

The transition temperatures of sodium carbonate were then found as follows :

	$10\text{H}_2\text{O}-7\text{H}_2\text{O}$	$10\text{H}_2\text{O}-1\text{H}_2\text{O}$	$7\text{H}_2\text{O}-1\text{H}_2\text{O}$
Uncorrected temperature.....	32.15	33.10	35.50
Correction, projecting column.....	+ .02	+ .03	+ .04
Correction, error of thermometer...	- .05	- .05	- .05
Correction, hydrogen scale.....	- .12	- .12	- .12
Corrected Transition Point.....	32.00	32.96	35.37

In comparing these transition temperatures with those mentioned at the beginning of the paper, it is seen that the first is very near Ketner's value. Ketner's transition temperatures do not agree at all with his solubility determinations, however, and it looks as if his acid must have been incorrectly standardized. The phases were not stated by Richards and Churchill but they evidently, at 35.2° , had an equilibrium between the heptahydrate and monohydrate. The point 32.96 between the decahydrate and monohydrate is new. In order to obtain it, the solution was heated a considerable time above 36° in order to destroy all heptahydrates, then cooled and inoculated with decahydrate. The point, once obtained, was fully as constant as any of the other transition points.

In conclusion, it may be observed that the transition points and solubility determinations are now in good accord.

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ON SOME FERROCYANIDES OF CALCIUM, BARIUM AND MAGNESIUM

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When potassium ferrocyanide is added to solutions of calcium, barium and magnesium salts, containing free ammonia or ammonium salts, difficultly soluble precipitates are obtained. Concerning the composition of these precipitates some confusion seems to have arisen. The general idea has been that they were double ferrocyanides of potassium and the alkaline earth metals. Tests, however, showed that the product always contained ammonia; hence, it seemed of interest to ascertain whether the precipitate was a definite chemical compound or a mixture of ferrocyanides.

H. Baubigny, in an article on the separation of calcium, barium and strontium¹, suggests that, after the removal of the barium as barium chromate, and after getting rid of the excess of the chromate, the calcium be precipitated by means of potassium ferrocyanide in ammonium chloride solution. On the authority of Rose, he calls this precipitate a potassium calcium ferrocyanide. He also recommends the use of potassium ferrocyanide as a test for calcium.

¹ Chem. News., 72, 27.

In the text book of qualitative analysis by Bailey and Cady (1st edition) the precipitation of calcium and magnesium by potassium ferrocyanide in the presence of ammonium salts is mentioned, and the fact pointed out that the precipitates contain ammonia. Recently Flanders¹ has suggested the use of potassium ferrocyanide in the presence of ammonium chloride as a test for calcium, and on the authority of Prescott and Johnson (1903 p. 212) calls the precipitate calcium potassium ferrocyanide.

Experimental.—The product formed by precipitating a calcium salt with potassium ferrocyanide in the presence of a large excess of ammonium chloride or nitrate, was thoroughly washed with hot water and dried first on a porous plate and then at 70° in an oven. Qualitative tests showed that the product contained potassium, ammonium, calcium, the ferrocyanogen ion and water. Analysis of various preparations gave results which correspond to the following formula: $K_2CaFe(CN)_6 \cdot 4(NH_4)_2CaFe(CN)_6 \cdot 2H_2O$.

	Found	Calculated
NH ₄	9.62	9.49
K	5.10	5.15
Ca	13.19	13.19
Fe	18.46	18.39
H ₂ O	2.24	2.37

When potassium ferrocyanide is added to a barium salt under similar conditions, a light yellow, heavy, granular precipitate falls which is soluble enough in hot water to admit of crystallization from that solvent. This fact was known to Thénard, since he suggests the separation of barium from strontium by precipitating the barium in ammoniacal solution by means of potassium chromate.² The analysis of the material, air-dried on a porous plate gave results corresponding to the formula, $K_2BaFe(CN)_6 \cdot 4(NH_4)BaFe(CN)_6 \cdot 15H_2O$.

	Found	Calculated
K	3.55	3.49
NH ₄	6.76	6.44
Ba	30.46	30.67
Fe	12.53	12.48
H ₂ O	11.80	12.06

Magnesium salts under these same conditions give a fine, white precipitate, difficultly soluble in water and acids. In Watts' Dictionary, Edition of 1869, a ferrocyanide of magnesium and ammonium is mentioned as having been obtained, but in an impure state. The cause of this lies in the carrying down of a slight excess of magnesium, probably due to the formation of a small amount of $Mg_2Fe(CN)_6$. The product carefully washed and air-dried to constant weight gave figures which correspond best to this formula: $K_2MgFe(CN)_6 \cdot 5(NH_4)_2MgFe(CN)_6 \cdot 10H_2O$.

¹ This Journal, 28, 1510.

² Children's translation of Thénard's Essay on Chemical Analysis, 1819, 123.

	Found	Calculated
K.....	3.85	4.22
NH ₄	9.79	9.72
Mg.....	8.43	7.87
Fe.....	17.96	18.06
H ₂ O.....	9.94	9.70

Experiment indicates that cadmium¹ forms compounds of a similar composition. The investigation of these products is being continued in this laboratory.

WASHBURN COLLEGE,
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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA
UNIVERSITY, No. 132.]

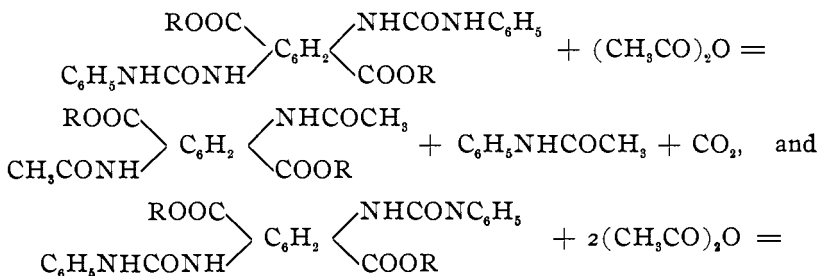
RESEARCHES ON QUINAZOLINES (19TH PAPER). THE SYNTHESIS OF 1,3,6,8-NAPHTHOTETRAZINES FROM PARADIAMINOTEREPHTHALIC ACID AND FROM CERTAIN OF ITS DERIVATIVES.²

BY MARSTON TAYLOR BOGERT AND JOHN MAURICE NELSON.

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Bogert and Dox prepared two naphthotetrazines from ethyl succinylsuccinate, one by condensation with guanidine³, the other by condensation with acetamidine⁴. Their attempts to obtain similar compounds from *p*-diaminoterephthalic acid resulted unsuccessfully. The authors of the present paper, as the result of further experimenting in this direction, have now succeeded in accomplishing this synthesis, and have prepared and studied several naphthotetrazines from *p*-diaminoterephthalic compounds. The experiments may be briefly summarized as follows:—

When ethyl *p*-diaminoterephthalate is treated with phenyl isocyanate, ethyl diphenyluraminoterephthalate results. By the action of acetic anhydride upon this phenyluramino ester, ethyl *s*-diacetyldiaminoterephthalate, and tetracetyldiaminoterephthalate are formed, according to the following equations:



¹ This has the composition K₂CdFe(CN)₆ · 4(NH₄)₂CdFe(CN)₆ · 2H₂O.

² Read at the Meeting of the New York Section, February 8, 1907.

³ This Journal, 27, 1127 (1905).

⁴ Ibid., 27, 1302 (1905).