret over mercury, and the remaining solution was collected to be weighed.

Measurements of the actual temperatures of the solutions were made with a portable type potentiometer using a calibrated copper–constantan thermocouple placed in the pyrometer well inside the vessel. The heating of the equilibrium vessel was controlled by a Leeds and Northrup recorder coupled with a Lindbergh controller. By maintaining a definite wall temperature, it was possible to control the equilibrium conditions to within one degree above the desired value. Some samples were withdrawn when the solution was two degrees above the equilibrium temperature, but the error could be tolerated since there is such a small effect on solubility due to temperature change between 75 and 120°.

A 20,000-lb. per sq. inch Bourdon type gage, G, indicated the approximate pressure in the system while a Crosby dead-weight pressure balance, I, measured the exact pressure when a sample of saturated solution was removed from the autoclave. This Crosby pressure balance could be used to measure pressures up to 25,000 lb. per sq.

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[2] Present address: Battelle Memorial Institute, Columbus, Ohio.

[3] J. K. Kennelly, "Limestone-Laden Clay Drilling Mud as Acidizing Acid," *California Oil World*, **35**, No. 17, 9–11 (1942).

[4] L. C. Chamberlain, Jr., and R. F. Boyer, *Ind. Eng. Chem.*, **31**, 400–406 (1939).

[5] J. B. Stone and D. G. Kefley, *The Oil Weekly*, Nov. **11**, p. 38 (1940).

[6] From thesis presented for the degree of Bachelor of Chemical Engineering, Case School of Applied Science, 1940 by B. N. Schrauf, C. F. Prutton and M. L. Riehl, "Solubility of Carbon Dioxide in Calcium Chloride Solutions" Progress Report, unpublished, 1940.

[7] MacKenzie, *Ann. Physik*, (2) **1**, 450 (1877).

[8] W. Sander, *Z. physik. Chem.*, **78**, 513–549 (1912).

[9] R. Wiebe and V. L. Gaddy, THIS JOURNAL, **61**, 315–316 (1939).

[10] Per K. Frolich, E. J. Tauch, J. J. Hogan and A. S. Peer, *Ind. Eng. Chem.*, **23**, 548 (1931).

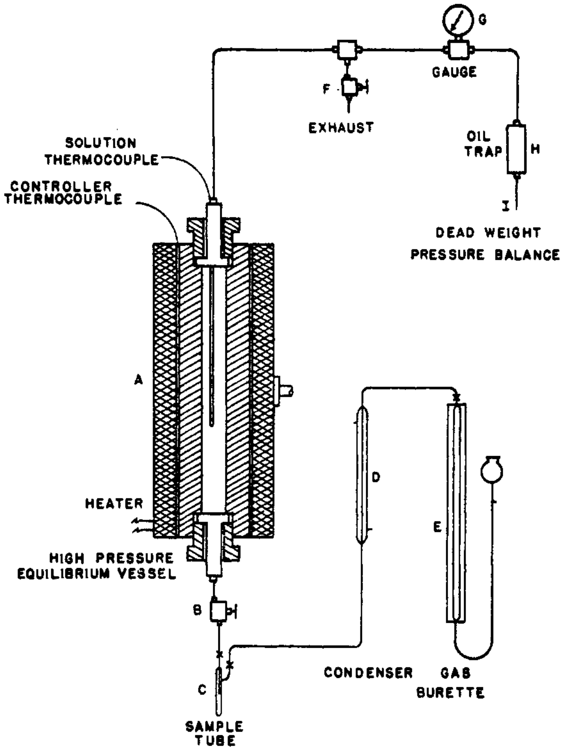

Fig. 1.—Diagram of gas solubility apparatus.

inch, pressure readings being duplicated to ±1 lb. per sq. inch at ten thousand. The manufacturer guaranteed for the gage a calibrated accuracy of ±0.25% but not better than ±1 lb.

The 20 and 30% calcium chloride stock solutions were made from the required amount of $CaCl_2 \cdot 2H_2O$ (Bakers c. p.) and some of the 20% solution was diluted to make a 10% stock solution. As determined on a Westphal balance, the density of the solutions indicated that the exact concentrations were 10.1, 20.2, and 30.2% calcium chloride. The carbon dioxide was a commercial gas for medicinal purposes (Ohio Chemical Company) and the solid calcium carbonate was small crystals of Iceland Spar (General Chemical Company).

Procedure

The method for determining the solubility of carbon dioxide in a calcium chloride solution consisted of allowing the carbon dioxide to come to equilibrium with the solution in the autoclave at the desired temperature, drawing off a sample of the solution, measuring the gas evolved at atmospheric pressure, and weighing the sample of solution from which the gas had been evolved.

After the vessel was thoroughly rinsed, the calcium chloride solution was drawn into the autoclave through the sampling valve, B, and the aspirator suction on the exhaust valve, F, was continued to remove any gases which would leave the solution at room temperature. In order to build up the desired pressure in the system, the carbon dioxide was pumped as a liquid from an inverted cylinder of gas into the autoclave at room temperature. A coil of copper tubing immersed in an ice–water-bath served as a feed line from the inverted carbon dioxide cylinder to the high pressure liquid proportioning pump, and high pressure tubing connected the pump to the sampling valve, B, at the bottom of the autoclave. An initial pressure of 3900 to 5500 lb. per sq. inch at room temperature yielded a pressure in excess of 10,000 lb. per sq. inch at equilibrium temperature.

Before the first sample was withdrawn from the equilibrium vessel, the system was held at the desired temperature for several hours, and a small amount of solution was run out, in case equilibrium had not been established in the short section of tubing between the autoclave and valve. This assured the presence of the saturated solution at the valve seat; failure to do so resulted in erratic values for the solubility.

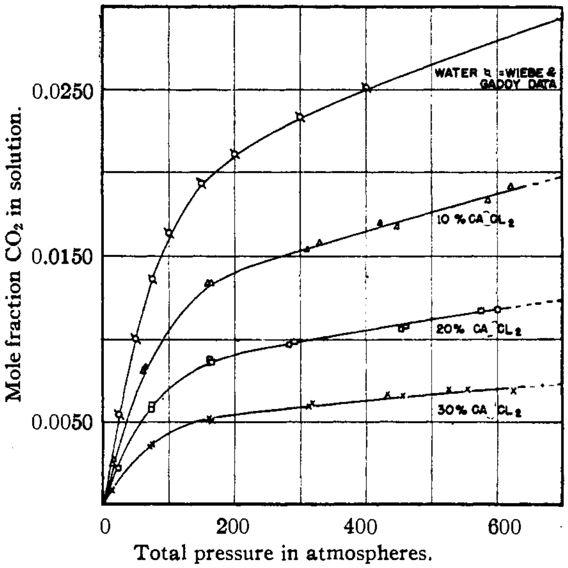

Fig. 2.—Solubility of CO_2 in calcium chloride–water solutions at 75°.

Immediately before sampling, the valve was again opened slightly, and the pressure in the system was restored by turning the capstan of the pressure balance. With the glass trap, C, connected to the high pressure valve, B, the sample of solution was collected to be weighed after the gas expanded into the buret system, D, E. During the three to six minutes required to collect the sample, the pressure in the system was maintained by turning the capstan on the pressure balance to force oil into the trap, H, to replace the volume of solution removed. The final measurement of the volume of carbon dioxide evolved was taken thirty to forty-five minutes later at the temperature of the water jacket on the buret system.

In order to obtain a series of solubility determinations at one equilibrium temperature, the pressure in the system was lowered after a sample had been taken, whereupon the solution was again agitated until it was in equilibrium with the gas phase. Duplicate samples could be collected by forcing more oil into the trap to maintain the pressure. Assurance that equilibrium had been attained was afforded by the concordant values from several samples collected when the system had come to equilibrium from a lower pressure.

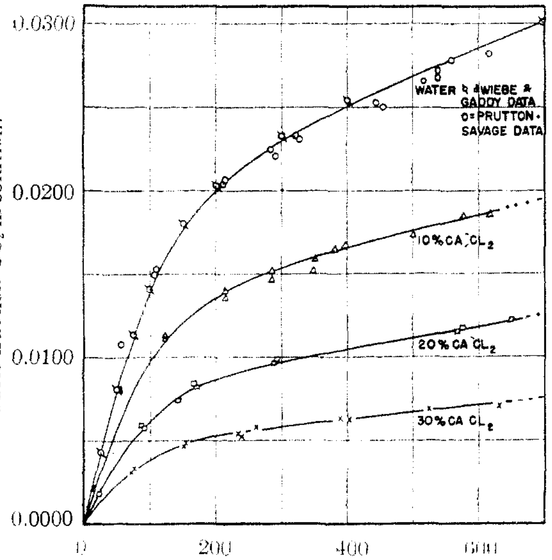

Fig. 3.—Solubility of CO_2 in calcium chloride water solutions at 100°.

For the measurement of the carbon dioxide evolved at atmospheric pressure, the volume of the liquid collected was subtracted from the gas buret reading. This resultant volume of carbon dioxide, corrected for the vapor pressure of the solution and reduced to standard conditions, was used to calculate the mole fraction of carbon dioxide in the solution. The temperature of the sample tube, C, was assumed to be that of the buret, and since there is an appreciable solubility of carbon dioxide in water at room temperature and atmospheric pressure, a correction was calculated from the Bunsen absorption coefficient (= 0.759 at 25°)[11] multiplied by the factor $[(\text{mm. Hg} - P_{H_2O})/760 d_{H_2O}]$. P_{H_2O} and d_{H_2O} were the vapor pressure and density of water at the temperature of the buret and mm. Hg was the barometric reading. A similar correction for the calcium chloride solutions was calculated from the values reported by MacKenzie[7] for the solubility of carbon dioxide in calcium chloride solutions at atmospheric pressure and room temperature. It was necessary to extrapolate his data to obtain a value for the solubility of carbon dioxide in 30% calcium chloride solutions. The same factor $(\text{mm.Hg} - P_{\text{soln.}})/760\ d_{\text{soln.}}$ converted the absorption coefficient to units consistent to the measurements used in this investigation. $P_{\text{soln.}}$ and $d_{\text{soln.}}$ were the calculated vapor pressure and the density of the calcium chloride solution at the temperature of the buret system.

The calculation of the first value in Table I is presented to show the method. After the sample was withdrawn from the equilibrium vessel, the gas volume in the buret was 90 ml. The volume at S.T.P., after correcting for the volume of liquid in the sample, vapor pressure of the solution, barometric pressure and temperature of the buret, was 76.3 ml. To this was added the volume of gas which was still dissolved in the 2.17 g. of water at the temperature of the buret. This volume was calculated from the Bunsen coefficient to be 1.5 ml. Dividing the sum of these two volumes by the molecular volume of carbon dioxide (= 22, 264) gave the moles of carbon dioxide in solution at equilibrium, and dividing this by the total of the moles of water plus carbon dioxide gave the mole fraction of carbon dioxide in solution.

A similar calculation for the solubility in calcium chloride solutions included the moles of calcium chloride dissolved in the sample.

In order to verify the accuracy of the experimental method, the solubility of carbon dioxide in water was determined at 100°, and the results compared with those of Wiebe and Gaddy,[9] who had used a flow system for the same measurement. Their experimental method consisted of bubbling carbon dioxide gas under pressure through the water in an equilibrium vessel until the liquid was saturated. The gas evolved from a sample of saturated solution was measured in a buret system where the volume of liquid was also measured. By means of the Bunsen coefficient a correction was made for the gas remaining in the water at room temperature under the partial pressure of the carbon dioxide in the buret.

Experimental Data and Results

In Table I are presented the solubility data for carbon dioxide in water at 100 and 120° and in calcium chloride solutions at 75, 100 and 120°. Total pressure was measured in lb. per sq. inch and converted to atmospheres. The weight of solution was taken after the gas had been evolved at atmospheric pressure and room temperature, the volume of carbon dioxide evolved being measured over mercury and the volume remaining in the water at atmospheric pressure calculated from the Bunsen coefficient for the solubility of carbon dioxide in water at the temperature of the water as was outlined in the description of the experimental procedure. This sum of the volume of gas evolved and the volume of gas dissolved at atmospheric pressure was used to calculate the mole fraction of carbon dioxide in the solution at the equilibrium pressure.

Discussion

Above 300 atm. total pressure the results were about 1% lower than those reported by Wiebe and Gaddy[9] for the solubility of carbon dioxide in water at 100° and below this pressure, where there was only one experimentally determined value, the deviation was somewhat greater. The difference may have been due to experimental

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(11) G. Geffcken, *Z. physik. Chem.*, **49**, 256 (1904).

TABLE I

SOLUBILITY OF CARBON DIOXIDE IN WATER AND CALCIUM CHLORIDE SOLUTIONS

Pressure, atm.	Mole fraction CO_2 in soln.
I. In Water	
t, °C. = 101 ± 1.0	
615	0.0282
558	.0278
518	.0266
452	.0251
443	.0253
325	.0231
320	.0233
290	.0221
283	.0225
212	.0207
210	.0205
109	.0153
107	.0150
57	.0108
t, °C. = 120 ± 1.0	
694	0.0300
646	.0299
570	.0290
562	.0288
360	.0250
353	.0248
187	.0200
186	.0193
69	.0105
68	.0100
23	.0040
23	.0038
II. In 10.1% $CaCl_2$	
t, °C. = 75.5 ± 1.0	
620	0.0192
585	.0184
446	.0168
426	.0170
328	.0158
310	.0154
163	.0133
162	.0133
63	.0083
62	.0081
16	.0027
16	.0026
t, °C. = 101 ± 1.0	
618	0.0186
575	.0185
500	.0174
394	.0168
380	.0165
352	.0159
347	.0162
286	.0152
286	.0147
213	.0140
213	.0135
120	.0113
120	.0112
56	.0081
17	.0022
17	.0021
In 10.1% $CaCl_2$ (*Contd.*)	
t, °C. = 121 ± 1.0	
703	0.0193
621	.0181
585	.0184
460	.0167
437	.0168
300	.0148
297	.0148
153	.0111
149	.0113
77	.0069
76	.0061
21	.0027
21	.0027
III. In 20.2% $CaCl_2$	
t, °C. = 76 ± 1.0	
600	0.0118
572	.0117
460	.0108
454	.0107
290	.0098
282	.0097
166	.0086
165	.0088
73	.0060
73	.0058
23	.0022
22	.0022
t, °C. = 101 ± 1.0	
648	0.0123
574	.0118
566	.0116
292	.0099
290	.0097
170	.0083
169	.0084
142	.0074
142	.0074
91	.0058
88	.0059
23	.0018
23	.0017
t, °C. = 121 ± 1.0	
659	0.0115
636	.0115
602	.0117
506	.0113
491	.0110
464	.0110
282	.0094
280	.0094
150	.0073
150	.0073
63	.0039
63	.0039
25	.0019
25	.0017
IV. In 30.2% $CaCl_2$	
t, °C. = 76 ± 1.0	
625	0.0069
554	.0070
525	.0070
455	.0066
431	.0067
319	.0061
314	.0060
163	.0051
161	.0052
74	.0037
73	.0036
15	.0009
15	.0009
t, °C. = 101 ± 1.0	
630	0.0071
525	.0070
402	.0063
389	.0064
388	.0064
261	.0058
238	.0052
234	.0054
154	.0049
151	.0047
76	.0033
74	.0031
t, °C. = 121 ± 1.0	
665	0.0074
510	.0069
494	.0065
468	.0061
450	.0063
302	.0058
296	.0058
150	.0045
148	.0045
85	.0031
83	.0031
V. In 10.1% $CaCl_2$ Solution with Solid $CaCO_3$ Present	
t, °C. = 120 ± 1.0	
874	0.0212
830	.0220
655	.0198
643	.0195
492	.0184
480	.0179
318	.0159
309	.0153
156	.0124
155	.0116
74	.0082
73	.0071
28	.0030
28	.0030

error, or it may have been due to possible differences in experimental procedure which may have occurred in the method used to maintain the pressure in the system while the sample was being withdrawn. Since the equilibrium was attained, and also disturbed, over a period of a few minutes' time, a lowering of the pressure during sampling could affect the results.

The values for the solubility of carbon dioxide in water at 120° are higher than the values at 100° at pressures in excess of 300 atm. and extend the data of Wiebe and Gaddy, confirming their observation that above 75°, the solubility in this pressure range increases with temperature. On this basis the results obtained by the two different methods were considered to be in close enough agreement to permit the use of the static method for the determination of the solubility of carbon dioxide in calcium chloride–water solutions.

A mean deviation of less than 3% was observed for the values obtained from the determination of the solubility of carbon dioxide in calcium chloride solutions and smooth curves resulted from plotting the solubility (mole fraction carbon dioxide) as a function of the pressure.

The change with pressure in the solubility of carbon dioxide in water approximately followed Henry's law up to pressures of about 100 atm., but a wide deviation occurred between 100 and 300 atm. Much greater deviations were observed for the solubility of carbon dioxide in the calcium chloride solutions in which there was a definite salting out effect. Sander[8] called attention to the fact that the compressibility maxima for carbon dioxide at temperatures from 50 to 100° lie between 100 and 200 atm., and that beyond this point the gas phase assumes the property of a liquid, being only slightly compressible. Wiebe and Gaddy[9] confirmed Sander's opinion that the mutual solubility of liquid in liquid is affected by pressure to only a slight extent.

Solid calcium carbonate in contact with the equilibrium solution resulted in a small increase of the concentration of carbon dioxide dissolved in a 10% calcium chloride solution. Figure 4 indicates that below 100 atm. pressure the solubility of carbon dioxide in the solution having calcium carbonate present was equal, within the limits of experimental error, to the solubility in the solution without the solid carbonate, and that between 100 and 700 atm. pressure the solubility increased by less than 4%.

The mole fraction of calcium chloride in the original stock solutions was about 0.018 in the 10% solution, 0.039 in the 20% solution and 0.065 in the 30% solution. A tabulation of the ratio of the moles of carbon dioxide in solution per mole of calcium chloride in the stock solution (Table II) shows that, even for the solutions containing only 10% calcium chloride, a pressure of over 600 atm. was needed in order to approach a mole to mole ratio of carbon dioxide to calcium chloride in solution which is the ratio in which they are formed during the reaction. At the higher concentrations of calcium chloride, the ratio of carbon dioxide to calcium chloride is much less than one to one. Generally, the acid used for the treatment of oil wells is about 15% hydro-

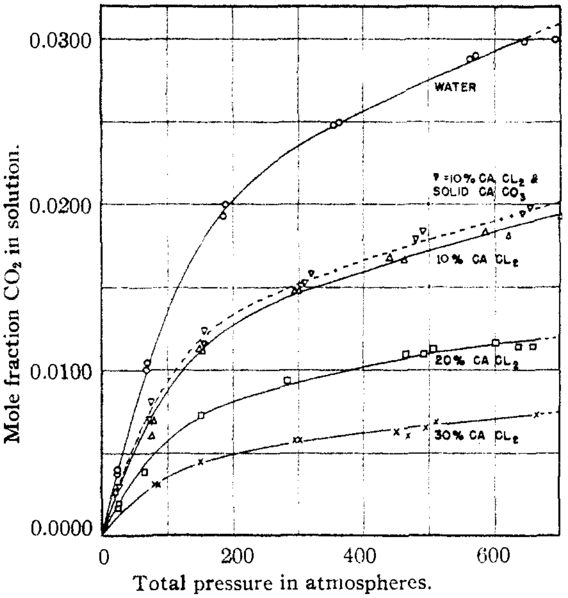

Fig. 4.—Solubility of CO_2 in calcium chloride–water solutions at 120°.

chloric acid and its action on calcium carbonate would result in the formation of a solution containing about 25% calcium chloride. The excess carbon dioxide from such a reaction solution would appear as gas bubbles to loosen drilling mud sheaths, and the reaction should go substantially to completion.

Table II

Moles of Carbon Dioxide in Solution per Mole of Calcium Chloride in the Original Solution at 75°

Pressure, atm.	10% $CaCl_2$ solution	20% $CaCl_2$ solution	30% $CaCl_2$ solution
700	1.10	0.32	0.110
400	0.91	.27	.100
300	.84	.25	.092
200	.76	.23	.083
150	.70	.21	.077
100	.59	.17	.065
75	.50	.15	.055
50	.37	.11	.040
25	.21	.06	.021

Summary

The solubility of carbon dioxide in 10, 20, and 30% calcium chloride–water solutions has been determined in a static system for temperatures of 75, 100, and 120°, and pressures up to 700 atm. There was a wide deviation from Henry's law above 100 atm., and this deviation increased with salt concentration.

The low solubility of the carbon dioxide in calcium chloride–water solutions even at high pressures indicates that the action of hydrochloric acid on calcium carbonate formations during the acid treatment of oil wells results in carbon dioxide being evolved during the reaction to provide some mechanical agitation for the dispersion of acid insoluble materials.

Cleveland, Ohio Received May 17, 1945

[Contribution from the Moore Laboratory of Chemistry, Amherst College]

The Determination of Small Surface Areas by Krypton Adsorption at Low Temperatures

By Ralph A. Beebe, John B. Beckwith and Jurgen M. Honig

Extensive use has been made of the method of Brunauer, Emmett and Teller[1] (B.E.T.) for the determination of surface areas of solids. This method consists in determining the volume (v_m) of a gas, usually nitrogen at liquid nitrogen temperature, necessary to complete an adsorbed monolayer. Making use of v_m and of σ_{N_2}, the estimated area occupied by each nitrogen molecule in the monolayer, it is possible to calculate the area of the solid under investigation.

The recent publications of Harkins and Jura[2] present a different approach to the problem. These authors have determined the area of a sample of crystalline, non-porous anatase (TiO_2) powder by an "absolute" calorimetric method, the results of which confirm the validity of the B.E.T. technique. They have also developed a "relative" method which does not require the use of an estimated value of σ_{N_2}.

Because of these developments it is possible to estimate with considerable confidence the areas of solids of moderately high specific surface area, let us say greater than one sq. m./g. of solid. However, in the case less porous or more coarsely crystalline solids of lower adsorptive capacity, none of the above methods using nitrogen as adsorbate is sufficiently sensitive. An important factor limiting the usefulness of the B.E.T. method and the Harkins and Jura "relative" method, both of which make use of the nitrogen adsorption isotherms up to fairly high relative pressures, is the large correction for unadsorbed nitrogen gas. This results from its high saturation pressure, which is approximately one atmosphere at liquid nitrogen temperature. This correction can be greatly reduced by carrying out the adsorption at temperatures well below the boiling

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[1] Brunauer and Emmett, This Journal, 59, 2682 (1937); Brunauer, Emmett and Teller, *ibid.*, 60, 309 (1938).

[2] Harkins and Jura, *ibid.*, 66, 1362 (1944); 66, 1366 (1944).