[CONTRIBUTION FROM COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Rate of Oxidation of Graphite by Steam

BY MARTIN A. MAYERS

The rate of oxidation of graphite by steam at atmospheric pressure at temperatures between 850 and 1160° has been measured under conditions which eliminate the effect of diffusion as the rate determining process. These conditions, and the criterion of their attainment, that the stream velocity coefficient of the observed rate of reaction vanish, were fully discussed in an earlier paper.[1] The same furnace and sample support, and the same lot of graphite, were used as for the previous work. The only modifications to the apparatus were those required for producing the stream of water vapor, and for analyzing the products of reaction, which, in this case, consisted of carbon monoxide, carbon dioxide, and hydrogen.

Steam was generated by an electrically heated nichrome coil in a glass boiler suspended in a steam-bath, and was conducted through a well-insulated glass tube to the furnace inlet. Since the boiler was maintained at 100° by the steam-bath, all the electrical energy dissipated by the nichrome coil appeared as latent heat of steam, and the rate of steam flow could be estimated from measurement of the power input of the boiler. The boiler feed was distilled water, boiled to remove dissolved oxygen and carbon dioxide, fed from a reservoir by displacement with mercury.

The effluent from the furnace was condensed and the water collected over mercury in a receiver from which the fixed gases were pumped off by a small Sprengel pump. The gases passed through a drying tower and an ascarite weighing tube to remove carbon dioxide, then through a copper oxide furnace to oxidize carbon monoxide to dioxide, and hydrogen to water vapor, which, finally, were removed in two more weighing tubes, one filled with dehydrite for water, and one with ascarite for carbon dioxide. The condensate was freed of dissolved gas and the system cleared by flushing with nitrogen bubbled through the condensate for a half hour after each run. This apparatus was found, by the analysis of known mixtures of gases, to give results correct to about 2%.

Results

The results of the measurements are given in Table I. A total of fifty-nine runs was made, of which thirty-four are entered in the table. The remainder were discarded, either as trial runs, because the sample was consumed, or because of failure of the temperature control. The data are arranged in groups according to the furnace temperature, while within each group the runs appear in the order of increasing gas velocity. All runs but one, No. 23, which was omitted from calculations, were made at steam flow velocities above the point at which the work with carbon dioxide indicated zero velocity coefficient. Since this limit is determined largely by hydrodynamic, rather than chemical, conditions, it is to be expected that it would be the same as for the previous work although the gases were different. Run 23 was about 40% lower than the average for that temperature, confirming the view that diffusion operated the same way in this reaction as in the carbon dioxide reaction.

TABLE I

Run	Furnace temp., °C.	Steam flow velocity 1/min. N. T. P.	Rate of formation of CO_2	H_2	CO	Rate of gasification of C	Ratio	Ratio
			mol. $\times 10^{-6}$/cm.² sec.	mole $\times 10^{-6}$/cm.² sec.	mole $\times 10^{-6}$/cm.² sec.	mole $\times 10^{-6}$/cm.² sec.	CO/CO_2	$H_2/(CO + 2CO_2)$
44	1181	18.3	6.65	14.31	1.97	8.62	0.297	0.938
52	1144	24.9	4.72	10.73	1.54	6.26	.326	.979
45	1155	29.1	5.66	12.88	1.55	7.21	.274	.998
51	1146	33.4	4.40	10.03	1.33	5.73	.302	.992
49	1074	10.7	3.12	5.17	0.96	4.08	.299	.717
46	1068	12.6	1.98	3.37	.64	2.62	.323	.733
48	1063	22.2	2.21	3.60	.64	2.85	.290	.711
10	1097	23.7	2.81	5.05	.85	3.67	.301	.782
50	1070	29.6	2.17	3.16	.64	2.81	.295	.633
47	1060	33.8	2.23	4.72	1.31	3.54	.588	.819
58	994	10.5	1.434	0.996	0.105	1.539	.073	.296
6	1014	12.3	1.186	2.573	.484	1.670	.408	.901
7	1013	17.0	0.998	1.735	.306	1.304	.337	.756
56	986	22.1	.964	1.771	.442	1.406	.459	.748
55	982	29.0	.843	1.497	.386	1.229	.458	.724
8	1004	30.4	.671	1.622	.434	1.105	.647	.914
57	982	33.6	.881	1.687	.426	1.307	.484	.772
23	974	2.3	.303	0.155	.030	0.333	.099	.244
19	976	5.0	.445	.534	.018	.463	.040	.589
20	976	10.7	.489	.925	.115	.604	.235	.847
21	985	10.7	.439	.722	.057	.496	.130	.772
14	980	15.4	.300	.667	.223	.523	.743	.810
18	958	22.4	.181	.473	.176	.357	.973	.880
15	955	25.6	.176	.521	.236	.412	1.34	.885
29	917	13.0	.103	.117	.052	.155	0.506	.453
30	898	29.6	.056	.122	.070	.126	1.24	.670
16	933	34.5	.118	.290	.158	.276	1.34	.736
22	937	34.8	.142	.368	.187	.329	1.32	.783
35	878	10.9	.106	.030	.038	.144	0.361	.110
26	885	18.5	.055	.058	.042	.097	.764	.383
25	889	18.6	.072	.043	.035	.107	.487	.239
34	857	25.9	.036	.018	.021	.057	.584	.193
36	841	29.9	.025	.017	.024	.049	.960	.239
27	861	30.3	.032	.050	.039	.071	1.22	.482

The first six columns of Table I contain the direct results and are self-explanatory. The

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(1) M. A. Mayers, THIS JOURNAL, 56, 70 (1934).

rates of appearance of carbon monoxide and of carbon dioxide vary rather widely within the same temperature group, especially in the low temperature range, but their sum, given in column 7, is found to be constant, making allowance for the variation of the actual temperature from the mean. This result had been anticipated and is considered to be justification for the view that the rate of oxidation of graphite by steam is given by the sum of the rates of appearance of the two oxides, but that, when secondary reaction is possible between the initial products of reaction and the gaseous atmosphere, the rate of appearance of either one of the oxides by itself is of no significance. The ratio CO/CO_2 of the products of reaction depends on the speed of the secondary reaction, in this case principally

$$CO + H_2O \longrightarrow CO_2 + H_2$$

and on the time during which the mixture of gases remains in the heated zone. That this view is correct is confirmed by the fact that the water gas constant found

$$K = (P_{CO} \times P_{H_2O})/(P_{CO_2} \times P_{H_2})$$

was above the equilibrium value for the corresponding temperatures and that the discrepancy increased with increasing stream velocity. If the water-gas constant were determined by the characteristics of the graphite oxidation, it would not have varied with gas velocity, and this would have required a decreasing value of the ratio CO/CO_2 with increasing gas velocity, but, as a matter of fact, the ratio increased in the low temperature range and remained approximately constant in the high temperature range.

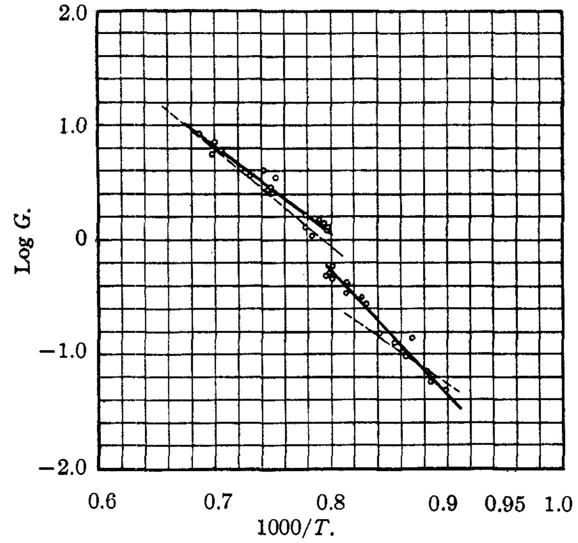

Fig. 1.—Rate of gasification of graphite at various temperatures. Points and full lines: rate of gasification by steam at approximately 745 mm. water vapor pressure. Dashed lines: rate of appearance of carbon as carbon monoxide from carbon dioxide at 1 atmosphere.

The results of the measurements could not be corrected to a standard pressure since the order of this reaction is not yet known. The atmospheric pressure in this Laboratory was about 745 mm. during the time the experiments were carried on. Variations in the atmospheric pressure and in the difference in pressure between the inside of the furnace and the atmosphere amounted to not over 3% of the total pressure. Thus if the reaction is of the first order, neglecting this correction introduces an error of ±3%, while if the reaction is of the second order, the error is about 6%. Of the thirty-three points that could be used for calculation of correlating equations, seventeen fell in the high temperature range (1000–1160°) for which G_1, the rate of oxidation of carbon by steam in micromoles per sq. cm. per second, may be represented by

$$\log G_1 = (6.20 \pm 0.25) - \frac{35130 \pm 50}{4.575\,T}$$

in which T represents the absolute temperature; and the other sixteen in the low temperature range (860–960°) represented by

$$\log G_2 = (8.42 \pm 0.30) - \frac{49720 \pm 50}{4.575\,T}$$

The constants in these equations and the magnitudes of their errors were determined by the method of least squares. The errors correspond to an uncertainty in a single observation of about 12%. The data are plotted with the correlating equations as full lines in Fig. 1, in which $\log G$ is plotted against $1/T$. It may be noted that the rate of oxidation of carbon in this reaction is of the same order of magnitude as the rate of appearance of carbon as carbon monoxide when graphite is oxidized by carbon dioxide, represented by the dotted lines of Fig. 1.

The hydrogen in the products of reaction was in every case less than the amount corresponding to the oxygen in carbon dioxide and carbon monoxide, as shown by the ratio $H_2/(CO_2 + 2CO_2)$ in the table, which is equal to 1 when all the hydrogen was recovered. In the high temperature range the discrepancy was usually small, but in the low temperature range sometimes only a fifth of the hydrogen expected from the oxygen balance was found. This may be due to the formation of methane which was not determined in these experiments. One milligram of methane per minute would have accounted for the largest discrepancies found. The formation of methane is not believed to have interfered with the oxidation measurements because, first, the observed rates of oxidation were the same at any temperature, regardless of the value of the ratio $H_2/(CO + 2CO_2)$ in the products, and, second, the concentrations of the products of reaction in the effluent gases were so small that the reaction between them must have been small by comparison with the reaction between hydrogen and the graphite with which it was in contact when it was formed.

Values of the heat of activation, which agree fairly well with those observed both for the steam and for the carbon dioxide oxidation reactions with graphite, may be calculated according to the principles enunciated by Hinshelwood.[2] The calculation involves the assumption that heats of adsorption found at room temperatures are valid at high temperatures. It also requires the assumption of mechanisms of reaction which may be subjected to experimental verification. The mere agreement of the experimental values of the heat of activation with such calculated values is not sufficient evidence for the acceptance of the assumptions, so detailed discussion of the mechanism of reaction will be deferred.

Summary

The rate of oxidation of graphite by steam has been measured under such conditions that the rate determining effect of diffusion has been eliminated. At about 745 mm. vapor pressure, the rate of gasification of carbon in micromoles per square cm. per second, in the high temperature range, from 1000 to 1160°, is given by

$$\log G_1 = 6.20 - (35{,}130/4.575\,T)$$

and in the low temperature range, from 850 to 1000°, by

$$\log G_2 = 8.42 - (49{,}720/4.575\,T)$$

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[2] C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 3d ed., Oxford University Press, 1933, pp. 349–355.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA AND OF THE COLLEGE OF ST. THOMAS]

Titration of Chloride and Bromide with Mercurous Nitrate Using Brom Phenol Blue as Adsorption Indicator

BY I. M. KOLTHOFF AND W. D. LARSON

Short notes on the titration of chloride and bromide with mercurous nitrate as a reagent using adsorption indicators for the detection of the end-point have been published in the literature. Burstein[1] used sodium alizarine sulfonate as indicator in the titration of bromide. Von Zombory[2] recommended brom phenol blue and brom cresol purple in the titration of chloride and bromide with mercurous nitrate or in the reverse titration. Recently von Zombory and Pollak[3] have also recommended chlor phenol red and brom cresol green for the same purpose. Each of the last four indicators remains in the yellow form in the solution when there is an excess of chloride or bromide, and is adsorbed with a lilac color when mercury is in excess. The color change is reversible; hence, if the end-point is overstepped one can back titrate with halide solution. After examination of many dyes as adsorption indicators for the various titrations, it appeared that brom phenol blue yielded the best color change, especially for titrations of chloride.

A more detailed study was made of the practical applicability of the chloride and bromide titration under varying conditions with mercurous nitrate, using brom phenol blue as adsorption indicator. The analytical results are reported in the first part of this paper, and in the second part the mechanism of the indicator action is discussed.

Materials Used

Mercurous Nitrate.—Mallinckrodt Analytical Reagent grade was used.

Potassium Chloride.—A C. P. product twice recrystallized and dried at 200°.

Potassium Bromide.—A chloride-free product was obtained by heating pure potassium bromate until all the oxygen was driven off. The resulting salt was recrystallized three times from water and dried.

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[1] R. Burstein, *Z. anorg. allgem. Chem.*, **168**, 325 (1927).

[2] L. v. Zombory, *ibid.*, **184**, 237 (1929).

[3] L. v. Zombory and L. Pollak, *ibid.*, **215**, 255 (1933).