that has yet been reported is 2.25, by Jolibois and Maze-Sencier.[4]

Because the figures in the eighth column of Table I seem to indicate the formation of precipitate with a higher ratio of Ca:P, an attempt was made to prepare precipitates having such high ratios. It seemed that this might best be accomplished by the addition of a phosphoric acid solution to a solution of calcium hydroxide (Table II). After thorough mixing in centrifuge tubes and standing for the times indicated, the tubes were centrifuged and the clear liquid was titrated with standard acid, using methyl red as indicator, and was also tested for the presence of phosphate by the method of Fiske and Subbarow.[5] None, or at most, inconsiderable traces of phosphorus were found. In a number of the mixtures, the analyses of which are not given, the precipitates could not be separated by centrifuging. This peptizing action of calcium hydroxide solution upon precipitates of calcium phosphate had previously been reported by Jolibois and Maze-Sencier.[4]

One such peptized mixture was prepared on a larger scale and was filtered through a dense paper, with almost complete exclusion of air. The first third was discarded. The filtrate subsequently obtained was crystal clear and contained no phosphate. The results of the analyses are given at the foot of Table II.

TABLE II

COMPOSITION OF PRECIPITATES OBTAINED WITH PHOSPHORIC ACID AND LARGE EXCESS OF CALCIUM HYDROXIDE

Experiment	Time, days	Initial $[Ca^{++}]$ 10^3	Initial $[P]$ 10^3	Final $[Ca^{++}]$ 10^3	Precipitate $[Ca]/[P]$
1	5	21.05	0.973	18.34	2.79
2	5	19.29	1.78	15.28	2.25
3	5	17.81	2.47	12.51	2.25
13	4	15.43	0.89	13.16	2.45
21	1	20.27	0.971	17.80	2.54
22	1	22.12	2.12	16.80	2.51

The ratios in this table are reasonably constant and are not appreciably greater than those reported by Jolibois and Maze-Sencier.[4] The higher ratios in Table I are probably erroneous. The first two deviations may very well be due to the small differences employed in the calculations: that in the third is almost certainly due to some gross error.

We may now picture the course of events as follows: after the first equivalent of calcium hydroxide has been added, the solution contains Ca^{++}, $H_2PO_4^-$ and $HPO_4^=$ ions. It also contains some undissociated $CaHPO_4$.[6] This may act as an acid and upon addition of $Ca(OH)_2$ give a precipitate of $Ca(OH)\cdot CaPO_4$, possibly occluding or adsorbing a little $Ca(OH)_2$ as well. Removal of $CaHPO_4$, lowers the value of $[H_2PO_4^=]$, of $[HPO_4^=]/[HPO_4^-]$, and, consequently, of *p*H. Upon standing, *if a crystal of* $Ca_3(PO_4)_2$ or related compound is present, the precipitate will gradually change to approximate this composition, and the solution will, accordingly, become more alkaline. If no such crystal is present, the metastable condition may persist indefinitely, as appears to have been the case in series M of the experiments of Holt, La Mer and Chown.

Summary

It is believed that the anomalous results obtained by others in the titration of phosphoric acid with calcium hydroxide can be explained by the formation of a precipitate having Ca:P = 2 or more, with a subsequent slow change to the usual 1.5.

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(4) P. Jolibois and J. Maze-Sencier, *Compt. rend.*, **181,** 36 (1925).

(5) C. H. Fiske and Y. Subbarow, *J. Biol. Chem.*, **66**, 375 (1925).

(6) I. Greenwald, J. Redish and A. Kibrick, *J. Biol. Chem.*, **135**, 65 (1940).

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, PITTSBURGH, PA.]

Pressure Dependence of the Rate of Gasification of Carbon[1]

BY B. R. WARNER[2]

In a previous publication[3] a mechanism of the steam-carbon reaction was postulated in which the rate of gasification was stated to be a function of an adsorption isotherm with a saturation pressure. This postulate was based on existing data[4] obtained in a system which was at a constant pressure and wherein the partial pressure of steam was varied by the change in the fraction of steam decomposed on altering the velocity of the steam passing through the carbon bed. It was found that the rate of gasification approached constancy with increase in the partial pressure of the steam. In these cases, however, the gaseous atmosphere surrounding the carbon is not pure steam but an admixture of steam and the reaction products, hydrogen, carbon monoxide, and carbon dioxide, any of which can be adsorbed in competition with the steam. A more rigorous proof can be obtained by changing the absolute pressure of the

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(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Presented at the 107th meeting of the American Chemical Society at Cleveland, Ohio, April, 1944. Not copyrighted.

(2) Associate physical chemist, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa. Present address: Gulf Research and Development, Harmarville, Pa.

(3) Warner, THIS JOURNAL, **65**, 1447 (1943).

(4) Brewer and Reyerson, *Ind. Eng. Chem.*, **26**, 734 (1934).

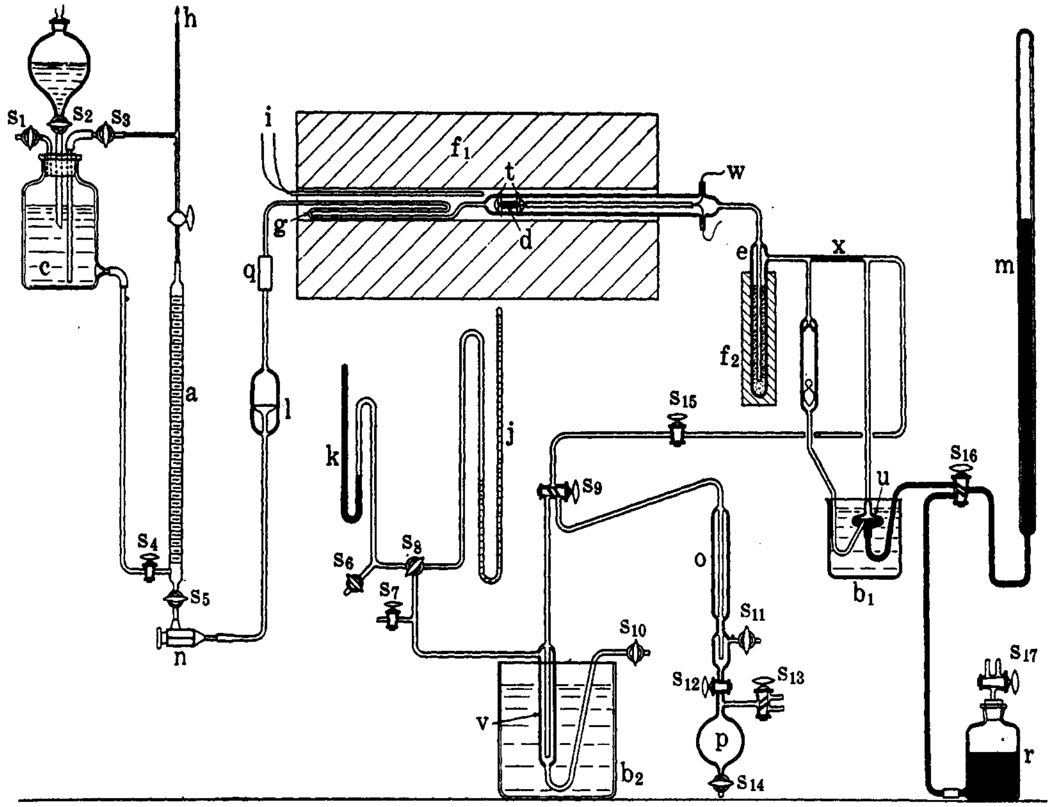

Fig. 1.—Apparatus for study of rate of gasification of carbon.

system and maintaining a steam velocity high enough to ensure an atmosphere consisting almost entirely of steam. The partial pressure of the steam is then equal to the system pressure. Since this reaction is typical of other gas–solid reaction systems, such as carbon dioxide–carbon, sulfur dioxide–carbon, etc., it seemed desirable to substantiate this point. It is also of importance in comparing carbons for reactivity in a water-gas generator, as saturation pressure may vary with different types of carbon as it does with temperature. Likewise, it would indicate no advantage in carrying out the reaction at super-atmospheric pressures if the saturation pressure is very low.

One of the unfortunate features in carbon reactivity studies is the variation between carbon samples from the same source.[5] It was therefore necessary to study a single sample of carbon over an entire pressure range, so that differences in carbons would not be involved in the measurements. This required an apparatus in which it was possible rapidly to change the pressure and steam velocity and a scheme for measuring the small amounts of gas formed in a very short time, so that the sample was not consumed to any appreciable extent between measurements. The problem was simplified by the fact that the gasification involves only the formation of carbon monoxide and hydrogen (the carbon dioxide being formed by the water-gas reaction[3]), so that by oxidizing these gases with copper oxide, only carbon dioxide and water were left. The rates were obtained by measuring the carbon dioxide pressure formed in a known volume after condensing the water. The apparatus used is described in Fig. 1.

Apparatus

Steam was generated by heating water in the quartz tube, q, which was maintained at red heat by means of an oxygen–gas flame. The water was supplied from the buret, a, its rate of flow being controlled by the sylphon bellows needle valve, n. The buret was filled from the water reservoir, c, in which the water was saturated with tank hydrogen connected at h. A hydrogen pressure was maintained in the buret to move the water from the buret to q. The fritted glass filter, 1, removed stopcock grease and other impurities from the water. The steam generated at q was superheated on passing through the quartz loops, g, and passed through the annulus formed by the carbon sample, d, and the enclosing quartz tube, all of which were heated by a platinum wire resistance furnace, f_1, whose temperature was controlled by hand by means of a variac and a rheostat. The carbon sample, d, was turned down from the larger diameter, leaving two smaller ends to fit into the quartz sample holder, t. Projections on this holder permitted the passage of steam. The diameter of the sample was 0.64 cm. and that of the reaction tube, 0.95 cm., resulting in an annulus of 0.39 sq. cm. cross section. Reaction temperatures were measured with thermocouples, W and i. W fitted onto the sample holder while i was outside the quartz tube over the sample. Samples were inserted into the quartz reaction tube and the system sealed off from the atmosphere, using quartz-to-pyrex and pyrex-to-soft glass graded seals so that the entire

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(5) Thiele and Haslam, *Ind. Eng. Chem.*, **19**, 882 (1927).

system could be made vacuum tight. The gas mixture then passed into the quartz tube, e, filled with copper oxide wire heated to 600–650° by the furnace, f_2. The hydrogen and carbon monoxide were oxidized to water and carbon dioxide and the gas continued through the capillary, X, and the pressure regulator,[6] u, the stopcock, S_{15}, acting as a further throttle to aid in the pressure regulation. Pressure in the system was read from manometer, m, the accuracy being ±5 mm. Condensation of steam was avoided by the use of a hot air-bath surrounding the apparatus from e to S_9 and a glycerol-bath, b_1, around the pressure reguator, u.

While steady state conditions were being attained, the steam was condensed in O, in which vacuum was maintained with an oil pump through S_{11} or an aspirator at S_{12}. The condensed water was removed from p by proper manipulation of stopcocks S_{12}, S_{13}, and S_{14}. When the steady state was reached, S_9 was turned so that the gas stream passed into V for a definite time interval determined with a stop watch. V was previously evacuated by an oil pump at S_6. The ice-bath, b_2, served to condense the water and the resulting pressure was read either on the mercury manometer, k, or on the butyl phthalate manometer, j. The volume of the system from S_9, including V and the manometer, was 105 cc. as determined by calibrating with a known volume.

From these pressures the vapor pressure of water at 0° was subtracted, the difference being that due to carbon dioxide. Some error was involved due to the solubility of carbon dioxide in water. As the area and volume of water exposed was about the same in all of the measurements, the amount of carbon dioxide dissolved should be directly proportional to the partial pressure of carbon dioxide, and therefore the percentage so lost should be approximately constant. It is also unlikely that under these conditions the equilibrium value for carbon dioxide solubility in water would be reached.[7] Measurements were limited to temperatures of 850–950°, since above these temperatures the rates of gasification became so great that the sample was rapidly consumed.

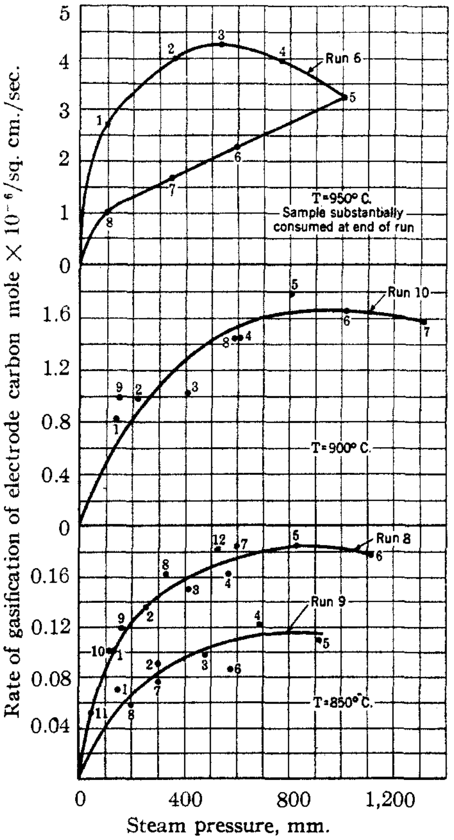

Fig. 2.—Rate of gasification of electrode carbon. Numbers on points indicate order in which they were obtained. Runs 8, 9, and 10 made on same sample of carbon.

Discussion

In Table I are shown the results of a typical complete run. With increase in pressure the rate of gasification increased at the lower pressures and then tapered off at the higher pressures. The results were reproducible on going from a lower to the highest pressure and then returning to the lower pressures, except in cases where the sample was greatly consumed. Figure 2 shows some of the typical results obtained. The curve obtained at 950° shows that the consumption of the sample makes it impossible to obtain reproducible results, while at the lower temperatures the points are in line and curves similar to adsorption isotherms are obtained. It should be noted that an aerodynamic effect such as Mayers[8] reported was not found. This is probably due to the fact

TABLE I

RATE OF GASIFICATION OF CARBON

Time	Temp., °C. Inner	Temp., °C. Outer	Av. steam flow over sample cc. H_2O/min.	Av. steam flow over sample Cm./sec.	Hg. system pressure mm.	CO_2 pressure in collecting system. mm.	Rate of gasification mole × 10^{-8}/sq. cm. sec.	Av.
1:51	853	851	0.9	282	130	2.5	8.7	
1:55	854	851	0.8	252		2.8	9.8	9.1
1:59	854	853	0.5	156		2.5	8.7	
2:05	853	853	1.0	160	255	3.9	13.6	
2:09	854	853	1.0	160		3.9	13.6	13.6
2:13	854	853	1.4	214		3.9	13.6	
2:19	854	852	1.4	136	420	4.3	15.0	15.0
2:23	854	853	1.4	136		4.3	15.0	
2:29	853	853	1.0	72	570	4.5	15.7	
2:33	852	851	1.5	84		4.4	15.3	16.6
2:37	851	852	1.5	84		5.1	17.8	
2:41	853	852	1.5	84		5.1	17.8	
2:51	858	857	1.2	60	830	5.3	18.5	
2:55	858	858	1.0	48		5.3	18.5	18.7
2:59	860	860	1.0	48		5.5	19.2	
3:10	860	860	1.6	58	1120	5.2	18.1	17.9
3:14	852	855	2.0	72		4.8	16.7	
3:21	853	851	0.6	40	600	5.3	18.5	18.5
3:25	858	860	0.6	40		5.3	18.5	
3:31	858	860	0.7	48	330	4.2	14.6	
3:35	862	862	0.7	48		5.0	17.4	16.4
3:39	861	861	0.7	48		4.8	16.7	
3:43	861	860	1.0	124		4.8	16.7	
3:48	859	860	0.7	180	160	3.4	11.9	11.9
3:53	854	851	0.7	180		3.4	11.9	
3:59	852	852	0.8	280	120	3.0	10.5	10.5
4:03	848	848	0.2	68		3.0	10.5	
4:08	843	844	0.5	420	50	1.7	5.9	5.8
4:12	844	844	0.5	420		1.6	5.6	
4:19	845	844	0.9	70	530	5.0	17.5	
4:23	844	844	0.9	70		5.2	18.2	18.0
4:27	844	843	0.4	32		5.2	18.2	

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(6) Warner, *Ind. Eng. Chem., Anal. Ed.*, **15**, 637 (1943).

(7) Markham and Kobe, THIS JOURNAL, **63**, 449–454 (1941).

(8) Mayers, *ibid.*, **56**, 1879 (1934).

that in these experiments the minimum average rate of steam flow over the sample was 32 cm. per second, as compared to Mayers' maximum flow of 30 cm. per second. The actual rates of gasification compare with those of Mayers as shown below.

RATE OF GASIFICATION IN MOLES × 10^{-6}/SQ. CM. SEC.

Temp., °C.	Warner (electrode carbon)[a]	Mayers (monolithic graphite)
850	0.18	0.09
900	1.8	0.22

[a] National Projector Carbon, National Carbon Co., Cleveland, Ohio.

Admitting the validity of these saturation pressures, there remain the problems of the activation energies and an explanation of why these pressures decrease with increase of temperature as was found in the treatment of the Brewer and Reyerson data (although not corroborated in the limited temperature range studied in the present experiments). The type of adsorption involved is most likely activated adsorption, so that the rate of adsorption should increase with temperature. Since it appears from the results that the adsorption equilibrum for those areas participating in the reaction is set up very rapidly there is no apparent reason for decrease in saturation pressure. It should be emphasized that in this case the adsorbing medium, carbon, is also participating in the reaction. Surface changes are continually taking place, and only the gross rate of reaction is measured. Certain areas may indeed lose activity due to a phenomenon similar to sintering of catalysts at high temperatures. At the higher temperatures the active areas which adsorb and react rapidly contribute most strongly to the gasification, while other less active areas may adsorb more slowly, and what appears to be a decrease in saturation pressure will necessarily follow. Because reaction is taking place, it is possible for unreactive areas to become active and *vice versa*.

No attempt has been made to calculate activation energies from these data since the unknowns involved preclude any such attempt. The true activation energy of this reaction may be very close to that obtained by Meyer and Sihvonen,[9] since in their experiments at very high temperatures (*circa* 2000° and 10^{-2}–10^{-4} min.) and low pressures, equal areas with low heats of adsorption would be participating in the reaction.

Acknowledgment.—The author wishes to express his appreciation to W. H. Tomlinson and Carl H. Noble for their aid in making the measurements, and to Dr. G. von Elbe with whom the author consulted during the course of the work.

Summary

New experimental proof has been obtained for the existence of isotherms and saturation pressures in the reaction between steam and carbon. These isotherms are of the form similar to the adsorption of a monomolecular layer of a gas on a solid adsorbent.

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[9] Meyer, *Trans. Faraday Soc.*, **34**, 1056 (1938); Sihvonen, *ibid.*, **34**, 1062 (1938).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Chloride as a Condensing Agent

BY J. H. SIMONS AND HAROLD HART

The use of hydrogen fluoride as a condensing agent has been demonstrated in this Laboratory,[1] and a study of the mechanism of the hydrogen fluoride catalyzed reaction between toluene and *t*-butyl chloride has been reported by Sprauer and Simons.[2] They have proposed an hypothetical mechanism which might be called a mutual acid-base catalysis[3] and have suggested that a similar mechanism might hold for other hydrogen fluoride catalyzed condensations.

Since the acidic and basic species involved in their mechanism are not ascribed to any specific chemical compound, it seemed logical that acids other than hydrogen fluoride might supply the acidic species. It was the purpose of this research to determine whether hydrogen chloride, under appropriate conditions, would have a catalytic activity similar to that of hydrogen fluoride.

The alkylation of the aromatic nucleus with certain alkyl halides and olefins and the acylation of the aromatic nucleus with an acyl halide have been accomplished successfully with the use of hydrogen chloride as the condensing agent. The reactions were carried out at temperatures varying from 75–235°, with initial hydrogen chloride pressures of 100–400 pounds per square inch. The yields in most cases were very good, with little or no tarry residues being formed. The reactions were homogeneous, which obviated the necessity of shaking.

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(1) J. H. Simons, *The Petroleum Refiner*, **22**, 83 and 189 (1943).

(2) J. W. Sprauer and J. H. Simons, THIS JOURNAL, **64**, 648 (1942).

(3) As the terms acid-base or acid-base catalysis have been used in the titles of articles published since our prior publication, for example, W. F. Luder and S. Zuffanti, *ibid.*, **66**, 524 (1944), and H. C. Brown, *et al.*, *ibid.*, **66**, 431 and 435 (1944), it is probably desirable to refer to the phenomenon which we have under discussion as the "Amphoteric Medium Effect."