

In the fusion of sodium anthraquinone  $\beta$ -monosulfonate with sodium hydroxide, oxidation occurs by means of the water reaction without the necessity of a previous oxidation by free oxygen.

It seems highly probable that the yield of  $\beta$ -naphthol would be increased by carrying out the fusion of the corresponding sulfonate with sodium hydroxide in the absence of free oxygen.

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## THE ADSORPTION OF ARSENIOS ACID BY FERRIC HYDROXIDE.

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In the course of the investigation of the catalysis of certain reactions by silicic acid and ferric hydroxide gels, the large adsorption of arsenious acid from solutions of sodium arsenite by ferric hydroxide was encountered.

Bunsen and Berthold<sup>1</sup> observed the great adsorption power of ferric hydroxide for arsenious acid, and considered the combination to be a basic ferric arsenite. Biltz<sup>2</sup> studied the reaction quantitatively and concluded that it was a case of adsorption and not chemical combination, since it followed the "adsorption law" expressed by the empirical and very flexible equation  $E = \beta A^p$ , where  $E$  is the concentration of adsorbed substance in the absorbing phase,  $A$  is the concentration of adsorbed substance in solution at equilibrium, and  $\beta$  and  $p$  are constants. Lockmann and Paucke<sup>3</sup>, and Lockmann and Lucius<sup>4</sup> studied the conditions under which the adsorption of arsenious acid from solution is complete. A comparison made in the latter paper shows that a given amount of arsenious acid is removed from solution by a considerably smaller amount of precipitate, when an exactly stoichiometric amount of ammonia is used than when twice that amount is used. They also observed that the adsorption of arsenious acid is considerably reduced by the use of potassium hydroxide or sodium hydroxide instead of ammonia. Mecklenburg<sup>5</sup> worked with ferric hydroxide and arsenious acid in demonstrating his principle of "affine Adsorptionskurven," *i. e.*, adsorption curves so related, each by a particular factor, to a unit curve, that the ordinate corresponding to any given abscissa on one of the curves may be obtained by multiplying, by the factor, the ordinate on the unit curve correspond-

<sup>1</sup> "Das Eisenhydroxyd," 1834.

<sup>2</sup> *Ber.*, 37, 3138 (1904).

<sup>3</sup> *Z. Chem. Ind. Kolloide*, 8, 273 (1911).

<sup>4</sup> *Z. Physik. Chem.*, 83, 735 (1913).

<sup>5</sup> *Ibid.*, 83, 609 (1913).

ing to the given abscissa. He showed that the adsorption curves obtained from differently prepared samples of hydrated ferric oxide were actually related in such a way to a unit curve, which he at first determined for one particular preparation.

We have studied (as far as seemed profitable for the purposes of our main investigation) the effects of sodium hydroxide and arsenious acid on the adsorption of each other by ferric hydroxide.

#### Description of Experiments.

The ferric hydroxide was prepared several months before the experiments by precipitation of ferric chloride solution with ammonium hydroxide. It was washed a great many times with tap water by decantation. Ammonium hydroxide was again added, and the gel again washed until the liquid gave only a very slight reaction for ammonia with Nessler's solution. The gel covered with water was kept so that it could be shaken up and poured.

The arsenious acid solutions were made by dissolving pure arsenious oxide in water. The normalities were determined by titration against standard iodine solution in the presence of sodium hydrogen carbonate.

The required amounts of arsenious acid and sodium hydroxide solution were mixed and made up to about 150 cc. in a 200 cc. standard flask. 31.5 cc. of the ferric hydroxide suspension carefully measured in a cylinder was added and the flask filled with water to the mark. Several determinations showed that this amount of ferric hydroxide contained 2.13 g.  $\text{Fe}_2\text{O}_3$ . To each flask of Series A was added one cc. of concn. sodium chloride solution and of Series B, 5 cc. of sodium chloride solution. These two series were allowed to stand for about two weeks with occasional shaking. When equilibrium had been attained (determined by titration of small portions withdrawn) the arsenious acid remaining was determined. The difference between the amount originally put in and the amount remaining in solution gave the amount adsorbed.

Series C and D were prepared similarly, but were allowed to stand a month with shaking every day or two. They were then allowed to stand for about 10 days to settle. In these two series although no sodium chloride was used, there was not very much difference in turbidity from A and B. In a few of the more concentrated solutions the turbidity was great enough to make the methyl orange end-point rather uncertain but the arsenite-iodine titration could be carried out without any serious difficulty. In those experiments where both sodium hydroxide and arsenious acid were used they were determined in the same sample, the alkali being titrated first.

Series A gives the adsorption of arsenious oxide in the absence of alkali. Series B gives the adsorption of arsenious oxide and of sodium hydroxide in the presence of varying amounts of sodium hydroxide and a constant

amount of arsenious oxide. These results are plotted in Fig. 1. Series C gives the adsorption of sodium hydroxide in the absence of arsenious oxide. Series D gives the adsorption of arsenious oxide and of

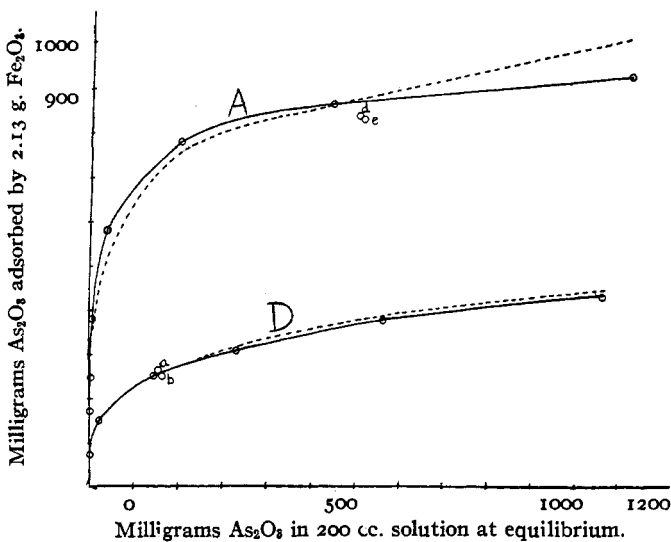


Fig. 1.

sodium hydroxide in the presence of varying amounts of arsenious oxide and a constant amount of sodium hydroxide. These results are plotted in Fig. 2. Series C and D were performed about a month

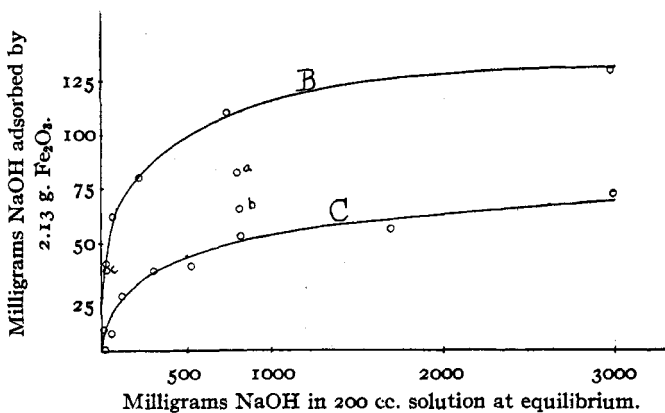


Fig. 2.

later than A and B. Following these, Series E was performed in order to determine whether the addition of sodium chloride had any effect upon the adsorption of arsenious acid or sodium hydroxide and also to determine whether these adsorptions were influenced at all by the somewhat greater age of the precipitate.

TABLE I.  
 Adsorption by Ferric Hydroxide.

Total As <sub>2</sub> O <sub>3</sub> .	As <sub>2</sub> O <sub>3</sub> adsorbed.	As <sub>2</sub> O <sub>3</sub> remaining.	Total NaOH.	NaOH adsorbed.	NaOH remaining.
Series A.—Pure Arsenious Oxide.					
73.5	73.5	0	..	...	..
172.1	172.1	0	..	...	..
246.4	244	2.38	..	...	..
384.7	378	6.73	..	...	..
393.1	384	9.1	..	...	..
614.1	578	36.1	..	...	..
987.5	784	203.5	..	...	..
1424.0	878	546	..	...	..
2175.0	955	1220	..	...	..
Series B.—Arsenious Oxide Constant.					
443.5	431	12.5	4	...	13
443.2	436	7.2	25.6	9.6	16
435.5	423	12.5	72	40	32
423.5	368	55.5	138	62	76
413	314	99	307	80	227
414	279	135	848	110	738
364	261	103	868	130	738
362	259	103	865	105	760
418	236	182	3010	130	2880
Series C.—Pure Sodium Hydroxide.					
..	...	...	25.24	0.24	25
..	...	...	75	8.0	67
..	...	...	149.8	24.8	125
..	...	...	349.4	36.4	313
..	...	...	568.8	38.8	530
..	...	...	874.4	52.4	822
..	...	...	1749	56.1	1693
..	...	...	3065	72.1	2993
Series D.—Sodium Hydroxide Constant.					
79.5	75	4.5	876	69	806
173.2	149	24.2	876	73	804
396	250	146	876	76	800
643	309	334	876	92	784
1049	381	668	876	88	789
1599	435	1164	876	104	773
449	250	199	1749	116	1633
450	233	217	3064	124	2940
Series E.—Effect of Sodium Chloride and Age.					
(a) 424.5	266.5	158	878	83	795
(b) 418	251.3	166.7	874	64	810
(c) 434.4	416	18.4	76.8	37.2	39.6
(d) 1456	846	610	..	...	..
(e) 1454	851	604	..	...	..

All values are expressed in milligrams and refer to 200 cc. solution and 2.13 g. Fe<sub>2</sub>O<sub>3</sub>.

5 cc. saturated sodium chloride in (a) and (c).

1 cc. saturated sodium chloride in (d).

TABLE II.  
Comparison of Observed with Calculated Values of  $E$  and  $\log E$ .

A.	$x = \log A.$	$E$ obs.	$E$ calc.	$y = \log E$ obs.	$y = \log E$ calc.
Series A—( $\beta = 127.7, p = 0.2102$ ).					
0	..	34.5	...	1.5378	..
0	..	80.8	...	1.9074	..
1.19	0.0755	114.6	132	2.0582	2.122
3.37	0.5276	177.5	165	2.2492	2.217
4.6	0.6628	180	176	2.2553	2.2455
18.05	1.2565	271.4	235	2.4436	2.370
101.8	2.0076	368	359	2.5658	2.555
273	2.4362	412	415	2.6149	2.6184
610	2.7853	448	492	2.6513	2.6917
Series D—( $\beta = 33.26, p = 0.2840$ ).					
2.25	0.3522	35.2	43.6	1.5465	1.6399
12.1	1.0828	70	70.4	1.8451	1.8474
73	1.8633	117.3	117.1	2.0693	2.0689
167	2.2227	145	148.2	2.1614	2.1709
334	2.5237	179	180.5	2.2529	2.2565
582	2.7649	204	211.3	2.3096	2.3251

TABLE III.  
Values of the "Mecklenburg Factor" for Series A and D.

100 cc. of solution contains $x$ mg. of $As_2O_3$ .	1 g. $Fe_2O_3$ holds $y$ mg. $As_2O_3$ .	Corresponding $y$ value of $M$ 's unit curve.	"Factor."
Series A.			
0	34.5	...	...
0	80.8	...	...
1.19	114.6	165	0.695
3.37	177.5	237	0.746
4.6	180	264	0.682
18.05	271.4	356	0.752
101.8	368	474	0.776
273	412	548	0.752
610	448	600	0.746
Series D.			
2.25	35.2	199.9	0.170
12.1	70.0	325.6	0.215
73	117.3	461.1	0.254
167	145	521.2	0.278
334	179	556.9	0.322
582	204	597	0.342

**Discussion.**

It is seen from Fig. 1, and Table I, Series A and D, that the adsorption of arsenious acid by ferric hydroxide is very considerably diminished by sodium hydroxide. Figs. 2 and 4 and Table I, Series B and C, show that the adsorption of sodium hydroxide by ferric hydroxide is somewhat increased by the simultaneous presence of arsenious acid.

Expts.  $a, b, d, e$ , in series E (points  $a, b, d, e$  Fig. 1) were performed for the purpose of determining whether the wide dif-

ferences in amounts of arsenious oxide adsorbed in the presence and in the absence of sodium hydroxide is due to the influence of sodium hydroxide or to the fact that the experiments were performed at an interval of a month, and that slightly different amounts of sodium chloride were used to diminish turbidity. The results show that the amounts

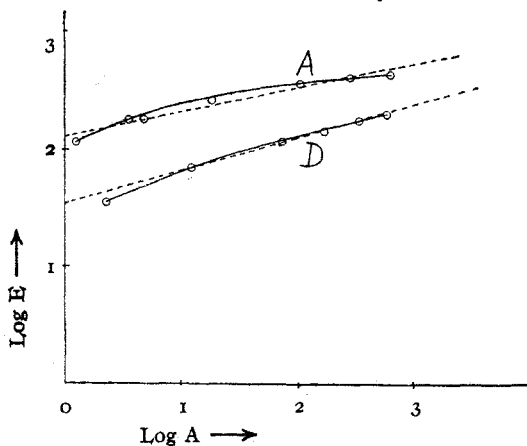


Fig. 3.

of arsenious oxide adsorbed by ferric hydroxide differed only slightly from those obtained in similar experiments performed with the same preparation of ferric hydroxide some two months previously. It seems then that conditions of precipitation are of very much greater influence on the adsorption than is the age of the precipitate. It is also evident that the effect of the salt used in these

experiments upon the adsorption is small.

Expts. *a, b, c*, Series E (points *a, b, c*, Fig. 2), performed for the similar purpose of verifying the results of Series B and C, Table I, on the adsorption of sodium hydroxide, do not definitely eliminate the somewhat greater age of the precipitate as a factor in the greater adsorption of sodium hydroxide in the presence of arsenious acid, points *a* and *b*, Fig. 2, falling midway between the two curves. However, Fig. 4, which refers to Series B and represents the variation of sodium hydroxide adsorbed with gradually increasing amounts of arsenious oxide present, makes it fairly certain that the general statement is correct that the adsorption of sodium hydroxide is increased by the presence of arsenious oxide.

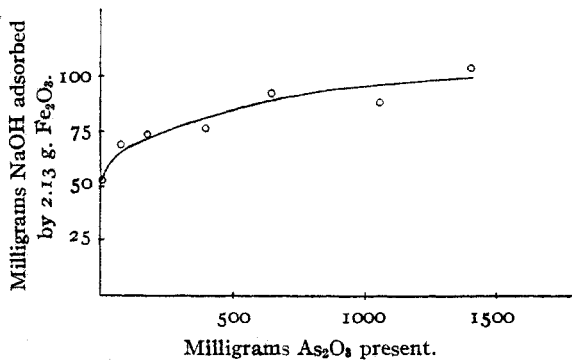


Fig. 4.

Consider the general adsorption equation  $E = \beta A^p$ . In the present case,  $E$  is the concentration of arsenious oxide on the precipitate,  $A$

is the concentration of arsenious oxide in solution, and  $\beta$  and  $p$  are constants. The corresponding logarithmic equation

$$\log E = p \log A + B \text{ or } y = px + B$$

represents a straight line. If the adsorption follows the equation, the experimental values when plotted will give a straight line, the tangent of whose angle with the  $x$  axis is the constant  $p$ , and whose intercept

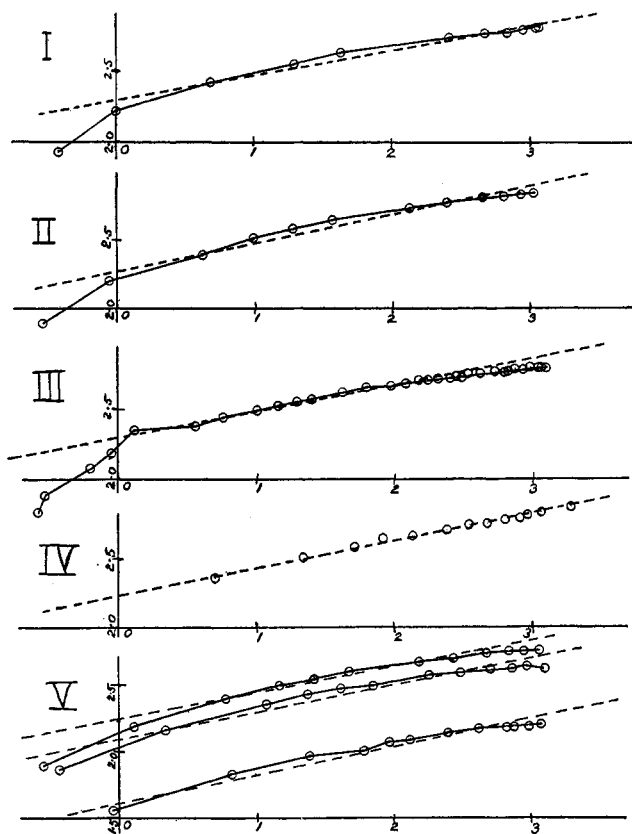


Fig. 5.

In each of the 5 diagrams the vertical axis represents  $\log E$ , *i. e.*, the logarithm of the concentration (milligrams per 1 g.  $\text{Fe}_2\text{O}_3$ ) of the arsenious acid in the solid phase at equilibrium; the horizontal axis represents  $\log A$ , *i. e.*, the logarithm of the concentration (milligrams per 100 cc.) of arsenious acid in the liquid phase at equilibrium. The dotted line in each case indicates the straight line to which the curve approximates and from which the constants  $\beta$  and  $p$  were determined as already described.

- Diagram I is for Mecklenburg's gel precipitated at  $1^\circ$ .
- "    II " " " " " " " "  $23^\circ$ .
- "    III " " " " " " " " "unit curve."
- "    IV " " " " " " " " "Biltz curve."

In " V the two upper curves are for Mecklenburg's gels precipitated at  $60^\circ$  and  $98^\circ$ , respectively, and the lowest curve is for the gel precipitated at  $98^\circ$  and heated subsequently.

on the  $y$  axis is the value of  $B$ . Fig. 2 shows that the plotted values approximate to straight lines. The constants  $p$  and  $\beta$  were calculated, as above described, and the corresponding values of  $A$  and  $E$  (for 1 gram ferric oxide and 100 cc. solution) were calculated for the several experiments. These calculated values along with the actual measurements are recorded in Table II. The curves obtained from these calculated values ( $E$  being multiplied by 2.13 and  $A$  multiplied by 2, corresponding with 2.13 g. and 200 cc. solution) are compared in Fig. 1 with the experimental curves.

A comparison of the curve for Series A with Mecklenburg's "affine Adsorptionskurven" shows a close agreement, the Mecklenburg "factor" for our preparation being about 0.75 or midway between the factors obtained by Mecklenburg for preparations precipitated at  $60^\circ$  and  $98^\circ$ . That our factor is not higher than 0.75 is probably due to the fact that the gel was comparatively old and probably had as a consequence become partially dehydrated, and partially lost its original amorphous condition. However it is seen from Table III that the curve for series D (adsorption of arsenious oxide in presence of sodium hydroxide) does not correspond at all with Mecklenburg's curve but that the "factor" increases steadily to twice its initial value. This observation corresponds to the fact that the exponential constant  $p$  is different for the two curves. Had D alone been different,  $p$  remaining the same, the curves would have been "affine." This may be seen from the equation  $E_1 = \beta_1 A_1^p$  and  $E_2 = \beta_2 A_2^p$ . If  $A_1 = A_2$ , then  $E_1 : E_2 = \beta_1 : \beta_2$  and the fraction  $\beta_1/\beta_2$  will be the Mecklenburg "factor" of one curve with respect to the other.

TABLE IV.  
Constants of the Equation  $E = \beta A^p$  for Ferric Hydroxide.

Series.	Precipitation temperature.	$p$ .	$\beta$ .
A .....	..	0.210	128
D .....	..	0.284	33.3
Mecklenburg's .....	$1^\circ$	0.183	195
Mecklenburg's .....	$11-12^\circ$	0.186	184
Mecklenburg's .....	$23^\circ$	0.197	184
Mecklenburg's .....	$45^\circ$	0.186	180
Mecklenburg's .....	$51^\circ$	0.195	170
Mecklenburg's .....	$60^\circ$	0.187	170
Mecklenburg's .....	$98^\circ$	0.195	120
(Mecklenburg) unit curve .....	..	0.188	200
(Mecklenburg) air dried .....	$98^\circ$	0.195	43
Biltz .....	..	0.198	170

From this it is seen that the only curve whose  $p$  value deviates very much from the average is that of Series D, which is the series where a constant amount of alkali was used.



### Summary.

The curves of the adsorption of arsenious acid by ferric hydroxide in the presence and absence of sodium hydroxide have been constructed. The adsorption of arsenious acid has been found to be diminished by the presence of sodium hydroxide.

The curves of adsorption of sodium hydroxide by ferric hydroxide in the presence and absence of arsenious acid have been constructed. The adsorption of sodium hydroxide has been found to be increased by the presence of arsenious acid.

Our measurements as well as those of Mecklenburg and Biltz indicate a deviation of the adsorption phenomenon from the simple adsorption equation.

An interpretation of the constants  $p$  and  $\beta$  in the adsorption equation  $E = \beta A^p$  is given and the connection between these constants and Mecklenburg's "affine Adsorptionskurven" is pointed out.

Mecklenburg's generalization is thus equivalent to saying that where the adsorption of a compound from solution follows the equation  $E = \beta A^p$ ,  $p$  is constant for the same adsorbing material, and that an adsorbent prepared under various conditions, or of various ages will vary only in the values of  $\beta$ .

The logarithmic curves plotted from our measurements although approximating to straight lines yet show unmistakably a concavity to the  $x$  axis, thus indicating a deviation of the adsorption phenomenon from the adsorption equation. In view of this fact it became desirable, especially since Mecklenburg makes no mention of the adsorption equation, to plot the corresponding logarithmic curves for Mecklenburg's results. Some of these as well as the curve for Biltz results<sup>1</sup> are shown in Fig. 5. In every case this same deviation from a straight line, and concavity to the  $x$  axis are found. There seems to be no doubt of the existence of a definite deviation from exact conformation with the equation. It would seem that the phenomenon of adsorption by gels from aqueous solutions has not the simplicity implied in the equation  $E = \beta A^p$ . What the theoretical significance of this deviation may be is not apparent. The equation however still serves as a simple approximation to the course of the adsorption.

That the exponent  $p$  remains constant for different preparations of ferric hydroxide where arsenious oxide alone is used, but changes when alkali is present, is shown in Table IV where the values of  $p$  and  $\beta$  have been calculated as already described.

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<sup>1</sup> *Ber.*, 37, 3138 (1904).