The Kinetics of Absorption of Oxygen by Catechol

BY M. A. JOSLYN AND G. E. K. BRANCH

The absorption of oxygen by polyhydric phenols and its catalysis by ferric and manganous ions, by alkali, and by plant phenolases is well known. However, the kinetics of the reaction in absence of any other catalyst but alkali have not been systematically investigated, except in the case of hydroquinone for which the results as to order of the reaction with respect to OH⁻ have been rather contradictory.[1,2,3,4,5,6,7]

In this paper we are reporting a study of the kinetics of the auto-oxidation of catechol in absence of any catalyst but alkali and in the absence of light.

A fairly stable p-quinone is formed in the oxidation of hydroquinone so that the kinetics of its auto-oxidation may be studied either by determining the rate of absorption of oxygen or the rate of formation of quinone. However, the o-quinone is much more unstable[8] and the auto-oxidation of catechol is more complex, yielding intensely dark brown products which are evidently compounds of considerable complexity.

Auto-oxidations in general involve a preliminary absorption of oxygen with the formation of peroxides, followed by secondary reactions. The initial rate of absorption of oxygen is a measure of the rate of the primary reaction. When the subsequent reactions do not involve oxygen gas, or are slow with respect to the primary reaction, and when no catalyst or inhibitor is produced during the reaction, the initial rate of absorption of oxygen remains constant over a measurable time during which absorption of appreciable quantities of gas occurs, and the rate of the primary reaction can be measured. It is evident that the primary reaction as defined above is not necessarily the first step in the reaction. For

instance, it cannot be the formation of active chain continuing molecules, for the time taken to reach a steady state of such active molecules is too short to be measured. It is probably the formation of peroxides no longer capable of continuing a chain leading to the absorption of oxygen.

In the auto-oxidation of catechol in buffered alkaline solution, easily measured quantities of oxygen are absorbed at a constant rate (see Fig. 2). Further evidence that this constant rate of absorption of oxygen is a measure of the rate of the primary reaction was given by the fact that the rate was unaltered in the presence of about 10% of freshly oxidized catechol. It was found also that the rate of the primary reaction could be measured in alkaline solutions even in absence of buffer.

The dependence of the primary reaction on such variables as H⁺-ion concentration, catechol concentration, partial pressure of oxygen, temperature and surface was studied, both in buffered and unbuffered solutions.

Experimental Part

Reagents.—A fresh stock of Eastman catechol was used without further purification. The crystals were perfectly colorless, gave a colorless solution, and melted sharply at 105°. The other chemicals used were of the purest commercial grade obtainable, either Eastman or analytical reagent grade.

Apparatus.—The rate of oxygen absorption was followed by measuring the rate of decrease in pressure, at practically constant volume, occurring when definite quantities of catechol dissolved in water, phosphate buffers or sodium hydroxide solutions, were rapidly shaken in an atmosphere of oxygen. The apparatus consisted essentially of two flasks, each connected to one arm of a manometer, to each other, and to an oxygen supply and a vacuum pump so that they could be at will flushed out and filled with oxygen at the desired pressure. Both flasks were connected to a metal swing and immersed in a darkened thermostat at 25 ± 0.03°. The manometer liquid was Brodies' solution[9] and the volume of the manometer was small, less than 0.1% of the volume of the flasks. During each individual experiment the concentration of catechol and the pressure of oxygen were practically constant as the total amount of oxygen absorbed was small with respect to both the oxygen and the catechol in the reaction vessel.

(1) Hans v. Euler and Ivan Bolin, Z. physiol. Chem., **57**, 80 (1908).

(2) Victor K. La Mer and Eric K. Rideal, THIS JOURNAL, **46**, 223 (1924).

(3) Hans v. Euler and Edvard Brunius, Z. physik. Chem., **139**, 615 (1928).

(4) Victor K. La Mer and J. W. Temple, Proc. Nat. Acad. Sci., **15**, 191 (1929).

(5) René Dubrisay and Albert Saint-Maxen, Compt. rend., **189**, 694 (1929).

(6) Albert Saint-Maxen, ibid., **191**, 212 (1930).

(7) W. Reinders and P. Dingemans, Rec. trav. chim., **53**, 209–230 (1934).

(8) For example see J. B. Conant and L. F. Fieser, THIS JOURNAL, **46**, 1858 (1924).

(9) R. Siebeck in Emil Abderhalden, "Handbuch der biochemischen Arbeitsmethoden," 1915, Vol. VIII, p. 25.

The rates are expressed in cc. of oxygen at 25° and 1 atmosphere absorbed by 125 cc. of solution.

The experiments were performed by introducing 100 cc. of the buffer solution or other substrate into one of the flasks, and 25 cc. of freshly prepared aqueous catechol solution (usually 0.5 M) into a small tube supported in the flask by a glass rod. Both flasks were evacuated and filled with oxygen. The system was then cut off from the oxygen supply and allowed to stand until temperature equilibrium was reached, usually one hour. The stopcocks connecting the two flasks were turned, the glass rod lifted to precipitate the catechol into the buffer solution and the shaker started. The shaking was sufficiently violent to shatter the tube, to cause practically immediate mixing, and to keep the solution in a state of froth. The empty thermostated flask attached to one arm of the manometer was found to effectively prevent movements of the manometer liquid other than those caused by the reaction.[10]
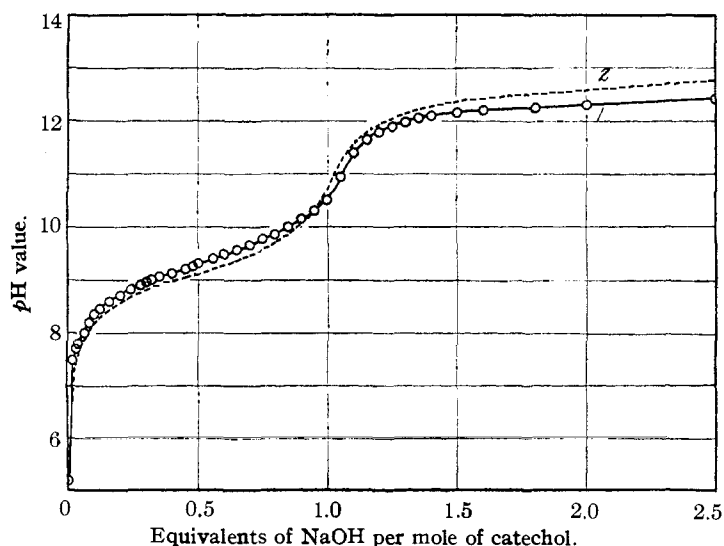

Fig. 1.—Titration curve: 1, pure catechol; 2, in presence 0.8 M KCl.

Measurement of pH.—The actual hydrogen-ion concentrations of the alkaline solutions of catechol used were measured by means of a Leeds and Northrup large bulb type glass electrode No. 7685 using an L and N saturated calomel electrode No. 7724, a type K potentiometer, and a 2500-f type R galvanometer. The glass electrode was used in preference to the hydrogen electrode, because of the difficulty of determining the pH of the alkaline catechol solutions by the latter, particularly in presence of the products of oxidation. However, by saturating the catechol solution with hydrogen and making the measurements in an atmosphere of hydrogen, it was found possible to measure pH values of unoxidized catechol solutions. The glass electrode was calibrated from pH 4 to 9 against buffers whose pH value was measured by a hydrogen electrode. The pH values above 9 were taken from an electrometric titration curve for unoxidized catechol determined in an atmosphere of hydrogen.

Accuracy.—Except in the most acid or most alkaline

regions studied, the rates were readily reproducible to well within an error of 5%, particularly in buffered solutions. The results for the rates lower than 0.02 or higher than 20 cc. per minute were less accurate. The pH values were reproducible to less than ±0.05 unit except in the most alkaline range, where the limit of error is probably 0.1 unit. The internal evidence of the accuracy of the measurements indicates an average error of 7%, most of which is due to error in pH measurement.

Data and Discussion

Titration Curve.—Catechol is capable of existing in alkaline solutions in three forms—undissociated molecule, monovalent ion, and divalent ion—and it is necessary to know the proportions in which these various substances are present in a given solution. The dissociation constant of 3.2×10^{-10} given in the "International Critical Tables" (Vol. VI, p. 259) is corrected for salt effect and it was desirable to determine this value under our conditions in sodium hydroxide solutions and in the presence of added potassium chloride. The electrometric titration curve (at $t = 23°$) constructed in part from data obtained by glass electrode and in part by hydrogen electrode, both in absence and presence of 0.8 M potassium chloride for 0.1 M catechol is shown in Fig. 1. The pK value of the first dissociation is 9.3 without added salt and 9.1 in presence of 0.8 M potassium chloride. These values neglecting the slight temperature correction[11] are in fair agreement with the value given in the literature ($pK = 9.5$). The difference of these results from each other and from the accepted pK value of 9.5 is evidently due largely to a salt effect. The titration curve does not show a break for the second dissociation. This is in agreement with the results obtained by Kolthoff, who found that the conductivity curve for catechol shows only one break.[12] The lack of a second break indicates a pK value greater than 12.5 for the second dissociation. Sheppard[13] gives 1.75×10^{-10} and 3.97×10^{-12} as the two dissociation constants for hydroquinone.

(10) The necessity for a thermobarometer to serve as a control is clearly pointed out by R. Siebeck, see reference 9, page 30.

(11) Following the procedure of Euler and Brunius³ the temperature correction was made by comparison with Lundén's values for phenol at various temperatures [Z. physik. Chem., 70, 249 (1910)]. The values for k decrease with decrease in temperature but the pK values increase. The correction in our case amounts to about −0.03 pK units which is within the limits of experimental error.

(12) I. M. Kolthoff, Z. anorg. allgem. Chem., 112, 187–195 (1920).

(13) S. E. Sheppard, Trans. Am. Electrochem. Soc., 39, 429–440 (1922).

Homogeneity of the Reaction.—The addition of large amounts of powdered Pyrex or soft glass had no appreciable effect on the rate of oxygen absorption; the reaction is thus homogeneous and free of wall effects.

Difference between Buffered and Unbuffered Solutions.—When the reaction is carried out in a well buffered solution, whether an external buffer is used or the concentration of sodium hydroxide is sufficient to nearly half neutralize the catechol present, more than 10 cc. of oxygen can be absorbed without any noticeable change in the rate. But when no external buffer and only a small amount of sodium hydroxide is used the rate decreases after the absorption of but little oxygen, and the initial rates must be obtained by extrapolation. Typical runs obtained in phosphate buffers prepared by mixing 1 M dipotassium phosphate and 1 M monopotassium phosphate and in sodium hydroxide solutions, shown in Fig. 2, illustrate this behavior. This is nothing but the usual phenomenon that is shown by any reaction whose rate depends on the concentration of hydrogen ion and in which the hydrogen-ion concentration changes. That it occurs in this reaction shows that the products of the auto-oxidation of catechol include an acid or acids stronger than catechol.

We have tested for other factors causing a reduction in rate in unbuffered solutions. No gas was formed in the reaction for the residual oxygen was found to contain no impurity.[14] No inhibitor was formed during the reaction. This was shown by oxidizing an alkaline solution 0.01 N with respect to catechol and then using the resulting solution as a substrate for a new experiment. Both in unbuffered and buffered solutions these new experiments gave the same rate of oxygen absorption as in experiments with clean substrate and pure catechol at the same pH value. These experiments also show that no catalyst is formed in the reaction.

Confirmation of the production of an acid or acids in the auto-oxidation was obtained by measuring the pH values present after reactions in which the rate had changed considerably. In these cases the observed decrease in pH was more than sufficient to account for the change in rate.[15]

(14) Carbon monoxide has been reported to be formed in the auto-oxidation of alkaline pyrogallol solutions.

(15) Alkaline solutions of catechol absorb oxygen so rapidly that an appreciable amount of reaction occurs between the cessation of rate measurements and measurement of pH values.

A similar decrease in rate was observed in the auto-oxidation of hydroquinone in unbuffered or slightly buffered solutions.[1,2,5] Dubrisay and Saint-Maxen[5] found that in presence of small amounts of sodium hydroxide the rate of oxygen absorption by hydroquinone rapidly decreases and finally tends to be practically zero, while the solution changes from alkaline to slightly acid.
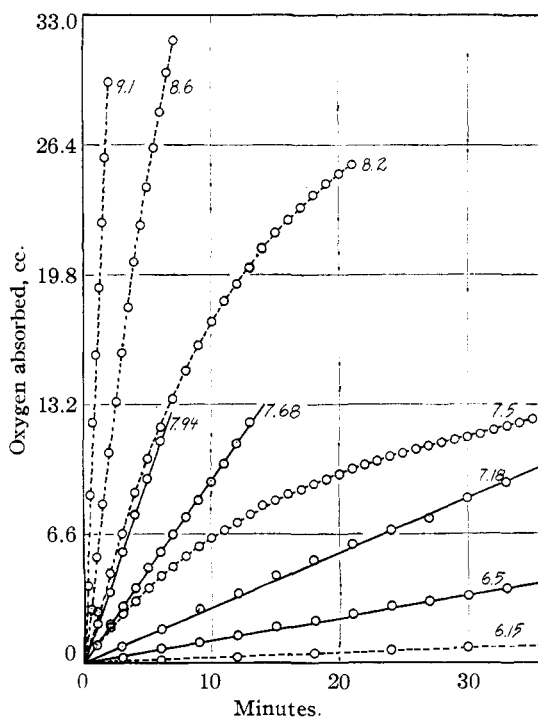

Fig. 2.—Rate of oxygen absorption at the pH values indicated on the curves: ——, in buffered solutions; ————, in NaOH solutions.

Variation of Rate with pH.—The results obtained for rates of oxygen absorption by a 0.1 M catechol solution in buffered solutions, and in sodium hydroxide solutions with and without added potassium chloride, at 1 atmosphere pressure of oxygen are shown in Tables I to V. The values of K were calculated on the assumption that the rate was directly proportional to the concentration of hydroxyl ions. It is seen that in all cases K is sensibly constant over a wide range of concentration. The average value of K in 0.8 M phosphate buffer solution is 1.46 × 10⁶ in the range pH 6.5 to 8.25; in sodium hydroxide solutions it is 1.07 × 10⁶ in the range pH 6.6 to 8.2; in sodium hydroxide solutions containing 0.8 M potassium chloride it is 1.89 × 10⁶ in the range, pH 6.68 to 8.74; in sodium hydroxide solutions containing 1.6 M potassium chloride it

is 1.95×10^6 in the range pH 6.54 to 8.74; and in solutions containing 2.4 M potassium chloride it is 2.54×10^6 in the range pH 6.12 to 8.55.

TABLE I

RATE OF OXYGEN ABSORPTION IN PHOSPHATE BUFFERS

pH	$K = $ rate in cm.³/min./ $(OH^-) \times 10^{-6}$	pH	$K = $ rate in cm.³/min./ $(OH^-) \times 10^{-6}$
4.0	8.8	7.43	1.39
4.1	13.1	7.65	1.37
5.9	2.01	7.83	1.38
6.2	2.27	7.98	1.34
6.5	1.59	8.08	1.50
6.72	1.51	8.15	1.47
6.90	1.48	8.20	1.59
7.15	1.36	8.25	1.56

Av. k in range pH 6.5–8.25 = 1.46×10^6.

TABLE II

RATE OF OXYGEN ABSORPTION IN SODIUM HYDROXIDE SOLUTIONS

pH	$K = $ rate (cc./ min.)/ $(OH) \times 10^{-6}$	$K' = $ rate/ $(Cat.^-)$	pH	$K = $ rate (cc./ min.)/ $(OH) \times 10^{-6}$	$K' = $ rate/ $(Cat.^-)$
5.23	4.65	932	8.45	0.937	214
5.30	5.00	1000	8.60	.852	204
5.40	4.54	907	8.80	.802	210
5.53	1.98	395	8.88	.783	217
6.15	1.56	312	9.00	.704	211
6.60	1.00	199	9.10	.702	228
6.91	1.03	206	9.26	.588	225
7.10	1.045	211	9.39	.517	230
7.22	1.06	214	9.53	.435	235
7.65	1.04	213	9.69	.337	232
7.80	1.01	208	9.85	.262	237
7.85	1.20	248	10.25	.121	240
7.96	1.10	230	11.1	.199	255
8.05	1.14	239	11.9	.0408	324
8.10	1.08	229	12.3	.01785	357
8.20	1.075	231	12.5	.01195	378
8.35	0.906	202	12.7	.0089	445

Average K in pH region 6.60 to 8.2 is 1.07×10^6.
Average K' in pH region 6.60 to 10.25 is 221.

At the higher pH values, particularly in the two cases carried into the strongly alkaline range, K rapidly decreases with increase in pH. But this decrease in K is to be expected in the reaction of an acid in the range where the alkali concentration is sufficiently large to neutralize an appreciable fraction of the acid. If we assume that the rate of oxygen absorption, V, is proportional to the concentration of the monovalent catechol ion (cat.$^-$), the rate law can be expressed as

$$V = K' \frac{k_a C}{k_a + (H+)}$$

where K' is the specific rate constant for the oxidation of cat.$^-$, k_a the first dissociation constant of catechol, and C the concentration of total cate-

TABLE III

RATE IN SODIUM HYDROXIDE SOLUTIONS IN PRESENCE OF 0.8 M POTASSIUM CHLORIDE

pH	$K = $ rate (cc./ min.)/ $(OH^-) \times 10^{-6}$	$K' = $ rate/ $(Cat.^-)$	pH	$K = $ rate (cc./ min.)/ $(OH^-) \times 10^{-6}$	$K' = $ rate/ $(Cat.^-)$
5.22	3.97	501	8.95	1.345	288
5.31	3.92	493	9.07	1.305	315
5.54	4.24	532	9.20	1.088	308
5.80	3.25	292	9.36	0.825	293
6.68	1.93	243	9.52	.598	273
7.02	1.97	245	9.69	.418	258
7.40	2.11	270	10.03	.232	241
7.75	1.80	236	11.90	.302	240
7.85	2.30	303	12.11	.189	244
8.05	1.89	257	12.22	1.55	257
8.18	1.78	250	12.29	.147	287
8.28	1.61	234	12.32	.135	281
8.38	1.80	270	12.40	.122	306
8.53	1.755	280	12.60	.0800	318
8.58	1.87	306	12.8	.0513	323
8.74	1.82	327			

Average K in pH region 6.68 to 8.74 is 1.89×10^6.
Average K' in pH region 6.68 to 12.2 is 270.

TABLE IV

RATE IN SODIUM HYDROXIDE SOLUTIONS IN PRESENCE OF 1.6 M POTASSIUM CHLORIDE

pH	$K = $ rate (cc./min.)/ $(OH^-) \times 10^{-6}$	pH	$K = $ rate (cc./min.)/ $(OH^-) \times 10^{-6}$
4.8	6.66	7.93	1.97
5.30	2.60	8.07	1.88
5.88	2.39	8.30	1.84
5.73	3.07	8.40	1.96
6.54	1.90	8.48	2.08
6.91	1.90	8.58	1.97
7.35	1.88	8.74	1.81
7.45	1.90	8.91	1.57
7.68	2.21		

Av. k in range pH 6.54–8.74 = 1.95×10^6.

TABLE V

RATE IN SODIUM HYDROXIDE SOLUTIONS IN PRESENCE OF 2.4 M POTASSIUM CHLORIDE

pH	$K = $ rate (cc./min.)/ $OH^- \times 10^{-6}$	pH	$K = $ rate (cc./min.)/ $OH^- \times 10^{-6}$
4.84	6.35	8.0	2.64
5.72	5.45	8.1	2.67
6.12	2.67	8.2	2.75
6.63	2.00	8.34	2.69
6.95	2.17	8.44	2.69
7.22	2.77	8.55	2.54
7.65	2.36	8.81	1.91
7.85	2.53	8.95	1.73

Average K in pH range 6.12–8.55 = 2.54×10^6.

chol ($= 0.1$ M). The values of K' calculated from the above expression are shown in column 3 of Tables II and III. It can be seen that these values are practically constant almost throughout

the entire range from slightly acid to strongly alkaline solutions. The average value of K' in absence of added salt is 221 and in presence of 0.8 M potassium chloride it is 270.

The constancy of K and K' suggests that the monovalent ion of catechol is the oxygen absorbing species. This is not strictly warranted because the product of (cat.) by (OH⁻) is proportional to the concentration of (cat.⁻) and the reaction may be one in which the OH ion acts as a basic catalyst for the oxidation of undissociated catechol.

In this case the negative ions of the phosphate buffer are also basic catalysts and the rate in buffered solution should be faster than in solutions in which the same pH values and ionic strength are obtained with sodium hydroxide and potassium chloride. This is contrary to the facts. It is, therefore, best to attribute the effect of alkali to the formation of the more reactive catechol ion from the less reactive undissociated catechol.

The constancy of K' from pH 6 to 10, shows that in this range absorption by the second ion of catechol is negligible, but in more alkaline solution there is a definite upward trend of the values of K' indicating that absorption of oxygen by the second ion has a greater specific rate than that by the first. If we assume that the absorption of oxygen by the second ion is first order with respect to its concentration, the rate in strongly alkaline solution (pH > 10) is given by the expression $V = K'(\text{cat.}^-) + K''(\text{cat.}^{--})$. On this assumption the rates in strongly alkaline solutions in the absence of potassium chloride correspond to values for K'' and the second dissociation constant of catechol having the orders of magnitude of 10^3 and 10^{-13}, respectively.

At low pH values, particularly below pH 6, K (and also K') is considerably higher than the average. This indicates that not only the ions but the undissociated catechol itself must be able to absorb oxygen. However, the rate of absorption of oxygen by the undissociated catechol molecule is very much less than that by the monovalent ion, since it only interferes with the constancy of K on the acid side of neutrality, that is, when the concentration of the monovalent ion is exceedingly small compared to that of catechol.

Salt Effect.—In the range pH 6 to 10, the rate of absorption of oxygen increases with added salts. The salt effect is not entirely determined by the ionic strength, for the rate in phosphate buffers is less than that in potassium chloride solutions of similar ionic strength. A large part of this salt effect is due to the influence of salt on the acidic strength of catechol. Thus K in 0.8 M potassium chloride is 77% greater than K in absence of extraneous salt, but K' which is independent of the strength of catechol is only 22% greater in 0.8 M potassium chloride than in 0.0 M potassium chloride.

Potassium chloride decreases the rate of absorption of oxygen by the second ion of catechol. This is shown by the fact that in strongly alkaline solutions the rate in the presence of potassium chloride falls below that in its absence.

Variation of Rate with Concentration of Oxygen.—Measurements of the rate of oxygen absorption by 0.1 M catechol solution in phosphate buffers at pH 8.40 were made at varying partial pressures of oxygen. These were produced both by making the runs in partially evacuated system and in presence of air at atmospheric pressure. The results obtained are shown in Table VI.

TABLE VI

RATE OF OXYGEN ABSORPTION AT VARYING PARTIAL PRESSURES OF OXYGEN

Partial press. of O₂, atm.[a]	Rate	$K = \text{rate}/(P_{O_2})$
0.082	0.220	2.78
.097	.260	2.68
.206[b]	.53	2.57
.206[b]	.56	2.72
.272	.790	2.90
.423	1.15	2.72
.439	1.38	3.14
.627	1.63	2.60
.792	2.07	2.61
.969	2.55	2.63

Average K = 2.72

[a] Corrected for vapor pressure of water.   [b] In air.

The constancy of the values of K calculated on the assumption that the rate of oxidation is proportional to the partial pressure of oxygen shows that over a more than tenfold range of oxygen pressure the reaction is directly proportional to the pressure of oxygen.

Variation of Rate with Concentration of Catechol.—To determine the effect of varying the catechol concentration at constant pH, the rate of oxygen absorption was measured at varying concentrations of catechol in a strongly buffered phosphate solution at pH 6.5 and in sodium hydroxide solutions in which the equivalence of sodium hydroxide added per mole of catechol was

maintained at 0.08 mole of sodium hydroxide per mole of catechol. The pH value of the sodium hydroxide solutions was practically constant at 8.20. The results obtained are shown in Table VII.

TABLE VII

RATE OF OXYGEN ABSORPTION AT VARYING CONCENTRATIONS OF CATECHOL

Concn. of catechol, M	Rate in phosphate buffer	Rate in NaOH	K_1 Buffer	K_1 NaOH	K_2 Buffer	K_2 NaOH
0.025	..	0.345	..	13.8	..	24.8
.05	0.0253	.782	0.506	15.6	7.08	21.9
.075	.041	..	.547	..	6.92	..
.10	.051	1.885	.510	18.9	6.12	22.7
.125	.071	..	.568	..	6.60	..
.15	.098	2.91	.652	19.4	7.42	22.1
.175	.107	..	.610	..	6.80	..
.20	.123	3.75	.614	18.8	6.77	20.7
.30	.202	..	.673	..	7.20	..
.40	..	8.00	..	20.0	..	28.7
				Average K_2 =	6.86	23.5

K_1 = rate/(concentration).
K_2 = rate × (concn. + 0.02)/(concn.)².

The rate is approximately first order with respect to catechol but it is slower than would be expected from this law at low concentrations of catechol. Thus, the values of K_1 calculated on the assumption that the reaction is first order with respect to catechol are over 30% lower at concentrations of catechol below 0.1 M. The rate obeys more exactly the law: rate = K_2 $(C)^2/(C + A)$, where C is concentration of catechol and A some constant. The K_2 values shown in Table VII were calculated using the same value of A, namely, 0.02 for both solutions.

By combining the results obtained by separately varying the pH value, the pressure of oxygen, and the total concentration of catechol, the rate of oxygen absorption in the range pH 6 to 10 is given by the expression

$$V\alpha(\text{Cat.}^-)(\text{O}_2) \times C/(C + A)$$

In view of the facts that A is approximately the same at two very different concentrations of hydroxide ion, and that the values of K' given in Tables II and III are constant over wide degrees of neutralization of the catechol, the concentration represented by C is to be taken as that of the sum of the concentrations of the undissociated catechol and of its first ion. The proportionality constant in the above expression is $K' \times$ (0.1 + 0.02)/0.1. This is 266 expressed in the units cc. of oxygen × atm.$^{-1}$ × mole^{-1} × liter ×

min.$^{-1}$, for solutions containing no extraneous salts.

Variation of Rate with Temperature.—The rates of oxygen absorption by 0.1 M catechol solution in phosphate buffers at pH 8.35 and in sodium hydroxide at pH 8.20 were measured at 20, 25, 30 and 35°. The results are shown in Table VIII. It is seen that the values for the phosphate buffer are somewhat more consistent. The average heat of activation is 12,900 calories for the phosphate solutions and 9400 calories for the sodium hydroxide solution. The temperature coefficient V_{35}/V_{25} is 2.16 for the phosphate solutions and 1.68 (corr.) for the sodium hydroxide solutions. These heats of activation include not only the heat of activation of the oxygen absorbing species but also the heats of neutralization of catechol by HPO$_4^=$ and OH$^-$, respectively. The difference in these heats of neutralization largely accounts for the higher heat of activation in the buffered solution.

TABLE VIII

EFFECT OF TEMPERATURE ON RATE OF OXYGEN ABSORPTION

Temp., °C.	Rate Phosphate	NaOH
20.0	1.76	1.35
25.0	2.51	1.70
30.0	3.74	2.22
35.0	5.22	3.00

Summary and Conclusions

The rate of oxygen absorption by catechol solutions has been studied under various conditions.

1. In the range of pH value 6.5 to 10, $V\alpha \times$ (Cat.$^-$) $\times$ O$_2$ $\times$ $C/C + A$.

2. In more acid solutions absorption of oxygen by the undissociated molecule is appreciable; and in more alkaline solutions the divalent ions also absorb oxygen.

3. In moderately alkaline solutions potassium chloride increases the rate of absorption, chiefly through a positive salt effect on the dissociation constant of catechol. In strongly alkaline solutions salt retards the reaction.

4. The heats of activation in sodium hydroxide solutions and in phosphate buffers were measured over the range 20 to 35°. The apparent heat of activation is higher in the phosphate buffer.

This difference can be accounted for by the difference between the heats of neutralization of

catechol by $HPO_4^=$ and OH^-, respectively.

BERKELEY, CALIFORNIA   RECEIVED MAY 22, 1935

The Adsorption of Methane by Coal[1]

BY J. BARTLETT SUTTON AND EARL C. H. DAVIES

Introduction

To determine the adsorption equilibrium between a highly adsorptive coal and methane, we have recently used an apparatus which contains a variable volume unit, by means of which the total system volume can be varied through four stages, enabling one to obtain adsorption values for four pressures with each gas sample and to check such values on both the adsorption and desorption side of the equilibrium point. The fact that approximately twenty-four hours were required for equilibrium conditions to be attained led us to enclose, in an electric refrigerator at constant temperature ($\pm$ 0.1°), not only the adsorption bulb but the entire apparatus.

Materials and Apparatus

The coal was obtained from the Carreta, West Virginia, mine of the Carter Coal Company, which is the most gassy mine in the world. It was of semibituminous rank and from the Pocahontas No. 4 seam. A ton sample, collected from all over the mine, was passed through a jaw crusher and then quartered several times to obtain a representative sample of fifty pounds. A portion of this was then ground in a "coffee mill" to approximately 100-mesh average size.

The analysis of this coal[2] as given by the Bureau of Mines was H, 4.4; C, 88.7; N, 1.3; O, 2.2; S, 0.5; H_2O, 0.4 and ash, 2.9. After refluxing with water for two weeks, we found the average density (nine determinations) to be 1.3521. The range of particle sizes, in the coal sample, as determined by the application of Stokes' equation to sedimentation data, was: 63.0%, 0.132 mm.; 10.0%, 0.045 mm.; 10.8%, 0.030 mm.; 10.2%, 0.021 mm.; 1.7%, 0.016 mm. and 4.3%, 0.007 mm. The coal received no preliminary heat treatment but was evacuated to 10^{-4} mm. for a period of seventy-two hours.

(1) This paper is from a dissertation submitted in June, 1935, by J. Bartlett Sutton to the Faculty of the Graduate School of West Virginia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) R. S. Selden. R. I-3233; U. S. B. M., June, 1934.

The methane was obtained from the Bureau of Mines at Pittsburgh, Pennsylvania. The higher hydrocarbons[3] had been removed from natural gas by passing it through 117 cm. of activated coconut charcoal.

The analysis of the methane[4] supplied by the Bureau of Mines was: CH_4, 97.8-98.0%; C_2H_6, 0.05%; O, 0.10% and N, 1.85%. The density found by the Regnault method was 0.7196. Traces of moisture were removed from the methane, before it was admitted to the system, by passing through a coil submerged in an ether–solid carbon dioxide mixture.
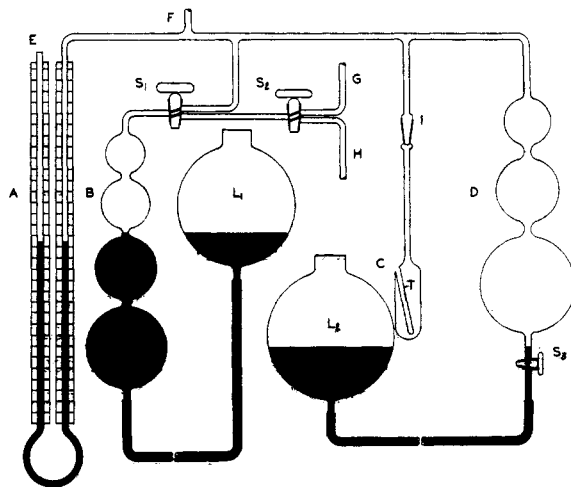

Fig. 1.—Adsorption apparatus with variable volume unit.

The apparatus (Fig. 1), designed and constructed in this Laboratory, consists essentially of the four units, A, B, C and D. A is the manometer, B the gasometer, C the adsorption bulb and D the variable volume unit. The volumes, between constricted portions, of both the gasometer and variable volume unit, as well as the total system volume, were accurately measured by the use of mercury. The temperature was determined by means of two ten-junction copper–constantan thermocouples, the hot junctions of which were en-

(3) H. H. Storch and P. L. Golden, THIS JOURNAL, 54, 4662 (1932).

(4) H. H. Storch, Bureau of Mines, personal communication.