TABLE III

PARTIAL MOLAL HEATS OF SOLUTION OF WATER AT 25°, IN JOULES PER MOLE

(a) %Zn(NO₃)₂	Molality	n_2/n_1	$\bar{H}_1 - H_1$
10.258	0.603	0.0109	−101
18.466	1.196	.0216	−254
25.577	1.815	.0327	−135
26.434	1.897	.0342	−132
32.354	2.525	.0455	−245
34.618	2.796	.0504	−282
35.079	2.853	.0514	−1,302
44.045	4.156	.0749	−1,417
53.236	6.011	.1083	−1,448
57.362	7.103	.1280	−2,660
63.150	9.048	.1630	−2,806
67.514	10.973	.1977	−4,979
72.713	14.070	.2535	−6,278
80.177	21.353	.3847	−9,172
82.375	24.677	.4446	−11,811

(b) %Cd(NO₃)₂	Molality	n_2/n_1	$\bar{H}_1 - H_1$
10.900	0.517	0.0093	−206
23.356	1.289	.0232	−271
28.908	1.720	.0310	−385
43.935	3.315	.0597	−592
49.615	4.165	.0750	−745
61.701	6.814	.1227	−1,548
65.357	7.980	.1438	−1,659
69.823	9.786	.1763	−1,615
73.501	11.731	.2113	−2,541
78.710	15.637	.2816	−3,442
81.218	18.290	.3295	−4,873
83.132	20.845	.3755	−4,711
85.176	24.303	.4378	−5,748
86.075	25.886	.4664	−5,803

partial molal heats of solution of water from vapor pressure data are tabulated in Table III for the concentrations on which vapor pressure measurements were made. These values are indicated by circles in Figs. 3 and 4 for sake of comparison with the calorimetric data.

The accuracy of the data presented is estimated to be about the same as that in the previous work which already has been discussed,[15,16,18] except for data involving the heat of solution of the anhydrous zinc nitrate. Due to the uncertainty as to the purity of this salt, the authors are unable to estimate the accuracy of its heat of solution.

Summary

A method for the preparation of anhydrous zinc nitrate has been devised.

The heats of solution of zinc nitrate and cadmium nitrate and their various hydrates have been measured.

Heats of dilution of the solutions of these two salts have been measured. The concentration range of these solutions extends into the extremely concentrated, and consequently supersaturated, range.

Certain thermodynamic quantities have been calculated from these data and comparisons made with values from vapor pressure data.

A Critical Study of the Thiosulfate Titration of Chlorine

BY F. J. HALLINAN AND W. R. THOMPSON

The iodine–thiosulfate reaction is one of the most widely used in analytical chemistry. A strongly acid system is usually employed, but titration at the pH of the sample, possibly either neutral or slightly alkaline, has been suggested in the appendix of "Standard Methods for the Examination of Water and Sewage,"[1] with an expressed hope that further study would be stimulated. The use of such systems has been reported elsewhere in the literature[2,3] as a means of estimating effective chlorine bactericidal agents

and of reducing interference by other compounds possibly present in natural waters. However, not only the oxidizing agents in the sample but the titration system itself are affected by pH change through varying proportion of thiosulfate conversion to tetrathionate ion and sulfate ion. Kolthoff and Furman[4] discuss some previous investigations which, however, were directed chiefly to the exploration of suitable ranges of hydrion concentration and other conditions separately, without any extensive consideration of the peculiarities of their interdependence. The object of the present communication is to present the results of a study of some of these relations which should be

(1) American Public Health Association, "Standard Methods for the Examination of Water and Sewage," American Public Health Association, New York, 1936, 309 pp.

(2) B. A. Skopintzew and F. J. Warfolomejewa, Z. anal. Chem., 88–89, 97–107 (1932).

(3) M. L. Koshkin, J. Am. Water Works Assoc., 29, 1761–1774 (1937).

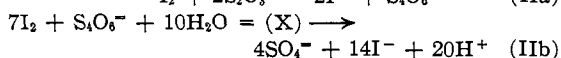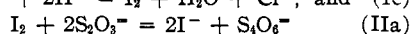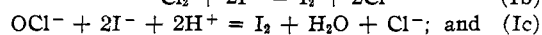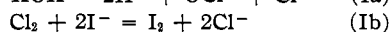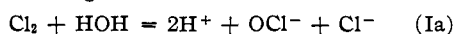(4) I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1929, 552 pp.

taken into account. In Part 1 the influence of *p*H and iodide concentration upon the titration of chlorine is considered, and in Part 2 an attempt is made to gage the effects of certain interfering substances, particularly manganese which occurs in many water supplies during seasonal overturns.

Part 1

The following stoichiometric reactions may be considered in regard to chlorine titration

$$Cl_2 + HOH = 2H^+ + OCl^- + Cl^- \quad \text{(Ia)}$$
$$Cl_2 + 2I^- = I_2 + 2Cl^- \quad \text{(Ib)}$$
$$OCl^- + 2I^- + 2H^+ = I_2 + H_2O + Cl^-; \text{ and} \quad \text{(Ic)}$$
$$I_2 + 2S_2O_3^- = 2I^- + S_4O_6^- \quad \text{(IIa)}$$
$$7I_2 + S_4O_6^- + 10H_2O = (X) \longrightarrow$$
$$4SO_4^- + 14I^- + 20H^+ \quad \text{(IIb)}$$

where X is a possible intermediate stage in the reaction IIb.

Chlorine solutions in distilled water, stabilized by storage for several days, were used in the titration study. Where dilutions were required chlorine-zero[5] water[1] was used. Except where noted otherwise, *p*H buffers consisted of mixtures of 5 *M* acetic acid with 5 *M* ammonium hydroxide of which one part was added to about forty parts of the sample to be titrated. Potassium iodide solutions were used in such concentrations that the required amount in any case was added in volumes equivalent to one-fortieth to one-eightieth that of the sample. {KI} will be employed to denote the grams of potassium iodide used per liter of sample. The potassium iodide solutions were always filtered through activated carbon and paper just before use to remove any preformed iodine possibly resulting from photochemical action. The titrating agent was 0.005 *M* sodium thiosulfate. The sample volume was usually such that 1 to 3 ml. of thiosulfate was required in titration. The indicator was arrowroot starch, 1% in water containing 1% zinc chloride, boiled ten minutes, and decanted after standing overnight. About 1 part of indicator was used to 100 of sample, added just before the end-point. The main study was made on 40-ml. samples of solutions containing between seven and twelve parts per million of chlorine. In that case end-point corrections were of minor importance, but the correction technique employed by Reith[6] under similar circumstances was used unless negligible. This correction (an addition to the direct reading) is obtained from

(5) The term "chlorine-zero" is used to designate water in which the chlorine demand has been satisfied and which contains no free chlorine.

(6) J. F. Reith, *Biochem. Z.*, **216**, 249–268 (1929).

titrations of serial dilutions of a chlorine solution with chlorine-zero water. In titrations the order of additions was sample, buffer, potassium iodide solution, and thiosulfate with starch indicator as mentioned. Titration was performed as rapidly as practicable.

In each case the titration of the sample at given *p*H and {KI} was divided by the titration of equal portions at a *p*H approximately 1.3 with {KI} >1, under which conditions sensibly the maximum titer was obtained. This ratio will be designated R'. A set of observations was made on the same chlorine solution (about 11.5 parts per million), and at each combination of *p*H and {KI} the mean of five titrations was used to obtain R'. The results are given in Table I together with p. e.$_{R'}$, the probable error of the mean R' in each case. A preliminary graph was made with values of R' plotted against log {KI} for each *p*H used. Inspection of the graphs suggested the possibilities of fitting a family of curves to the observations, as the graphs appear almost linear and of nearly the same slope. It appeared furthermore that about the same value of R' was found when log {KI} was increased about 1.5 times as much as *p*H was decreased, or vice versa, even closer when the ratio

TABLE I

COMPARISON OF OBSERVED AND CALCULATED RELATIVE TITERS WITH CHLORINE CONCENTRATION APPROXIMATELY 10 P. P. M.

*p*H	{KI} g. per liter	$100R'$ obsd.	P. e.$_{(100R')}$	$\dfrac{100R'^a}{R \text{ (calcd.)}}$
1.3	1.0	100	0.25	(100.03)
6.57	0.1	73.1	1.8	112
6.57	1.0	82.4	1.3	101
6.57	10.0	91.5	1.5	100
6.57	125.0	101.5	1.3	(105)
6.30	0.1	75.4	1.7	104
6.30	1.0	81.5	0.59	95
6.30	10.0	94.6	.38	101
5.47	1.0	96.1	.48	101
5.47	0.1	90.4	.47	103
4.98	.1	91.5	.3	98
4.98	.05	91.9	.42	101
4.98	1.0	98.1	.73	101
4.59	0.05	90.0	.67	95
6.88	5.0	83.9	1.1	99
6.88	50.0	96.1	0.64	103
6.88	19.0	89.2	1.8	99
6.7[b]	19.0	85.4	1.3	99
6.7[b]	22.5	95.4	0.66	103
6.7[b]	22.5	89.2	0.95	97
7.47	20.0	73.9	2.8	90

[a] Mean = 99.8; standard deviation = 4.6, p. e. = 3.1.
[b] Sodium potassium tartrate, ten grams per liter sample as buffer.

20/14 ≅ 1.428 was used instead of 1.5. This is the ratio suggested by equation IIb if it is assumed that the intermediate products (X) are 14 I^- + $20H^+$ and a precursor of sulfate ion. Since some of these reactions are not sensibly reversible, the ratios R' may depend more upon relative velocity coefficients of the reactions involved than upon constants of equilibrium, and as far as we know these constants have not been determined.

It seemed worth while to approximate R' by a function of $20pH - 14 \log \{KI\}$. If the final products of thiosulfate oxidation are tetrathionate and sulfate, then $1 \geqq R' \geqq \frac{1}{8}$. Accordingly, an attempt was made to approximate R' by R where the function, $f(R)$, is taken as

$$\log \frac{1 - R}{R - 0.125} = K_1(20pH - 14 \log \{KI\}) - K_2 \quad (1)$$

and the coefficients, K_1 and K_2, were determined to minimize $\Sigma[f(R)-f(R')]^2$ over the observed values of R' less than unity. This gave $K_1 \cong$ 0.028059 and $K_2 \cong 4.2604$. Furthermore, the limiting values ($\frac{1}{8}$, 1) are the same for R as for R' by the device used in choosing $f(R)$ as given above. Values of $100R'/R$, thus calculated, are given in Table I for comparison. The square root of the mean $[f(R)-f(R')]^2$ was 0.165; and the correlation coefficient r, found incidentally in the calculation, between $f(R')$ and $(20pH-14 \log \{KI\})$ was 0.881. Considering only the nineteen values of Table I used in fitting equation (1), the mean value of $100R'/R$ is 99.8 with p. e. $\cong$ 3.1. A graph of R as a function of $(20pH - 14 \log \{KI\}$ is given in Fig. 1 together with observed values, R'.

The data already treated are each a mean of five observations. As a further test of the formula (1) additional data from 63 single titrations have been used to compare observed and calculated values of R. More than half the observed values, R', lie within 5% of the calculated value, and if results with $\{KI\} < 0.5$ are excluded, then two-thirds of the values are within this range. Other values with very low chlorine concentrations are given in Table II. Koshkin[3] has published the results of a series of titrations of chlorine solutions which also contained ammonia, at varying pH. His results, similarly treated in Table III, indicate an excellent agreement between calculated and observed values of R for this system.

One of Koshkin's objectives was to indicate activity or availability of the chlorine bactericidal

TABLE II

ADDITIONAL COMPARISON OF OBSERVED AND CALCULATED RELATIVE TITERS WITH LOW CHLORINE CONCENTRATIONS, 0.5 P. P. M. to 2.3 P. P. M.

pH	$\{KI\}$	$100R'$ (obsd.)	$100R'/R$	Chlorine, p. p. m.
6.88	1.25	68.7	89.5	2.3
6.88	25.0	84.8	92.8	0.79
4.5	1.43	100	101.4	.5
6.3	1.43	79	90.0	.5
6.7	1.43	72	88.7	.5
7.4	1.43	58	89.9	.5
8.0	1.43	51	107.4	.5

Mean, 95.5.

TABLE III

DATA BY M. L. KOSHKIN[a] RECALCULATED TO INDICATE OBSERVED AND CALCULATED RELATIVE TITERS (R)

pH	$\{KI\}$	$100R'$ (obsd.)	$100 R'/R$	Chlorine, p. p. m.
4.0	1.0	86.6	87.3	0.479
7.0	1.0	63.7	88.2	.602
7.6	1.0	59.4	106.3	.618
7.9	1.0	47.8	100.9	.634
8.1	1.0	45.3	108.4	.634

Mean = 98.2.

[a] Table IV in ref. 3.

agents at various pH values, particularly that of the original water sample. It appears, however, that variation in the thiosulfate titration results largely from the peculiarities of relative extent of oxidation of this reagent with respect to variation in pH and $\{KI\}$. It is noteworthy that when a low titration is obtained by such variation (R' low), then further additions of acid, potassium iodide, or both, do not make possible a continuation of titration to give $R' \cong 1$. On the contrary,
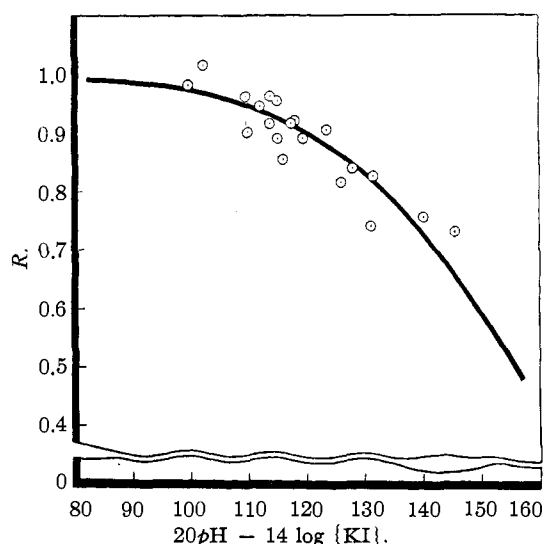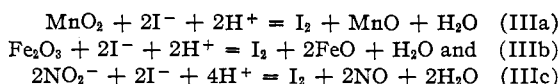

Fig. 1.—A representation of relative titer R as a function of a single variable, $20pH - 14 \, 1 \, g_{\bar{4}}\{KI\}$.

practically no more iodine is liberated for titration. Furthermore, the amount of sulfate ion formed in the titration should be greater the slower it is performed, and the titer correspondingly lower. This is roughly in agreement with our general experience.

Part 2

The possibilities of interference of manganese dioxide, ferric oxide, and nitrites have been studied. Iodine may be liberated by these substances in accord with the following stoichiometric equations

$$MnO_2 + 2I^- + 2H^+ = I_2 + MnO + H_2O \quad \text{(IIIa)}$$
$$Fe_2O_3 + 2I^- + 2H^+ = I_2 + 2FeO + H_2O \text{ and} \quad \text{(IIIb)}$$
$$2NO_2^- + 2I^- + 4H^+ = I_2 + 2NO + 2H_2O \quad \text{(IIIc)}$$

The reaction IIIa was studied over approximately the same range of pH and iodide concentration as in the thiosulfate oxidation experiments. A manganese dioxide sol was produced according to Mellor's description[7] of Forchhammer's method. Nineteen hundred milliliters of solution was prepared containing 0.66 mg. of manganese added as manganous sulfate. To this was added 2.91 ml. of one-eightieth normal potassium permanganate solution with rapid stirring, and the mixture was then diluted to 2 liters to form a brown sol, which had a color equivalent to 162 on the platinum–cobalt scale[1] and which remained unchanged by passage through Whatman no. 40 filter paper. Particle size was not determined, but probably a finer suspension was obtained than is usually encountered in water supplies. The oxidizing capacity of the sol was measured by the o-tolidine method[1] with a five-minute reaction time, and found equivalent to that of 0.65 part per million of chlorine.

A series of 50-ml. portions of this sol was adjusted to various hydrogen and iodide ion concentrations, in a manner similar to that employed for the thiosulfate titrations. One per cent. of a 0.2% alcoholic solution of α-naphthoflavone (20 parts per million) was added as an extremely sensitive[8] acceptor of iodine formed, and an observation made of the time, t', required for development of a color matching a standard which was approximately the color obtained by the liberation of an amount of iodine equivalent to 0.05 p. p. m. chlorine at pH = 6.7 and $\{KI\} = 18$, with compensa-

(7) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Company, New York, N. Y., Vol. XII, 1932, p. 261.

(8) George Barger, "Some Applications of Organic Chemistry to Biology and Medicine," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, 186 pp.

tion for natural color and turbidity.[9] The results are given in Table IV. Although t' must be considered a crude estimate of the time required for liberation of a given amount of iodine by the interfering substance in a thiosulfate titration, it was hoped to obtain in this way some indication of the extent of its influence.

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED TIMES FOR STANDARD COLOR DEVELOPMENT

{KI}	t', obsd.	t, calcd.	{KI}	t', obsd.	t, calcd.
	pH 4.62			pH 6.62	
0.1	12	24.5	3.0	16	13.1
.1	18	24.5	5.0	9	7.9
.3	5	8.2	7.0	7	5.6
.5	4	4.8	9.0	6	4.4
1.0	1	2.4	14.0	2	2.8
	pH 5.0			pH 6.92	
0.5	10	8.3	7.0	11	8.5
1.0	7	4.1	9.0	6	6.6
1.0	5	4.1	12.0	6	5.1
2.0	2	2.1	15.0	4	4.1
3.5	2	1.2	18.0	2	3.4
	pH 5.5			pH 7.53	
0.5	26	16.5	10.0	21	13.4
1.0	10	8.3	13.0	18	10.8
5.0	3	1.7	16.0	12	8.8
6.0	1	1.3	19.0	8	7.5
	pH 6.35			pH 7.77	
1.0	25	26.8	20.0	15	9.9
3.0	10	9.0	25.0	8	8.0
5.0	5	5.5			
8.0	3	3.4			
8.0	4	3.4			

For given pH values the logarithms of observed values of t' were plotted against log $\{KI\}$, yielding very roughly an approximation to a set of straight lines of nearly the same slope, about 45°. This suggested fitting a function of the type

$$x^a y^b t = k \quad (2)$$

where $x = C_{H^+}$, $y = \{KI\}$ and a, b and k are constants. To find values of a, b and k to minimize $\Sigma(\log t - \log t')^2$ would be a straightforward procedure, but it seemed better to consider t' as equally subject to error regardless of magnitude; i. e., to attempt to minimize $\Sigma(t - t')^2$. To deal simultaneously with a, b and k would be difficult. However, within each subset wherein x was constant a good fit was obtained with $b = 1$, but log k appeared to increase successively about as did 0.4 log x. This suggested a trial value of $a = 0.6$,

(9) F. D. Snell and C. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., New York, N. Y., Vol. I, 1937, pp. 11–12.

with $b = 1$; and the corresponding value of k to minimize $\Sigma(t - t')^2$ was found to rough approximation to be $k = 4.14 \ (10^{-3})$. From this formula, $x^{0.6}yt = k$, the calculated time t is given in Table IV for comparison with the observed t'. Equations (1) and (2) have been used to develop the nomogram given in Fig. 2, in which the parallels for given R demark on a logarithmic scale corresponding values of pH and $\{KI\}$ from equation (1), and the t-parallels demark a corresponding relation from equation (2). Thus, if arbitrary values of R and t are prescribed, the intersections of nomogram lines indicate the corresponding pH and $\{KI\}$ to be used. In the procedure in "Standard Methods"[1] the amount of potassium iodide used is 0.75 g. per liter of sample; whence for $R = 0.97$ the pH should be approximately 4.92 and t would be 5. Obviously, a buffer should be used to hold the required pH, for which acetates should be appropriate. The system ammonia–acetic acid–water was found satisfactory in the present work, having appreciably no influence upon blank corrections. The value $t = 5$ indicates that manganese dioxide interference comparable with that induced by the sol used in the present investigation would be negligible.

Extensive study of possible interference by nitrite ion and ferric oxide has not been made, but a brief survey indicated that conditions sufficient to repress manganese dioxide interference would also make negligible interference by these other agents. Usually no attempt is made to differentiate the iodine formed by the system chlorine–ammonia–water; but the situation is complicated considerably in the presence of organic chloroamines or possibly chlorine adsorption products, which are considered relatively ineffective as bactericidal agents.[3,10,11] Unfortunately, there appears to be no combination of pH and $\{KI\}$ available where a measure of the iodine-forming capacity of the chlorine–ammonia–water system may be made satisfactorily with the thiosulfate titrating agent without risking considerable interference by these other ineffective chlorine derivatives if present. It is important not to misinterpret decreases in thiosulfate titer obtained by reduction in $\{KI\}$ or increase in pH which could be obtained similarly in simple titration of chlorine–water.

(10) W. L. Mallman, "The Germicidal Activity of Available Chlorine as Measured by the Orthotolidine and Iodometric Tests for Chlorine," Michigan Engineering Experiment Station, Bulletin 59, 1934, 15 pp.

(11) David Charlton and Max Levine, "Germicidal Properties of Chlorine Compounds," Iowa Engineering Experiment Station, Bulletin 132, 1937, 60 pp.
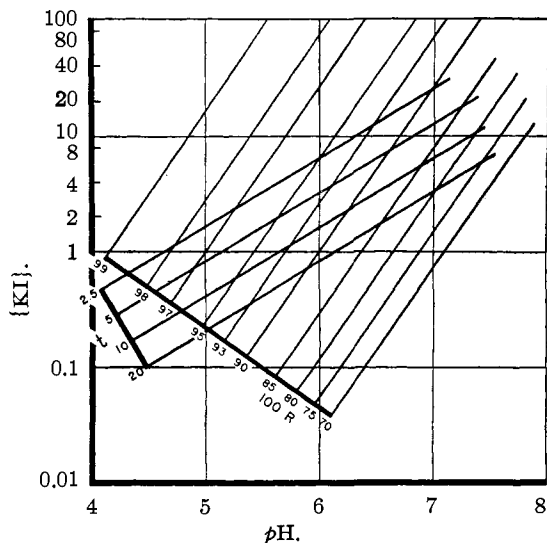

Fig. 2.—Nomogram presenting relations between relative titer R, reaction time t, potassium iodide concentration $\{KI\}$ and pH value.

Summary

The influence of hydrogen and iodide ion concentrations upon oxidation of thiosulfate induced by chlorine, and the oxidation of iodide by oxidized manganese have been studied. With pH between 4.6 and 7.7 and potassium iodide concentration between 0.05 and 100 g. per liter of sample, and under the other experimental conditions described, the results may be represented approximately by the equations

$$\log \frac{1 - R}{R - 0.125} = 0.02806 \ [20pH - 14 \log \{KI\}] - 4.260 \quad (1)$$

and

$$\log t = 0.6 \ pH - \log \{KI\} - 2.383 \quad (2)$$

where R is the ratio of observed to maximum titer, $\{KI\}$ is the weight of potassium iodide in grams used per liter of sample, and t is the time required to produce sufficient iodine by introduction of 0.5 part per million of manganese in a prepared sol to color an α-naphthoflavone indicator as much as would 0.05 part per million of chlorine under the standard conditions of pH and potassium iodide concentrations.

These equations have been used to develop a nomogram which may serve as guide to chlorine titration with thiosulfate in the presence of manganese dioxide. By taking advantage of the moderate difference in slopes of the R and t nomogram lines, it should be possible to choose conditions where sulfate formation and manganese interference are negligible.

Less extensive studies of the effect of hydrogen and iodide ion concentrations on the action of other interfering substances indicate that conditions satisfactory in the presence of manganese dioxide would suffice for nitrite or iron. Some organic chloramines or chlorine derivatives of low bactericidal potency, if present, will be partially measured as chlorine under any conditions suitable for thiosulfate titration. Any values of pH and {KI} taken from the nomogram for use should be subjected to direct tests by a definite procedure, to determine the accuracy of chlorine titrations in the concentrations to be employed and the rate of reaction of amounts of interfering substances likely to be encountered.

ALBANY, N. Y.   RECEIVED AUGUST 23, 1938

The Sorption of Hydrogen on Supported Nickel

BY CARROLL W. GRIFFIN

Introduction

In an earlier paper the writer[1] pointed out that the low-pressure increase in the adsorption of hydrogen by copper which had been poisoned with a small amount of carbon monoxide appeared to be due either to the ability of the monoxide molecule to link several hydrogen atoms to itself, or to an increased activity of the copper centers in proximity to the adsorbed monoxide. White and Benton,[2] after studying the poisoning action of a small amount of carbon monoxide on the adsorption of hydrogen by nickel, concluded that the increased adsorption of hydrogen caused by the monoxide was due to an increased activity of the most active centers of the metal, that is, an enlargement of the active areas following the poisoning. With both metals larger amounts of carbon monoxide caused a smaller increase of hydrogen adsorption, and, at higher pressures, the poison often decreased the adsorption. In both of the above studies the adsorption was of the activated type, the measurements being carried out at 0°.

In the extensive investigations of Benton and White on the sorption of gases at low temperatures[3] where the adsorption was largely of the physical type it was revealed that carbon monoxide caused an immediate decrease in the adsorption of hydrogen. Furthermore, at −183° this low-pressure decrease is exactly equal to the volume of poison employed provided, of course, the amount of poison used is not greater than the low-pressure adsorption of hydrogen itself. However, in their low temperature studies, Benton and White did not use less than 1.0 cc. of the poison; and since previous experience had always shown that much more than 0.04 cc. of carbon monoxide caused a decrease in hydrogen adsorption, it seemed worth while to investigate the effect of a progressive poisoning of nickel with the smaller amounts of the monoxide at low temperature. In addition, by employing a supported nickel adsorbent two other points could be observed, namely, whether or not a supported sample shows the step-wise discontinuities which characterize many of the isotherms for gases on massive metals as shown by Benton and White, and the result of "experiments with temperature variation."[4]

Experimental Part

The apparatus, the purification of hydrogen and the procedure for making a run have been described.[5] Helium, used as a reference gas, was purified by passing over hot copper and copper oxide and over active charcoal cooled in liquid nitrogen. The method of preparation of the supported nickel has been reported.[6] Fifty grams of brick was used to support the nickel in the ratio of two moles of nickel to a thousand grams of brick.

The low temperature measurements were carried out with the adsorbent in a bath of liquid nitrogen. The temperature was determined by use of a platinum resistance thermometer connected to a Leeds and Northrup Mueller type temperature bridge. The resistance thermometer was calibrated at 100, 25, 0° and at −78.5, −191.5 and −196°. The absolute temperature of the experiments at the lowest temperature may be in error by 0.5° or less, but variations in temperature amounting to 0.001° could be detected. The blade of the thermometer was approximately the same length as the bulb containing the adsorbent and was placed alongside the latter. For experiments at −78.5° solid carbon dioxide and alcohol were employed; for 0°, ice and water. The volume of the free

(1) Griffin, THIS JOURNAL, 49, 2136 (1927).

(2) White and Benton, J. Phys. Chem., 35, 1784 (1931).

(3) Benton and White, THIS JOURNAL, 53, 3301 (1931).

(4) Benton and White, ibid., 54, 1379 (1932).

(5) Pease, ibid., 45, 1196 (1923).

(6) Griffin, ibid., 59, 2431 (1937).