tirely to the sodium form with it, and then precipitated from solution with methanol. The resulting product was sodium trimetaphosphate. This means that the original salt is a trimetaphosphate.

Since the original salt is not destroyed by dissolution and may be precipitated from solution with methanol, it is possible to prepare the original salt in aqueous solution as well as from a melt. A solution of sodium trimetaphosphate was prepared by dissolving 51.0 g. of sodium trimetaphosphate in 300 ml. of water to which 12.4 g. of potassium chloride and 2.0 g. of KOH were added. Methanol was added to the solution until precipitation ceased. The white precipitate was redissolved and reprecipitated. It was dried at 30° and X-rayed. The X-ray pattern was identical to the pattern obtained from the original $3NaPO_3 \cdot KPO_3$ which had been dissolved in water and precipitated from solution with methanol. This is proof that the salt prepared by Morey is a trimetaphosphate which may be prepared from a melt or from an aqueous solution.

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Activity of Hydrochloric Acid in Mixtures with Cobalt(II) and Nickel(II) Chlorides

BY FRANK DYER, E. H. GILMORE AND T. E. MOORE

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Of the various methods for the determination of the activity of hydrochloric acid, measurement of the electromotive force of cells employing hydrogen and silver–silver chloride electrodes has proved to be the most satisfactory up to comparatively high acid concentrations. The cell $H_2/HCl\ (m_1),\ MCl_x\ (m_2)/AgCl-Ag$ has also been used extensively to determine the activity of hydrochloric acid in hydrochloric acid–salt mixtures.[1] However, in general there has been no independent confirmation of the activity values in such acid–salt systems by another method.

Recently the activity of hydrochloric acid in mixtures with cobalt and nickel chlorides has been determined by vapor pressure measurements,[2] and since the results seriously disagreed with some activity values obtained by the electromotive force measurements of an earlier investigation, it seemed worthwhile in view of the importance of the above cell to reexamine its suitability for activity measurements in these transition metal halide solutions at high salt and acid activities. As an independent check on the results the hydrochloric acid activities were also determined from the distribution coefficients of HCl between benzene and the aqueous mixtures.[3]

Experimental

Solutions.—The salt–acid mixtures were prepared 7 molal in HCl and analyzed as described elsewhere.[2]

Electromotive Force Measurements.—All experiments were made at 30°. The hydrogen electrodes were of the usual platinized platinum type. Silver–silver chloride electrodes were constructed by electrolytically depositing silver on platinum spirals and chloridizing according to the recommendations of Janz and Taniguchi.[4] In order to prevent diffusion of silver ions to the hydrogen electrode, the silver–silver chloride electrode was enclosed in a tube fitted with a fine-porosity fritted-glass disc at one end. Silver chloride-saturated solution was aspirated up until the level inside the tube was slightly below that outside.

The partial pressure of the presaturated hydrogen gas was calculated from the barometric pressure and the data of Moore, *et al.*,[2] for the water and HCl vapor pressures. Approximately two hours were required to saturate the solutions with hydrogen.

Potential comparisons were made using a Rubicon Type B potentiometer. A value of 0.21912 volt was taken as the standard potential of the cell.[5] The value of the neglected liquid junction potential was probably small in all cases.[6]

Distribution Experiments.—Equal volume (50 ml.) amounts of benzene and the acid–salt mixtures were sealed in glass tubes and agitated mechanically for 24 hours at 30°. The shaking was stopped and the solutions allowed to stand for an additional 12 hours before sampling for analysis.

Weighed samples of the benzene phase were re-extracted with known amounts of aqueous potassium nitrate solution, and samples of the resulting aqueous phase were then titrated potentiometrically with silver nitrate to a null endpoint by the procedure of Kolthoff and Kuroda.[7] Since it has been shown that over the molality range of 7.2×10^{-6} to 2.73×10^{-1} in benzene the aqueous phase activity of HCl is proportional to its concentration in benzene,[3] the HCl activities were calculated according to the equation

$$a(\mathrm{HCl}) = 2.96 \times 10^{6} m(\mathrm{HCl}) \qquad (1)$$

Discussion of Results

Reasonably good agreement was obtained among all three methods (Fig. 1). These results confirm the vapor pressure measurements previously reported[2] and independently demonstrate the suitability of the electromotive force method in determining hydrochloric acid activities in transition metal salt solutions of high acid and salt activity.

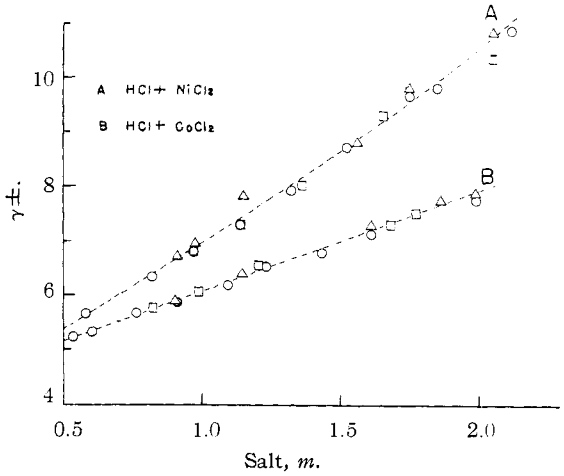

Fig. 1.—HCl activity coefficients of 7 molal HCl in presence of $CoCl_2$ and $NiCl_2$: ○, vapor pressure measurements; △, benzene extraction measurements; □, electromotive force measurements.

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The Preparation of Complex Compounds of Certain Organic Bases with Nickel(II) and Cobalt(II) Oxalate and Phthalate and the Determination of Their Heats of Formation[1]

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The effect of the negative ions in nickel(II) and cobalt(II) salts upon the heat of formation of pyridine complexes of these salts and the effect of the character of the complexing amine upon the heat of formation of complexes with nickel(II) thiocyanate have been reported.[3] A new series of nickel and cobalt compounds have been prepared to determine the effect of aromatic and aliphatic dibasic negative groups upon the heat of formation of the complexes. The heats of formation of the complexes were calculated according to the equation

$$\Delta H_f = L_S + L_A - L_C$$

from the observed values of the heats of reaction of the simple salt, the amine and the complex with 2 *N* HCl.

Preparation of the Compounds

Nickel(II) and Cobalt(II) Oxalates.—These salts were prepared by conventional methods and analyzed for metal content. *Anal.* Calcd. for NiC_2O_4: Ni, 40.04. Found: Ni, 39.85. Calcd. for CoC_2O_4: Co, 40.10. Found: Co, 40.32.

Nickel(II) and Cobalt(II) Phthalates.—The phthalates were prepared by refluxing for six hours a mixture of nickel or cobalt carbonate with an equivalent amount of phthalic acid solution. Any residue remaining after six hours was removed by filtration and the filtrate evaporated to dryness. Nickel phthalate formed as yellow green crystals; the cobalt phthalate as lavender crystals. *Anal.* Calcd. for $NiC_8H_4O_4$: Ni, 26.34. Found: Ni, 26.25. Calcd. for $CoC_8H_4O_4$: Co, 26.42. Found: Co, 26.68.

Oxalatodipyridinenickel(II) and Oxalatodipyridinecobalt(II); Oxalatobis(β- or γ-picoline)-nickel(II) and Oxalatobis(β- or γ-picoline)-cobalt(II).—The complex salts were formed by adding excess of each of the amines to the metal oxalates. The light blue crystals of nickel complexes and the rose-colored crystals of cobalt complexes formed by the evaporation of excess amine were stored in desiccators until equilibrium was reached. *Anal.* Calcd. for $NiC_2O_4 \cdot 2C_5H_5N$: Ni, 19.25. Found: Ni, 19.36. Calcd. for $NiC_2O_4 \cdot 2\beta C_6H_7N$: Ni, 17.63. Found: Ni, 17.70. Calcd. for $NiC_2O_4 \cdot 2\gamma C_6H_7N$: Ni, 17.63. Found: Ni, 17.50. Calcd. for $CoC_2O_4 \cdot 2C_5H_5N$: Co, 19.31. Found: Co, 19.22. Calcd. for $CoC_2O_4 \cdot 2\beta C_6H_7N$: Co, 17.69. Found: Co, 17.79. Calcd. for $CoC_2O_4 \cdot 2\gamma C_6H_7N$: Co, 17.69. Found: Co, 17.54.

Phthalatotetrapyridinenickel(II) and Phthalatotetrapyridinecobalt(II).—The phthalate pyridine–metal complexes were prepared in a manner identical to that described for the complex oxalates. These complexes were soluble in chloroform and could be recrystallized from that solvent with no change in composition. The complex containing nickel formed as bright blue crystals; the cobalt complex was rose-colored.

Phthalatotetrakis-(β- or γ-picoline)-nickel(II) and Phthalatotetrakis(β- or γ-picoline)-cobalt (II).—These were prepared by adding a slight excess of each of the amines to water solutions of the metal phthalates. The resulting complex compounds were extracted with chloroform. The crystals resulting from the evaporation of the solvent were freed from excess amines and stored in desiccators. The color of the phthalato-β-picolinenickel complex was light blue; the analogous compound containing γ-picoline formed blue-green crystals. The color of both of the cobalt complex compounds was deep red. *Anal.* Calcd. for $NiC_8H_4O_4 \cdot 4C_5H_5N$: Ni, 10.88. Found: Ni, 10.66. Calcd. for $NiC_8H_4O_4 \cdot 4\beta C_6H_7N$: Ni, 9.86. Found: Ni, 9.67. Calcd. for $NiC_8H_4O_4 \cdot 4\gamma C_6H_7N$: Ni, 9.86. Found: Ni, 9.80. Calcd. for $CoC_8H_4O_4 \cdot 4C_5H_5N$: Co, 10.92. Found: Co, 10.88. Calcd. for $CoC_8H_4O_4 \cdot 4\beta C_6H_7N$: Co, 9.90. Found: Co, 9.98. Calcd. for $CoC_8H_4O_4 \cdot 4\gamma C_6H_7N$: Co, 9.90. Found: Co, 10.07.

Determination of Heats of Reaction.—A method similar to that reported earlier[3] was used to determine the heats of reaction of the simple salts, the amines and the complexes with 2 *N* HCl. The values of the heats of reaction obtained and the calculated heats of formation are recorded in Table I.

TABLE I

Substance	Heat of soln., cal./mole at 25° [a]	Heat of formation, cal./mole at 25° [a]
Pyridine[b]	− 8,530 (± 10)	
β-Picoline	− 9,210 (± 30)	
γ-Picoline	− 9,400 (± 20)	
NiC_2O_4	− 3,460 (± 20)	
$NiC_3H_4O_4$	−10,940 (± 30)	
CoC_2O_4	− 5,070 (± 30)	
$CoC_8H_4O_4$	− 7,010 (± 20)	
$NiC_2O_4 \cdot 2Py$	− 1,340 (± 10)	19,200
$NiC_2O_4 \cdot 2\beta Pic$	− 2,020 (± 20)	19,900
$NiC_2O_4 \cdot 2\gamma Pic$	− 2,210 (± 20)	20,000
$NiC_8H_4O_4 \cdot 4Py$	−10,260 (± 40)	34,800
$NiC_8H_4O_4 \cdot 4\beta Pic$	−12,500 (±100)	35,300
$NiC_8H_4O_4 \cdot 4\gamma Pic$	−19,440 (± 20)	29,100
$CoC_2O_4 \cdot 2Py$	− 1,280 (± 40)	20,800
$CoC_2O_4 \cdot 2\beta Pic$	− 4,500 (± 90)	19,000
$CoC_2O_4 \cdot 2\gamma Pic$	− 5,080 (± 10)	18,800
$CoC_8H_4O_4 \cdot 4Py$	−12,340 (± 30)	28,800
$CoC_3H_4O_4 \cdot 4\beta Pic$	−12,710 (± 30)	31,100
$CoC_3H_4O_4 \cdot 4\gamma Pic$	−13,080 (±100)	31,500

[a] Averages obtained from 2 to 4 determinations on each compound. [b] Corrected value (ref. *3b*).

The heats of formation of the oxalate complexes formed with each of the three amines and nickel(II) or cobalt(II), Table I, show no great variance between the metals used nor with the amines added to form the complexes. These results are in agreement with the work previously reported.[3a,b]

The heats of formation of the phthalato complexes show less uniformity in the values observed. The heat of solution of phthalatotetrakis(γ-picoline)-nickel(II) appears to be anomalously high resulting in a low calculated heat of formation of the complex. Since the phthalato complex contained four molecules of the bases, a direct comparison with the oxalates cannot be made to determine the effect of the negative group. However, in comparing the heats of formation of the three phthalatotetraaminenickel(II) complexes with the corresponding thiocyanatotetraaminenickel(II) complexes reported earlier,[3b] it is observed that the heats of formation of the thiocyanato complexes are higher.

It has been noted[3b] that when attempts were made to crystallize the thiocyanate complexes of β- and γ-picolinenickel(II) from chloroform solution some entrapment of chloroform within the crystals was observed. In the preparation of the oxalate and phthalato complexes, it was thought that perhaps the dibasic organic negative groups might increase the entrapment of the solvent. No similar

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[2] This article is based on a thesis submitted by Albert B. Costa in partial fulfillment of the requirements for the degree of Master of Science, Oregon State College.

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