

waxy soap and from subwaxy to waxy soap the heat effect is large and varies with the chain length. At the higher temperature transitions the heat effect is small and relatively independent of the chain length. The conclusion is that the low temperature transitions are probably due

to changes in the arrangement of the hydrocarbon chains while the high temperature transitions are due to rearrangement of the polar heads of the molecules.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED JUNE 2, 1941

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Analytical Procedures Employing Karl Fischer Reagent. VIII. The Determination of Water of Hydration in Salts

BY W. M. D. BRYANT, J. MITCHELL, JR., DONALD MILTON SMITH AND E. C. ASHBY

The advantages of using Karl Fischer reagent for the quantitative determination of the water content of organic compounds have been discussed in earlier papers from this Laboratory¹ as well as by other investigators.^{2,3,4} In the inorganic field the reagent affords a valuable means of determining the water present in hydrated salts or adsorbed on the surfaces of solids. Preliminary evidence to this effect was given by Karl Fischer in his original paper.² The writers have found the method to be precise and to have a wide range of application. Of course there are a number of inorganic materials that react abnormally with Fischer reagent to indicate a fictitious water content, but these compounds are readily classified and are in most cases subject to precise correction.

This titration method for water is more rapid and direct than the commonly used thermal drying procedures and is free from some objectionable features of the latter, namely, the difficulty of finding a safe drying temperature corresponding to a complete loss of moisture and the danger of losing other volatile constituents as a result of hydrolysis during drying. It is perhaps not immediately evident how Fischer reagent at room temperature can achieve results equivalent and often superior to those obtained by the older more tedious procedures based on weight loss. At least part of the explanation lies in the fact that the removal of water from hydrated salts and similar

materials is greatly facilitated by the large excess of methanol normally present in the reagent. Where coordination affinity and adsorption are great, methanol is believed to readily replace water and so reduce the mass action or corresponding surface effects opposing the removal of water. For example, it was shown in an earlier paper⁵ that methanol extraction combined with the Fischer titration would remove more water from native and processed cellulose than could be safely removed by thermal drying. Here the reagent was scarcely ever used in the direct presence of cellulose but instead was confined to analysis of the methanol extracts. A distribution equilibrium was evidently established between moisture in the solvent and in the pores of the solid.

In the present paper the writers have studied the behavior of twenty-five hydrated salts (see Table I) where there was no interference from side reactions. In many cases parallel analyses were made by titration, and by weight loss after oven-drying at specified temperatures. Although the hydrated salts available did not in all cases conform to the exact stoichiometric compositions, the effectiveness of the Fischer procedure was shown by the comparative analyses. The titration results were in most cases numerically greater and closer to theory.

The behavior of a large number of "reactive" inorganic compounds with Karl Fischer reagent was observed in an effort to obtain useful generalizations regarding interfering substances. The generalizations are as follows (a more detailed account of this work will appear in the next paper of the series). The ease with which hydrate water is titrated by Karl Fischer reagent depends

(1) (a) Smith, Bryant and Mitchell, *THIS JOURNAL*, **61**, 2407 (1939); (b) *ibid.*, **62**, 3504 (1940). The reagent (a solution of iodine with excess sulfur dioxide and pyridine in dry methanol) combines directly with water to form pyridine methyl sulfate and hydriodide, the color changing from brown to yellow. The reagent is added to the sample from a buret until the brown color is just restored. Except for examples to be discussed, the method is specific for water.

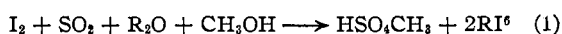
(2) Karl Fischer, *Angew. Chem.*, **48**, 394 (1935).

(3) Zimmermann, *Fette u. Seifen*, **46**, 446 (1939).

(4) Almy, Griffin and Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **12**, 392 (1940)

(5) Mitchell, *ibid.*, **12**, 390 (1940).

more upon the solubility of the initial or final material in the reaction environment than upon the thermal stability of the hydrate. Many hydrates of high stability are rapidly attacked by the reagent. Even relatively insoluble hydrates are broken down provided the sample is finely ground and the mixture shaken mechanically with excess reagent. The use of auxiliary solvents such as glycol is sometimes beneficial. The most frequent type of interference is that produced by base metal oxides, either free or as hydroxides or salts of weak acids. Here a stoichiometric reaction analogous to the regular one with water occurs



R in reaction (1) may be hydrogen, sodium, potassium, etc. Other oxides and their salts may react, but low solubility often renders this interference negligible. Some amphoteric or weakly acidic oxides react, but the more strongly acidic members are without action upon the reagent. Strong oxidizing and reducing substances will usually interfere, but here again the reaction tends to be stoichiometric, hence subject to correction. Precautions should of course be taken to avoid potentially hazardous compounds like the perchlorates.

The successful use of Fischer reagent with the salts in Table I suggested the possibility of assaying desiccants of the anhydrous salt or adsorbent gel type. Samples of activated alumina, silica gel, anhydrous calcium chloride and partly dehydrated calcium sulfate (Drierite) after exposure to moist air were analyzed for moisture by the Fischer titration and by weight loss on heating. As indicated in Table II, the first three gave excellent results.

Reagents.—The preparation and standardization of Karl Fischer reagent is outlined in the first paper of this series.^{1a} A standardized solution of water in methanol (approximately 0.15 M) was employed in back-titrating an excess of reagent. Du Pont synthetic methanol (<0.1% water) was used as a suspending solvent. The salts investigated were from freshly opened bottles of analytical quality reagents and were used without recrystallization.

Analytical Procedure.—A quantity of the finely powdered salt equivalent to 5–10 millimoles of water was suspended in 25 ml. of methanol (<0.1% water) in a 250-ml. glass-stoppered volumetric flask and the sample titrated with standard Karl Fischer reagent to the usual light brown end-point. An end-point stable for fifteen minutes usually indicated complete reaction. Fine grind-

(6) Pyridine has been omitted from this equation for the sake of simplicity.

ing was necessary only when the salt is insoluble in methanol. If the initial titration was incomplete as indicated by a changing end-point, then the mixture was titrated at about ten-minute intervals until a permanent brown color was reached. The analysis of an insoluble material could be expedited by shaking the mixture with a moderate excess of Karl Fischer reagent on a Boerner shaking apparatus⁷ finally back-titrating the unused reagent with a standard solution of water in methanol.

Analyses employing Fischer reagent completed within four hours gave the best results. Longer standing encouraged side reactions, the most conspicuous of which caused a slow regeneration of iodine in the spent or partly spent reagent. The nature of this reaction is unknown but it is believed to involve the slow reduction of sulfur dioxide to hydrogen sulfide by the hydriodic acid present.

The water content of the suspending methanol was determined by a blank titration of a 25-ml. portion and the titer of the sample was diminished by this amount. The corrected titer was equivalent to the available water in the sample. Other inert suspending media besides methanol were sometimes useful. Ethylene glycol, for example, exerted a greater solvent action upon some salts.

Results.—Inspection of Table I shows the close agreement between the results by the Fischer titration and by weight loss on oven drying at 110° in those cases where the latter method is known to succeed. A more critical test of the titration method is found in the group of hydrated sulfates of the metals extending from manganese to zinc in the periodic table. These hydrated salts retain the last mole of water up to temperatures approaching 300°; the titration with Fischer reagent was rapid and complete. Other sulfates of this group not tabulated were titrated successfully but required an additional correction for their oxidizing effect. Another class of hydrates, readily analyzed by the present technique but not by thermal drying, is that of salts undergoing chemical changes such as hydrolysis, disproportionation or pyrolysis on heating; for example, stannic chloride, monocalcium hydrogen phosphate⁸ and cobaltous nitrate. The hydrates of potassium fluoride, barium chloride, monocalcium hydrogen phosphate and calcium sulfate were slow in their reaction with Karl Fischer reagent. In all cases mechanical shaking and a fine state of division were beneficial. Further improvement was observed with the first two hydrates on suspending the sample in ethylene glycol instead of methanol. Both dissolve appreciably in this solvent.⁹

(7) Item No. 8927, Arthur H. Thomas Co., Philadelphia, Pa.

(8) Friend, "A Text-Book of Inorganic Chemistry," Volume III, Part I, Charles Griffin & Co., Ltd., London, 1925, pp. 91-95.

(9) Shreve and Prichard, *Ind. Eng. Chem.*, **27**, 1488 (1935), discuss solubility of barium chloride.

TABLE I
 ANALYTICAL DATA FOR HYDRATES

Hydrate	Moles of water in hydrate		Thermal stability, literature ^a
	Fischer titration	Wt. loss 110°	
NaOCOCH ₃ ·3H ₂ O	2.99	3.00	
NaH ₂ PO ₄ ·H ₂ O	1.01		anh. 100°
Na ₂ HPO ₄ ·12H ₂ O	11.04	11.07	anh. 99.5°
NaHSO ₄ ·H ₂ O	1.08		anh. 50°
Na ₂ S ₂ O ₄ ·2H ₂ O	1.69	1.69	
(NH ₄) ₂ C ₂ O ₄ ·H ₂ O	1.01		anh. 100° ^b
KF·2H ₂ O ^c	1.98		
K ₄ Fe(CN) ₆ ·3H ₂ O	3.11		anh. 110°
MgSO ₄ ·7H ₂ O	6.98	5.00	anh. 280°
CaH ₄ (PO ₄) ₂ ·H ₂ O ^c	0.98		decomp. 152°
CaSO ₄ ·2H ₂ O	1.47	1.06	
SrCl ₂ ·6H ₂ O	5.86	5.87 (132°)	anh. above 130°
BaCl ₂ ·2H ₂ O	1.98	1.96	anh. 100°
Ba(OCOCH ₃) ₂ ·H ₂ O	0.27	0.24	anh. 41° ^b
ZnSO ₄ ·7H ₂ O	6.94	5.70	anh. 280-300°
CdCl ₂ ·2.5H ₂ O	2.55	2.50 (132°)	anh. 120-130°
SnCl ₄ ·5H ₂ O	4.97		decomp.
Pb(OCOCH ₃) ₂ ·3H ₂ O	3.02		anh. 100° ^b
MnSO ₄ ·4H ₂ O	4.03		anh. 280°
FeSO ₄ ·7H ₂ O	7.00		monohyd. 140° <i>vacuo</i>
FeSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	6.01		
Co(NO ₃) ₂ ·6H ₂ O	6.06		decomp.
CoSO ₄ ·7H ₂ O	6.99		monohyd. 100°
NiSO ₄ ·6H ₂ O	6.11		anh. 280°
UO ₂ (OCOCH ₃) ₂ ·2H ₂ O	2.00		

^a Data from J. Newton Friend, "A Text-Book of Inorganic Chemistry," Charles Griffin and Co., Ltd., London, except where noted. ^b Data from Meyer and Jacobson, "Lehrbuch der organischen Chemie," 2d ed., Veit & Co., Leipzig.

^c Slow reaction, probably due to insolubility in methanol.

Caspari¹⁰ has effectively demonstrated that the supposed lower hydrates of calcium sulfate (*e. g.*, 2CaSO₄·H₂O) are merely zeolitic adsorption complexes involving water and a trigonal modification of anhydrous calcium sulfate more reactive than the better known orthorhombic mineral, anhydrite. Although in the present research treatment of the dihydrate for one hour with excess reagent left a balance of 0.53 mole of water per mole of salt, prolongation of the treatment for four hours reduced the water content of the salt to 0.36 mole, hence there was no real evidence of hemihydrate formation. Caspari's calculations suggest that the entry or departure of zeolitic water from the trigonal calcium sulfate lattice would be slow because of the small interatomic clearance. The sluggish action of Karl Fischer reagent may be due to the much greater difficulty of replacing water by the more bulky methanol molecule.

Although Fischer had already shown that adsorbed moisture in fuller's earth could be titrated,² it appeared desirable to test the efficacy of the method as applied to other desiccants. The results are given in Table II.

(10) Caspari, *Proc. Roy. Soc. (London)*, **A155**, 41 (1936).

 TABLE II
 ANALYTICAL DATA FOR DESICCANTS

Material	Weight per cent. water found		
	This procedure	Thermal drying 104° (4 hr.)	Thermal drying 150° (4 hr.)
Activated alumina ^a	7.02±0.00 ^b	5.37±0.06	6.12±0.01
Silica gel	5.48±0.01	4.32±0.08	4.71±0.19
Calcium chloride	11.28±0.08	2.08±0.06	10.75±0.09
"Drierite"	5.31±0.05 ^c	5.50±0.10	6.42±0.12

^a Grade D supplied by Aluminum Ore Co., East St. Louis, Ill. Reaction complete in half hour. ^b Average deviation for duplicate analyses. ^c Slow reaction characteristic of calcium sulfate; four hours.

The above materials were powdered, exposed to moist air, then analyzed in the usual manner, but without mechanical shaking. The success of the titration method in the first three cases is outstanding, while the less satisfactory behavior of "Drierite" is consistent with the data for pure calcium sulfate in Table I.

Summary

1. The successful use of Karl Fischer reagent for the titrimetric determination of water in hy-

drated salts has been demonstrated by analyses of twenty-five typical hydrates.

2. The value of the reagent in determining the

water content of inorganic desiccants has been verified.

WILMINGTON, DELAWARE

RECEIVED JULY 24, 1941

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

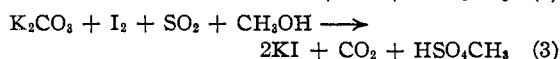
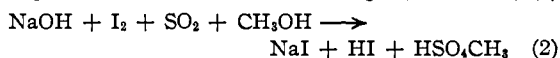
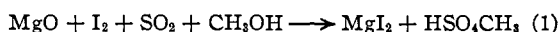
Analytical Procedures Employing Karl Fischer Reagent. IX. Reactions with Inorganic Oxides and Related Compounds. Oxidation and Reduction Reactions

BY J. MITCHELL, JR., DONALD MILTON SMITH, E. C. ASHBY AND W. M. D. BRYANT

Karl Fischer reagent is known to provide a rapid and highly specific quantitative means of determining water in organic materials and is useful in determining the water content of many hydrated inorganic salts.¹ Its value in inorganic analytical work is potentially great although interference from side reactions is more frequent, and consequently a well-defined knowledge of the nature and stoichiometry of these reactions is essential for its successful use.

In addition to iodine, sulfur dioxide and pyridine the methanol solution of the reagent contains considerable amounts of the pyridine salts of hydroiodic and methylsulfuric acids arising from preparative side reactions.² These latter constituents ordinarily have no effect on the titration of water. However, hydroiodic acid, even when buffered by pyridine, has a marked solvent action upon metal oxides and in attacking these compounds normally liberates one mole of water for each oxygen atom removed. (This reaction was verified stepwise in the case of zinc oxide.) This action involves simple neutralization either with or without complex ion formation. If the metal is capable of existence in other valence states then hydrogen iodide may reduce or iodine may oxidize the ion as soon as it is formed with additional effect upon the apparent water titer. Although Karl Fischer reagent is always standardized by titration of solutions of known moisture content, this really means that the iodine content of the solution has been established. Hence it is apparent that disappearance of iodine may measure either water content or reducing ability, while the oxidizing capacity of the material is measured by an increase in iodine content of the solution.³

The reaction producing water by the action of hydroiodic acid upon oxygen-containing inorganic compounds is fairly general. The oxides and hydroxides of the alkali and alkaline earth metals react without difficulty. In fact, the alkali salts of weak oxygen acids behave like a mixture of the respective oxides. It is convenient to consider the over-all reaction of Karl Fischer reagent with the oxides and their derivatives rather than the preliminary step involving only hydrogen iodide. For example

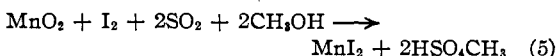


The salt-forming function of pyridine has been ignored in order to simplify formulation. On this basis the regular reaction with water is as follows

$$\text{H}_2\text{O} + \text{I}_2 + \text{SO}_2 + \text{CH}_3\text{OH} \longrightarrow 2\text{HI} + \text{HSO}_4\text{CH}_3 \quad (4)$$

Oxides of less electropositive metals are less reactive although cuprous, zinc, silver and mercuric oxides are readily converted. Aluminum, nickel, cupric and plumbous oxides on the other hand are unreactive. Some weakly acidic oxides of nonmetals (*e. g.*, As_2O_3 and B_2O_3) are reactive but the more strongly acidic oxides do not in general interfere.

The oxidizing-reducing properties of an iodine-iodide couple are well known and it is not surprising to find this action present in Karl Fischer reagent. Reactions of this character are conditioned by the properties of the metal ion present and hence differ from the oxide reactions described above, although the gross reaction may involve both effects



If the metal ion is associated with an anion not affected by hydroiodic acid, the reaction is

(1) Bryant, Mitchell, Smith and Ashby, *THIS JOURNAL*, **63**, 2924 (1941).

(2) Smith, Bryant and Mitchell, *ibid.*, **61**, 2408 (1939).

(3) The iodine of the reagent is relatively inactive toward organic compounds; see reference 2.