determination of the specific surface have been applied to products of lead chromate of different age and degree of perfection. The agreement between the results is very satisfactory, as is evident from the summarized data in Table VII. In terms of mg. of wool violet per gram the surfaces of the various products were: Product A, 4.8; B, 4.1; C (six minutes old), 38; C (eight minutes old), 35; D, 17.2; E, 15.4. These values were

TABLE VII

SPECIFIC SURFACE EXPRESSED IN MG. OF Pb P. G. OF DIFFERENT SAMPLES OF LEAD CHROMATE BY VARIOUS METHODS

Sample	W. V. method	Adsorption lead acetate from alcohol	——Thorium B methods—— In water	In ethanol	Dye coated products
A	2.6	2.1	2.6	2.1	2.7
			2.9[a]		
B	2.2		2.2[a]		
C[b]	20.5			25	
C[c]	19	18.9			27
D	9.3	8.7	7.5	8.7	
E	8.3		7.4		

[a] No correction was made for the slight amount of lead adsorbed. The values reported may be slightly high for this reason. [b] Product was six minutes old. [c] Product was eight minutes old.

converted into the units of Table VII by means of the factor 0.54. One mg. of wool violet is equivalent to 0.54 mg. of lead in the surface according to the results obtained with product A.

Summary

1. The wool violet method is very suitable for the determination of the specific surface of lead chromate. Equivalent amounts of dye and lead are removed from the solution. On the saturated surface one wool violet ion is adsorbed per 2 molecules of lead chromate. The mechanism of the dye adsorption has been discussed.

2. Lead acetate is adsorbed in a monomolecular layer on the surface of lead chromate from dilute solutions of the salt in 95% ethanol. Use of this fact has been made in the development of a new method for the determination of the specific surface.

3. Two new procedures have been described for the determination of the specific surface of fresh and imperfect precipitates of lead chromate by the radioactive method.

The Systems Magnesium Chromate–Water and Ammonium Chromate–Water from 0 to 75°[1]

BY ARTHUR E. HILL, GLENN C. SOTH AND JOHN E. RICCI

In connection with certain phase rule studies involving magnesium and ammonium chromates the aqueous solubilities of these salts were determined in the temperature range 0 to 75°.

I. The literature contains little information on magnesium chromate and its hydrates. The only figure on the solubility of the salt appears to be that of Kohlrausch,[1a] who reported that at 18° 100 ml. of saturated solution contained 60 g. of magnesium chromate. Kopp[2] reported that magnesium chromate crystallized from aqueous solution at room temperature as the heptahydrate; according to Wyrouboff[3] the pentahydrate could be prepared by allowing the heptahydrate to stand in air, or by recrystallization from water above 30°.

The present measurements were made on "Analyzed" grade magnesium chromate recrystallized as follows. A quantity of the salt was dissolved in water and filtered by gravity to remove the insoluble material. The solution was evaporated on a steam-bath under reduced pressure, at about 60°, until crystals began to form in the solution. The material was poured out immediately into a beaker and allowed to cool to room temperature with continuous stirring for twelve hours. The precipitated salt was filtered by suction, centrifuged for twenty minutes, and air-dried for three days. It was then kept in a desiccator over some partly dehydrated salt. This gave, after a week, magnesium chromate pentahydrate of sufficient purity (100.0 ± 0.1% by chromate analysis). The treatment described is rendered necessary by the fact that the concentration of solutions of magnesium chromate by normal boiling causes the precipitation of a solid phase of still unknown composition which may possibly be a basic product of hydrolysis. Concentrated solutions of the salt, moreover, have high viscosity, so that adequate stirring to prevent superheating and serious bumping of the solution during recrystallization is difficult.

The solubilities were determined from both super- and

(1) This paper is being published, following the death of Professor Hill, by his collaborators.

(1a) Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, London, 1931, p. 275.

(2) Kopp, Ann., 42, 97 (1842).

(3) Wyrouboff, Bull. Soc. Min., 12, 69 (1890).

under-saturation, using the usual methods of stirring in closed Pyrex tubes to obtain equilibrium. The temperatures were constant within 0.1° at the extremes, 0 and 75°, and within 0.01° at 25 and 35°. The samples for analysis from the 75° solutions were withdrawn into glass-jacketed pipets preheated to the same temperature and filled with isoamyl alcohol to act as an insulator and as a heat reservoir. The analyses were based on the determination of chromate by the usual iodometric method, using 0.15 N sodium thiosulfate solution standardized against pure potassium dichromate, following the procedure of Kolthoff and Furman.[4]

To determine the hydrates in equilibrium with solution at 0° and at 25°, complexes containing excess magnesium chromate pentahydrate were rotated at those temperatures for two weeks; the solid phase was then filtered off by suction, centrifuged for ten minutes and analyzed immediately, with the following results:

Temp., °C.	MgCrO₄ (found), %	MgCrO₄ (theoretical), %
0	51.46	52.67 (for $MgCrO_4 \cdot 7H_2O$)
	51.88	
25	59.67	
	59.53	60.90 (for $MgCrO_4 \cdot 5H_2O$)

These analyses of the damp residues show the stable solid phases in equilibrium with saturated solution to be the heptahydrate at 0° and the pentahydrate at 25°. The solubility curve of the heptahydrate was then determined by using solid prepared from pentahydrate and water at 0°.

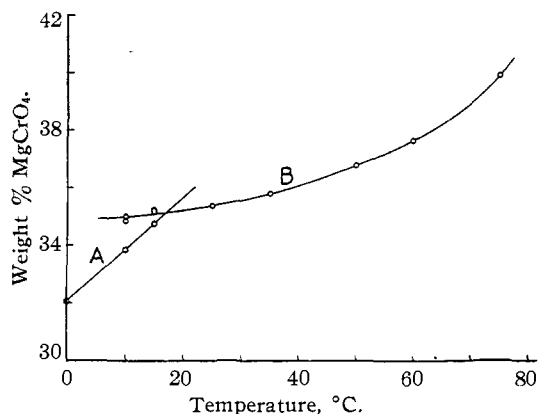Fig. 1.—System MgCrO₄–H₂O from 0 to 75°: A, Mg-CrO₄·7H₂O; B, MgCrO₄·5H₂O.

By extrapolation of the solubility curves, as shown in Fig. 1, the transition temperature for the two hydrates in contact with solution was found to be 17.2°, at a concentration of 35.15% MgCrO₄.

The pentahydrate curve is shown extending to 75°, but this last point may possibly be metastable in respect to a solid phase not yet identified. Prolonged stirring at this and slightly higher tem-

(4) Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York. N. Y., 1929, p. 371.

TABLE I
SOLUBILITY OF MgCrO₄ IN WATER

Temp., °C.	S[a]	U[b]	Mean	Solid phase
	Wt. % of MgCrO₄			
0	32.05	32.07	32.06	⎫
10	33.85	33.90	33.87	⎬ MgCrO₄·7H₂O
15	34.77	34.79	34.78	⎭
10 (m)[c]	35.01	34.86	34.94	⎫ MgCrO₄·5H₂O (m)[c]
15 (m)[c]	35.18	35.18	35.20	⎬ (m)[c]
	35.25			⎭
25	35.39	35.39	35.39	⎫
35	35.82	35.80	35.81	⎪
50	36.83	36.82	36.82	⎬ MgCrO₄·5H₂O
60	37.70	37.66	37.68	⎪
75	39.92	39.99	39.96	⎭ (m?)[c]

[a] S, from super-saturation.   [b] U, from under-saturation.
[c] m, metastable.

perature yields a very finely divided solid which is extremely difficult to filter, and which has not been analyzed; it may be either a lower hydrate or a basic product of hydrolysis, with a solubility known to be lower than that listed for the pentahydrate at 75°.

For further information on the hydrates of magnesium chromate, the thermal decomposition of MgCrO₄·5H₂O was investigated, with respect to both temperature and time, on exposure to ordinary laboratory air. Although the actual aqueous vapor pressure on the system was therefore not strictly controlled, the results are nevertheless of significance, as the figures and curves show.

Wyrouboff[3] reported that MgCrO₄·7H₂O lost two moles of water in air (at room temperature), and three more at 120°, but that the complete expulsion of water at higher temperatures was accompanied by decomposition of the salt. According to Kopp,[2] however, complete dehydration is possible without decomposition.

As already indicated, the present study showed the pentahydrate to be the stable form of magnesium chromate exposed to air at room temperature. The decomposition of this hydrate was studied by the following procedure. A weighed amount of MgCrO₄·5H₂O was placed in an oven at room temperature and the temperature was increased at intervals until a decrease in weight was observed. When a noticeable loss of weight resulted after at least ten hours at a given temperature, that temperature was maintained until a new constant weight was approached, corresponding to a new hydrate. The temperature was then increased further, and the process repeated.

The following is a résumé of the observations. A loss of water of 23.45% was recorded at 60–70°, the weight then remaining constant up to 100° (theoretical loss for three moles of water from the pentahydrate = 23.46%). A second constant weight was obtained at about 110°, representing a total loss of 30.57% water, while prolonged heating up to 180° left the weight practically constant, the loss reaching only 31.74% (theoretical loss for four moles of water = 31.28%). The weight remained constant at 210°. But at 275°, the last mole of water was expelled (observed loss, 39.07%; theoretical, for five moles of water, 39.10%), leaving the weight constant at that temperature.

The data show the existence of the following forms of magnesium chromate, therefore, in addition to the heptahydrate, which is stable in contact with saturated solutions below 17.2°: $MgCrO_4 \cdot 5H_2O$, $MgCrO_4 \cdot 2H_2O$, $MgCrO_4 \cdot H_2O$ and $MgCrO_4$ anhydrous. In view of the close agreement between the observed and the theoretical loss of weight for the complete dehydration to anhydrous $MgCrO_4$, the loss of the last mole of water is evidently not accompanied by any decomposition of the salt, in contradiction to the report of Wyrouboff,[3] but in agreement with the work of Kopp.[2]

The transition temperatures in the decomposition of the pentahydrate, under ordinary atmospheric conditions, can be roughly estimated from the data to be 50–60° for $MgCrO_4 \cdot 5H_2O \rightleftharpoons MgCrO_4 \cdot 2H_2O + 3H_2O$, 100–110° for $MgCrO_4 \cdot 2H_2O \rightleftharpoons MgCrO_4 \cdot H_2O + H_2O$, and 160–170° for $MgCrO_4 \cdot H_2O \rightleftharpoons MgCrO_4 + H_2O$.

II. Although the solubility of ammonium chromate had already been reported, at 0, 25, 50 and 75°, by Gerasimov,[5] the system was repeated for greater accuracy and to make sure of the attainment of equilibrium. The salt used was a recrystallized analyzed grade of ammonium chromate. Although there is an appreciable loss of ammonia from hot concentrated solutions of the salt, consideration of the system CrO_3–NH_3–H_2O at 30°, studied by Schreinemakers,[6] shows that the normal salt can be precipitated from solutions containing excess of ammonia. The recrystallization was therefore carried out by cooling a saturated solution, containing excess ammonia, from near boiling to room temperature, with constant stirring, until precipitation appeared to be complete. The crystals were filtered by suction, cen-

(5) Gerasimov, J. Gen. Chem. (U. S. S. R.), 4, 721 (1934).
(6) Schreinemakers, Z. physik. Chem., 55, 71 (1906).

trifuged and kept over solid potassium hydroxide. Analysis of the dry salt showed a purity of 100.0 ± 0.1% based on determination of chromate. The loss of ammonia from the solid salt itself, during the brief handling required for the preparation of the solubility complexes, was negligible, as verified by repeated analysis of the salt. The loss from hot solutions was kept at a minimum by reducing the free space in the solubility tubes. In order to estimate the loss of ammonia from saturated solutions during sampling, tests were made at 50°, to determine any error from this source. After the initial samples were taken, the solubility tubes were left suspended in the thermostat, open to the air; further samples were then taken one hour and two hours later. From the figures given in Table II, it is seen that the actual loss during the three or four minutes required during sampling must be negligible.

TABLE II

SOLUBILITY OF $(NH_4)_2CrO_4$ IN WATER, SOLID PHASE, $(NH_4)_2CrO_4$

Temp., °C.	S	Wt. % $(NH_4)_2CrO_4$ U	Mean
0	19.79	19.77	19.78
15	24.14	24.12	24.13
25	27.04	27.00	27.02
35	30.01	29.98	30.00
50	34.38	34.42	34.40
50 (exposed 1 hr.)	34.21	34.17	
(exposed 2 hrs.)	33.80	33.83	
60	37.22	37.19	37.21
75	41.19	41.21	41.20

The solubilities given in Table II are all based on chromate determinations, with the exception of some values at 50°. At this temperature, the values given for the concentration after exposure to the air are based on the ammonia determination alone. Ammonia was determined by distilla-
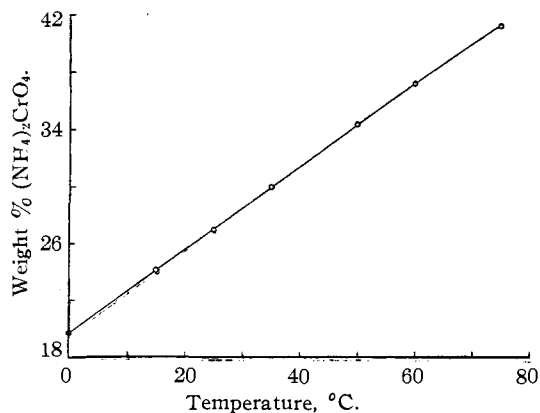

Fig. 2.—System $(NH_4)_2CrO_4$–H_2O from 0 to 75°.

tion into standard acid and titration of the excess acid. The solubility curve is shown plotted in Fig. 2, together with the values reported by Gerasimov[5] and the determination of ·Schreinemakers at 30°. The present values fall on a straight line up to 60°, with only a slight falling off above that temperature.

Summary

1. The aqueous solubility of magnesium chromate has been determined from 0 to 75°; the saturating phases in this temperature range are $MgCrO_4 \cdot 7H_2O$ and $MgCrO_4 \cdot 5H_2O$. Two other hydrates, $MgCrO_4 \cdot 2H_2O$ and $MgCrO_4 \cdot H_2O$, also have been detected, in the thermal decomposition of the pentahydrate in air. Anhydrous magnesium chromate can be prepared by complete dehydration.

2. The aqueous solubility of $(NH_4)_2CrO_4$ has been determined from 0 to 75°.

[CONTRIBUTION FROM MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Heats of Adsorption of Gases on Iron Synthetic Ammonia Catalysts at Low Temperatures[1]

BY RALPH A. BEEBE AND NELSON P. STEVENS

Emmett and Brunauer[1a] have developed a method for measuring surface areas of adsorbent materials based on the analysis of the low temperature van der Waals adsorption isotherms of gases near their boiling points. For any given adsorbent, the values for the surface area calculated from the van der Waals isotherms of different gases are generally in good agreement. When the method was applied to several iron catalysts[2] the apparent areas were anomalously high for certain gases such as carbon monoxide and carbon dioxide as compared with nitrogen and argon. This discrepancy was attributed to the presence of chemisorbed oxides of carbon in addition to a van der Waals adsorbed monolayer. By determining the amount of adsorption in excess of that necessary to fill the van der Waals monolayer, it was possible to estimate the quantity of chemisorbed gas present. The chemisorbed volume was also estimated from the volume of gas which, once adsorbed, could not be removed at a temperature considerably above the adsorption temperature. These data were used as a basis for certain important conclusions concerning the preferential concentration of alkali in the surface of alkali promoted iron catalysts.

Although the above method of estimating the fraction of chemisorption appeared to be justifiable, it seemed desirable to obtain an independent experimental check on the method. In a number of investigations in this Laboratory the heats of adsorption have been used in differentiating between van der Waals adsorption and chemisorption. Therefore, at Dr. Emmett's suggestion, we have measured the heats of adsorption in the temperature region of 0 to −183° for several gases on two iron catalysts, one doubly promoted and the other unpromoted. In anticipation, it may be said that our results substantiate in general the conclusions of Emmett and Brunauer as regards the magnitude of the chemisorption processes on these surfaces.

Experimental

Apparatus.—The general apparatus assembly in the present measurements has been described in earlier publications.[3,4] The calorimeter is shown in Fig. 1 of the paper by Beebe and Orfield. In the final experiments on the iron catalysts (Series B on 931 and 973), the calorimeter was modified slightly to permit sending a continuous stream of hydrogen through the catalyst mass during the period of activation. This modification involved the substitution of a metal tube without perforations in the place of the perforated tube D shown in Fig. 1 (Beebe and Orfield). This tube was seated at the lower end in such a way that the incoming hydrogen passed down through the tube D and then up through the catalyst and out through a side tube (not shown in the figure) at the top of the glass mantle. This outlet tube was closed by a glass tap during the adsorption measurements.

In the final experiments with catalyst 931, the assembled calorimeter contained the following materials: platinum calorimeter and cover 34.09 g., platinum side tube 1.14 g., copper tube and vertical vanes 42.45 g., copper shot 14.61 g., iron-nickel tubes 3.65 g., iron catalyst (unreduced oxide)[5]

(1) Supported by a grant from the Penrose Fund of the American Philosophical Society.

(1a) Brunauer and Emmett, THIS JOURNAL, **59**, 2682 (1937).

(2) (a) Emmett and Brunauer, ibid., **59**, 310 (1937); (b) **59**, 1553 (1937); (c) **62**, 1732 (1940).

(3) Beebe and Orfield, ibid., **59**, 1627 (1937).

(4) Beebe and Dowden, ibid., **60**, 2912 (1938).

(5) All catalyst weights given in this paper are those of the unreduced oxides.