Knowing the total quantity of periodate, the volume of solution, how the assumed values for γ_1 and γ_2 vary with ionic strength, and how the ratio of M_2:M_1 varies with ml. of base added, the condition where Eq. 7 is satisfied was evaluated by a series of successive approximations. This condition was found to occur where $\sqrt{\mu}$ was *ca.* 0.25 and

$$\frac{M_2}{M_1} = \frac{\gamma_1}{\gamma_2} = \frac{0.805}{0.428} = 1.88$$

This molar ratio corresponds to *p*H values of 8.24 and 8.26 on curves 1 and 2, respectively, in Fig. 4. This gives a value of $K_2 = 5.6 \times 10^{-9}$ which, in view of the uncertainties involved in γ_1 and γ_2, is in good agreement with the value of $K_2 = 4.35 \times 10^{-9}$ obtained from the spectrophotometric studies.

The value of K_3, also a new constant, agrees, within experimental error, with the value of K_3 obtained from K_1 and K_2 using the method of Hill.[6]

Activity Coefficients.—The magnitudes of the differences between Curves 1 and 2 in Fig. 3 are much greater than predicted differences due to such changes in ionic strength, using normal γ_1 and γ_2 values. This suggests an abnormal decrease of the actual activity coefficients of the $H_4IO_6^-$ and $H_3IO_6^=$ ions, particularly the latter, with increasing ionic strength. For this reason values of K_1 and K_2 were calculated from the data for low ionic strength where errors due to such abnormalities would be very small. Estimates of the actual γ_1 and γ_2 values at the ionic strengths indicated may be made from the magnitudes of the differences between the two curves.

Analytical Significance.—From these studies it is quite obvious that for the analytical determination of periodate (in the absence of interfering substances) spectrophotometrically, *p*H is a very important factor. Inspection of the plot of optical density at 222.5 mμ *versus* *p*H shows clearly that a *p*H of *ca.* 5.0 is the optimum *p*H to use in acid solutions for this determination. For solutions of low ionic strength *p*H values of 5.0 ± 1.5 are quite satisfactory, the optical density not varying appreciably in this region. Concentrations as low as 10^{-7} molar in periodate should be detectable using 5.00-cm. silica cells. In the event that it is desirable to determine periodate spectrophotometrically in alkaline solutions, *p*H values between *ca.* 10.5 and 12.5 are desirable. Such analysis leads to a sacrifice in sensitivity of the method at 222.5 mμ because of the lower molecular extinction coefficient of the $H_3IO_6^=$ ion as compared to that of the $H_4IO_6^-$ ion used in the lower *p*H range. This disadvantage may be eliminated by simply carrying out the analysis at a somewhat lower wave length, *i. e.*, at a wave length nearer to or at which the $H_3IO_6^=$ ion shows an absorption maximum.

Summary

It was shown that most probably any equilibria involving the formation of the dimesoperiodate ion, $I_2O_9^{4-}$, is of no importance in dilute aqueous solutions. Three simple equilibria involving stepwise dissociation of paraperiodic acid, H_5IO_6, account completely for the variation of the ultraviolet absorption spectra of dilute aqueous solutions of periodate with *p*H. K_1[4,5] was substantiated and new estimates of K_2 and K_3 were made from spectrophotometric studies. K_2 was substantially confirmed by potentiometric studies and K_3 was confirmed by the method of Hill.[6] Evidence was shown for abnormal activity coefficients of $H_4IO_6^-$ and $H_3IO_6^=$ ions with increasing ionic strength. Recommendations were made for the spectrophotometric determination of periodate in slightly acid and alkaline solutions.

AMES, IOWA RECEIVED APRIL 4, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORQUIMA S. A., SÃO PAULO, BRAZIL]

The Acid Properties of Iron Tetracarbonyl Hydride

BY P. KRUMHOLZ AND H. M. A. STETTINER

It has been shown previously[1] that the reaction between iron pentacarbonyl and alkalies does not produce, as assumed by Hieber,[2] the free iron tetracarbonyl hydride but its monobasic salts. The acid behavior of iron carbonyl hydride could be confirmed later by preparing salts with complex amine cations.[3] Some of them, as shown by Hieber,[4] behave in solution as strong electrolytes. Meanwhile Hieber[4] stated that structures as $[Fe(CO)_4H]^-$ are not stable and only can be stabilized by the formation of salts with complex cations, that the alkaline solutions of the hydride contain aquo salts rather than normal salts not yet prepared,[5] and that the formation of metal derivatives of $Fe(CO)_4H_2$ is by far not as general as it is supposed to be in an ordinary formation of salts.

In order to destroy any doubts regarding the behavior of iron carbonyl hydride as an ordinary acid we tried to determine its dissociation constant[6] by potentiometric titration of its salts with

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[1] F. Feigl and P. Krumholz, *Monatsh.*, **59**, 314 (1932).

[2] W. Hieber and F. Leutert, *Z. anorg. Chem.*, **204**, 145 (1932).

[3] F. Feigl and P. Krumholz, *ibid.*, **215**, 242 (1933).

[4] W. Hieber and E. Fack, *ibid.*, **236**, 83 (1938).

[5] The monosodium salts prepared by F. Feigl and P. Krumholz, ref. 1, as alcoholates could not be freed completely from alcohol.

[6] A. A. Blanchard, *Chem. Rev.*, **21**, 3 (1937), assumed that the dissociation constant of cobalt tetracarbonyl hydride should be about 10^{-5}.

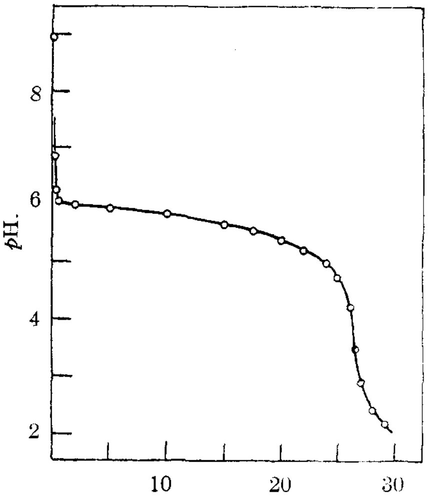

Fig. 1.—Titration of 0.055 m. $[Fe(CO)_4H]_2Ba$ with 0.57 *N* HCl; initial volume 135 cc., $T = 17.5°$.

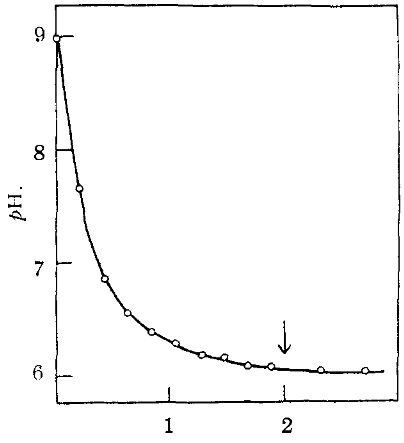

Fig. 2.—Titration of 0.055 m. $[Fe(CO)_4H]_2Ba$ with 0.57 *N* HCl.

HCl. Figs. 1 and 2 show the change of *p*H during the titration of a solution of the barium salt $[Fe(CO)_4H]_2Ba$ obtained by allowing barium hydroxide to react upon an excess of iron pentacarbonyl[1] according to

$$2Fe(CO)_5 + 3Ba(OH)_2 = [Fe(CO)_4H]_2Ba + 2BaCO_3 + 2H_2O \quad (1)$$

Those diagrams represent typical titration curves of salts of a weak acid of low solubility, since, immediately after starting the titration, the initially steep slope of the titration curve turns suddenly flat. At this point the initially clear solution becomes turbid due to the separation of free iron carbonyl hydride (the point where the first visible turbidity appears is indicated by an arrow in Fig. 2). From this part of the titration curve the molar solubility of $Fe(CO)_4H_2$ (at 17.5°) may be calculated as about *1.8* × *10*$^{-3}$. The *p*H at the endpoint of the titration is 3.60; it corresponds to a thermodynamic dissociation constant[7] of ≈*3.4* × *10*$^{-5}$ (at 17.5°). Computing the dissociation constant from *p*H values at different concentrations of $[Fe(CO)_4H]^-$, and assuming that the concentration of undissociated $Fe(CO)_4H_2$ remains constant, we obtained as mean value $K_1 = 4.15 \times 10^{-5}$ (Table I).

Table I

$C_{Fe(CO)_4KH}$	*p*H	$K_1 \times 10^5$
1×10^{-1}	6.00	4.17
7.5×10^{-2}	5.88	4.13
5.3×10^{-2}	5.71	4.31
4.3×10^{-2}	5.63	4.20
2.3×10^{-2}	5.36	4.14
8.4×10^{-3}	4.95	3.92

The titration curve shows furthermore that the reaction between barium hydroxide and excess $Fe(CO)_5$ proceeds to an extent of at least 99.8% according to (1).

Solutions of the mono potassium salt of iron carbonyl hydride prepared by allowing $Fe(CO)_5$ to react with potassium and barium hydroxide in quantities corresponding to the equation

$$Fe(CO)_5 + KOH + Ba(OH)_2 = Fe(CO)_4KH + BaCO_3 + H_2O \quad (2)$$

behave in a similar way.

As iron carbonyl hydride also forms bibasic salts with some heavy metals,[3,8] and as Blanchard[9] recently assumed the formation of a bibasic potassium salt $Fe(CO)_4K_2$, we submitted solutions prepared according to

$$Fe(CO)_5 + 2KOH + Ba(OH)_2 = Fe(CO)_4K_2 + BaCO_3 + 2H_2O \quad (3)$$

to potentiometric titrations. As shown in Fig. 3 the *p*H values in the first moiety of the diagram are lower than the corresponding values of potassium hydroxide of equal concentration (represented by the dotted line in Fig. 3). This proves the formation of the dibasic salt, hydrolyzed to an extent of about 45% in 0.18 molar solution. We computed the second dissociation constant of iron carbonyl hydride from the hydrolytic equilibrium of the bibasic salt according to[10]

$$K_2 = K_{H_2O} \times \frac{C_{K_2X} - (OH^-)}{[C_{KHX} + (OH^-)](OH^-)} \times \frac{\gamma_{bi}}{(\gamma_{mono}^2)}$$

where C_{K_2X} and C_{KHX} represent the analytical concentrations of the bibasic and monobasic salt, $K_{H_2O} \approx 5.6 \times 10^{-15}$ (at 17.5°) and γ the activity coefficients of the ions.[11] We obtained

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[7] Assuming the activity coefficient of $[Fe(CO)_4H]^-$ to 0.75 and γ_H to 0.80 at the ionic strength of 0.15.

[8] H. Hock and H. Stuhlmann, *Ber.*, **61**, 2097 (1928).

[9] A. A. Blanchard and G. W. Coleman, "Inorganic Syntheses," vol. 2, p. 243 (1946).

[10] *Cf.* I. M. Kolthoff and H. A. Laitinen, "*p*H and Electro Titrations," John Wiley and Sons, New York, N. Y., 1941.

[11] The initial ionic strength of the solution is 0.46, diminishing during the titration, mainly due to the disappearance of the bivalent ion $[Fe(CO)_4]^=$, reaching the value of 0.33 at the first equivalence point. We assumed (from known activities of salts of bibasic acids) at the beginning of the titration $\gamma_{mono} = 0.66$ and $\gamma_{bi} = 0.20$ and at the equivalence point $\gamma_{mono} = 0.70$ and $\gamma_{bi} = 0.24$.

the OH⁻ concentrations by comparing the measured potentials with those of potassium hydroxide solutions containing the same amount of K^+ (as KCl) as the solution of the iron carbonyl salt.[12]

The mean value (Table II) of the second dissociation constant of iron tetracarbonyl hydride at 17.5° thus obtained is $K_2 = 3.7 \times 10^{-14}$.

TABLE II

$c_{Fe(CO)_4K_2}$	$c_{Fe(CO)_4KH}$	(OH^-)	$K_2 \times 10^{14}$
1.8×10^{-1}	0	7.8×10^{-2}	4.25
1.13×10^{-1}	6.15×10^{-2}	4.5×10^{-2}	3.7
8.2×10^{-2}	9.05×10^{-2}	3.0×10^{-2}	3.8
4.1×10^{-2}	1.27×10^{-1}	1.45×10^{-2}	3.45
1.6×10^{-2}	1.50×10^{-1}	5.5×10^{-3}	3.40

The *p*H of the second equivalence point is 3.56 corresponding to a value of $K_1 = 3.7 \times 10^{-5}$. The mean value of this constant computed from *p*H values between the first and the second equivalence point[13] (Table III) is $K_1 = 4.3 \times 10^{-5}$.

TABLE III

$c_{Fe(CO)_4KH}$	*p*H	$K_1 \times 10^{-5}$
1.47×10^{-1}	6.11	4.45
1.25×10^{-1}	6.04	4.42
9.8×10^{-2}	5.94	4.37
6.3×10^{-2}	5.78	4.06
1.7×10^{-2}	5.20	4.16

The experimental error of the indicated values amounts to ±10%. The assumed values of the activity coefficients, specially of the bivalent ion, may be wrong to an extent of about 10–20%. A further error may be due to differences in the liquid junction potentials, so that the obtained values of the dissociation constants may be uncertain within ± one unit.

For the dissociation constants of iron tetracarbonyl hydride at 17.5° we can assume the approximate values

$$K_1 = 4 \times 10^{-5} \text{ and } K_2 = 4 \times 10^{-14}$$

exact within about ± one unit.

Thus, iron carbonyl hydride as monobasic acid is stronger than acetic acid, while the relation between the two dissociation constants reaches the extremely high value of $1:10^9$.

Furthermore, we tried to prepare the solid alkali salts from solutions obtained according to equations (2) and (3). These solutions, if prepared and kept under complete exclusion of oxygen, are only slightly brownish or pink and perfectly stable.

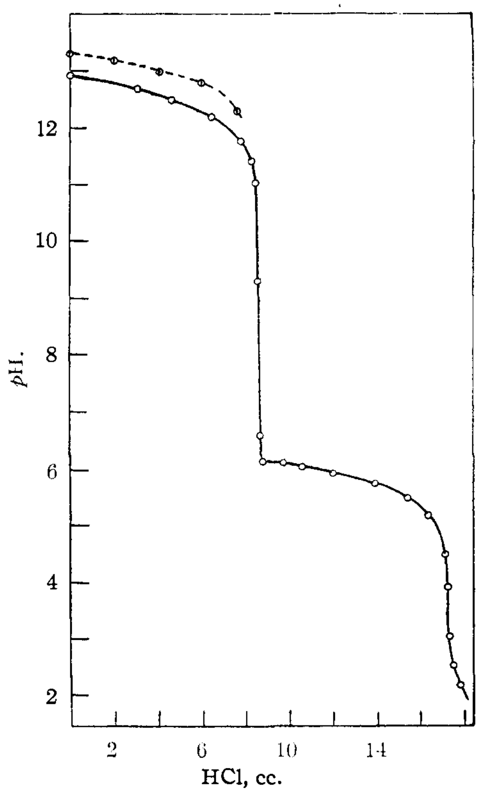

Fig. 3.—Titration of 0.18 m. $Fe(CO)_4K_2$ with 2 *N* HCl; initial volume 96 cc., $T = 17.5°$. Dotted line: titration of 0.18 *N* KOH + 0.18 *N* KCl with 2 *N* HCl.

On concentrating the solution of the bibasic salt at a low temperature, colorless crystals appear when the volume is reduced to a few cc. A slightly brownish mass remains when dried over phosphorus pentoxide at 0.5 mm; its analysis corresponds closely to the bibasic anhydrous salt $Fe(CO)_4K_2$. The salt is very soluble in water, producing a brownish solution due to an unavoidable small decomposition. Such a solution reacts with mercuric chloride according to

$$Fe(CO)_4K_2 + 2HgCl_2 = Fe(CO)_4Hg_2Cl_2 + 2KCl \quad (4)$$

yielding 98% of the theoretical amount of the mercuric salt.

These results allow no further doubts as to the existence of the anhydrous salt $Fe(CO)_4K_2$. They also exclude the possibility that the product obtained represents a mixture of $Fe(CO)_4KH$ and potassium hydroxide, specially as a potassium hydroxide solution retains about 2 molecules of water when dried under similar conditions over phosphorus pentoxide.

Treating solutions of the monobasic salt in an analogous way one obtains no separation of crystals, but the residue of the evaporation solidifies over phosphorus pentoxide to a brownish amorphous substance, with analytical data corresponding to the anhydrous salt $Fe(CO)_4KH$. This salt is extremely hygroscopic and, like the

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(12) The ionic strength of the potassium hydroxide solution is smaller (initially 0.36) than the ionic strength of the carbonyl solution. As the activity coefficients of OH⁻ vary less within those limits than the experimental error of the *p*H measurements, we assumed that equal potentials do not only correspond to equal values of the activities, but also to equal values of the concentrations of OH⁻.

(13) Assuming $\gamma[Fe(CO)_4H]^- = 0.70$ at the ionic strength of about 0.30.

bibasic salt, very sensitive to oxygen. Its brownish solution reacts with mercuric chloride according to

$$Fe(CO)_4KH + 2HgCl_2 = Fe(CO)_4Hg_2Cl_2 + HCl + KCl \quad (5)$$

yielding 97% of the theoretical amount of the mercuric salt, but only 92% of the theoretical amount of hydrogen chloride due to a loss of the very volatile $Fe(CO)_4H_2$ through hydrolysis of the monobasic salt and to a simultaneous formation of $Fe(CO)_4K_2$.

Since at least 97% of the substance consists of $Fe(CO)_4KH$ and $Fe(CO)_4K_2$, as shown by the reaction with mercuric chloride, it seems certain that $Fe(CO)_4KH$, too, exists as an anhydrous salt. It is possible, of course, that the ions $[Fe(CO)_4]^{=}$ and $[Fe(CO)_4H]^-$ are hydrated in aqueous solution. No further doubt may exist as to the rather peculiar fact that iron tetracarbonyl hydride behaves as an acid forming "normal" salts not only with amine cations but also with alkali metals.

The acidic behavior of iron carbonyl hydride—formation of hydrogen ions (or hydroxonium ions) in aqueous solution—is in contradiction to the easy decomposition of the hydride to molecular hydrogen explained by Hieber[2] with the formulation of $Fe(CO)_4H_2$ as a true hydride with direct iron-hydrogen bond. But this formulation explains hardly the acidic functions of $Fe(CO)_4H_2$. Furthermore, electron diffraction studies by Evans and Lister[14] seems to indicate that the hydrogen atoms are fixed on the oxygen atoms according to the formula $Fe(CO)_2(COH)_2$.

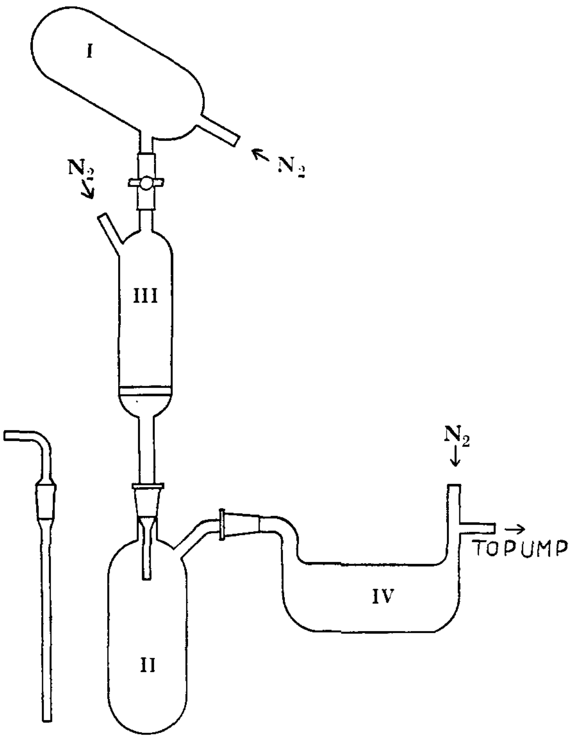

Fig. 4.—I, Reaction vessel; II, filter vessel; III, filter tube; IV, trap.

This formulation, especially in the electronic expression like $Fe^{=}:C:::{}^{++}O:H$ or $Fe^{-}::C::{}^{+}\underset{..}{O}:H$, might explain the acid behavior of the hydride as the positively charged oxygen atoms must repel protons.[15]

But neither of both formulations is able to explain by itself the experimental facts, that iron carbonyl hydride may lose neutral hydrogen atoms as well as protons.

The structural problems in question will be discussed further in a later paper.

Experimental Part

Due to the enormous sensitivity of iron carbonylhydride and its salts to oxygen, all operations have to be performed under nitrogen absolutely free from oxygen, taking extreme care to exclude air during the manipulations.

We prepared the solutions for the potentiometric titrations in a modified Schlenck apparatus,[1] by shaking for three hours excess $Fe(CO)_5$ with a 0.33 *N* solution of barium hydroxide, or, according to equations (2) and (3) exact quantities of $Fe(CO)_5$ with solutions containing 0.18 mole of barium hydroxide and 0.18 or 0.36 mole of potassium hydroxide, respectively, in 1000 ml. and filtering the solution from the precipitated barium carbonate. The filtered solution was transferred to a titration vessel consisting of a 500-cc. erlenmeyer flask containing the glass and reference electrodes, buret, thermometer and inlet and outlet tubes for nitrogen. The titrations were performed with hydrochloric acid to 17.5 ± 0.2° after calibrating the glass electrodes with buffer solutions. It is known that glass electrodes show large alkali errors at *p*H above 10, even in potassium salt solutions. To eliminate these errors we calibrated the electrode in the strongly alkaline range with potassium hydroxide solutions containing the same amount of K^+ (as KCl) as the titrated solution. The reproducibility of the potentials during calibration and over the whole range of the titration —excepting perhaps the immediate proximity of the first equivalence point—was better than 1 mv. In order to obtain this accuracy in the strong alkaline range one has to wash the electrodes before every use for at least six hours in pure water, particularly after being used in acid solutions, and to wait about five minutes before taking the first reading. If oxygen is not entirely excluded, it is impossible to obtain constant readings near the first equivalent point, the liberated $Fe(CO)_4H_2$ being immediately destroyed by oxidation.

As already stated, soon after the first equivalence point, there appears free $Fe(CO)_4H_2$ at first in the form of a milky turbidity, separating later as a yellow oily layer that soon turns deeply red by decomposition. This decomposition however does not influence the titration. Apparently enough hydride always remains to give a saturated solution as shown by the constancy of the potentials, and the fact that calculated values of K_1 are constant within the limits of accuracy over the whole range of titration. Only at a temperature of over 25° does the decomposition become great enough in more acid solutions so that one is no longer able to determine the second equivalence point exactly.

Preparation of the Potassium Salts.—We prepared the solutions of the potassium salts by a procedure similar to that used for the potentiometric titration, using the apparatus shown in Fig. 4. The solution prepared in the

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[14] R. V. G. Evans and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

[15] See the similar formulation of carboxyl groups by L. Pauling, "The Nature of the Chemical Bond," 2nd ed., p. 202.

reaction vessel I was filtered through the filter tube into the previously weighed vessel 2 connected with an ice cooled trap. After having exchanged the filter tube for a gas inlet tube, the vessel was immersed in a water-bath at 20° and evaporated at about 5 mm. in a slow stream of nitrogen. After the evaporation the trap was exchanged for one filled with phosphorus pentoxide, and evacuated at less than 0.5 mm. to constant weight.

For analysis the content of the weighed vessel was dissolved in water and decomposed by slow addition of neutral 10% hydrogen peroxide, boiling finally until the iron tetracarbonyl formed had disappeared completely. To prevent loss by volatilization of iron carbonyl the vessel was connected with a wash bottle containing 0.2 *N* alcoholic potassium hydroxide and a small quantity of hydrogen peroxide. The solution filtered from the iron oxide contains the potassium as carbonate. The carbonate was determined by acidimetric titration. The iron was determined in the residue on the filter and in the contents of the washing bottle.

$Fe(CO)_4K_2$.—The solution was prepared from 1 ml. = 0.0074 mole $Fe(CO)_5$ and 40 ml. of a solution containing exactly 0.0074 mole of $Ba(OH)_2$ and 0.0148 mole of KOH. *Anal.* Calcd. for $Fe(CO)_4K_2$: Fe, 22.70; K, 31.78. Found: Fe, 22.89, 23.30, 22.73; K, 31.3, 31.45. 1.316 g. of the dry salt was dissolved in 50 ml. of water freed from air and poured under nitrogen into a saturated solution containing 5 g. of mercuric chloride. The mixture was shaken for thirty minutes to complete the reaction, then filtered, washed with water, dilute hydrochloric acid, alcohol and ether (to remove small quantities of iron tetracarbonyl) and dried *in vacuo*, giving 3.4484 g. of the yellow $Fe(CO)_4Hg_2Cl_2$. *Anal.* Calcd.: Fe, 8.72; CO, 17.51. Found: Fe, 8.65, 8.63; CO, 17.08, 16.98. Calculating the amount of pure mercuric salt from the found CO value the relation $Fe(CO)_4K_2:Fe(CO)_4Hg_2Cl_2$ is 1:0.98.

$Fe(CO)_4KH$.—Prepared from 1.5 cc. of $Fe(CO)_5$ (excess) and 40 cc. of a solution containing exactly 0.0074 mole of $Ba(OH)_2$ and 0.0074 mole of KOH. *Anal.* Calcd. for $Fe(CO)_4KH$: Fe, 26.85; K, 18.80. Found: Fe, 27.35, 26.87; K, 18.89.

The reaction of 0.845 g. of this salt with $HgCl_2$ yields 2.5716 g. of the mercuric salt. *Anal.* Found: Fe, 8.54; CO, 17.05. In the filtrate from the mercuric salt we determined the HCl by acidimetric titration. The relation $Fe(CO)_4KH:Fe(CO)_4Hg_2Cl_2:HCl$ is 1:0.97:0.92 if the salt is calculated as pure $Fe(CO)_4KH$. As the salt contains about 5% $Fe(CO)_4K_2$ this relation is still about 1% nearer to the theoretical amount.

Summary

The dissociation constants of iron tetracarbonyl hydride at 17.5° have been determined to $K_1 = 4 \times 10^{-5}$ and $K_2 = 4 \times 10^{-14}$.

The molar solubility of iron carbonyl hydride at 17.5° is about 1.8×10^{-3}.

The anhydrous salts $Fe(CO)_4K_2$ and $Fe(CO)_4KH$ (the latter containing about 5% of $Fe(CO)_4K_2$) have been prepared.

RECEIVED OCTOBER 21, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Disperse Structure of Manganese Oxides and a Magnetic Method for Studying Depolarizer Action in the Leclanché Cell[1]

BY P. W. SELWOOD, R. P. EISCHENS,[2] MARYLINN ELLIS AND KATHRYN WETHINGTON

The object of this work was to explore the possibility of using magnetic methods for the study of chemical changes occurring *in situ* in the dry cell. Manganese is the only paramagnetic constituent in the cell, and the number of unpaired electrons increases as tetravalent manganese is reduced. Consequently it was considered possible to follow the valence changes of the manganese during cell discharge and recovery by observing changes of magnetic susceptibility.

Magnetically dilute tetravalent manganese has three unpaired electrons and a well established, spin-only, magnetic moment of about 3.9 Bohr magnetons. Similarly, manganese in the oxidation states of three and two has magnetic moments of 4.9 and 5.9, respectively. With adequate magnetic dilution the susceptibility at any one temperature is virtually linear with oxidation state.

Unfortunately, the crystalline transition group oxides are so magnetically concentrated that large interactions occur between adjacent paramagnetic ions. Thus, the susceptibility at 25° for crystalline *pyrolusite* is 27×10^{-6}, that for the crystalline sesquioxide (*bixbyite*) is 89×10^{-6}, but for the monoxide (*manganosite*) it is only 67×10^{-6}. Furthermore, all these substances show large and uncertain values for the Weiss constant, and, at lower temperatures, wide deviations from the Curie–Weiss law.

These effects eliminate the possibility of using crystalline *pyrolusite* as depolarizer in quantitative magnetic studies. Attention was, therefore, turned to supported oxides, which have been shown to approach high magnetic dilution at moderately low concentration.[3]

A series of studies on manganese oxides on various supports showed that the oxidation state of supported manganese was determined in part by the crystal structure of the support, and this observation led to the general principle of valence inductivity, as previously described.[4] It was established that the experiment on the dry cell could be carried out if the manganese depolarizer were supported on high-area titania, in the *rutile* modification.

At this point in the work it was discovered that many laboratory prepared samples of manganese

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(1) This paper describes, in part, work performed under contract with the Squier Signal Laboratory, Signal Corps Engineering Laboratories, as part of their program for the improvement of dry cells.

(2) Present address: The Texas Company, Beacon Laboratories, Beacon, N. Y.

(3) Selwood, Hill and Boardman, THIS JOURNAL, **68**, 2055 (1946).

(4) Selwood, *ibid.*, **70**, 883 (1948).