has been shown by stretching elastic gels in which the dye was dissolved.[2] It is feasible that with increased viscosity reducing rotational and other brownian movement, effective reduction of the total absorption might occur. Alterations of *relative* intensity distribution in the full band can bring about, because of band-overlap, apparent changes of infraband intervals. Such alterations may be interpreted in terms of the relative "weights" of a principal electronic transition itself, and of higher[7] frequency members of a band spectrum produced by coupling thereof with vibrational quanta, such as that proper to a —C=C— bond.[4] How an enhancement of certain of these may be produced by difference in solvent, or by change of temperature of the same solvent, is not yet clear, and should be profitable to study.

Conclusions and Summary

Some effects of change of temperature on the absorption spectra of cyanine dyes in organic solvents have been measured over a temperature range from *ca.* 300 to 90°K. In this range the ionized cyanine dyes showed no appreciable displacement of the wave lengths of maximum absorption. The spectra became appreciably sharper as the temperature fell, which is attributed to suppression of rotational and low order vibrational energies. Temperatures were not reached sufficiently low to eliminate the vibrational quanta responsible (by coupling with the electronic transition) for the auxiliary absorption bands. The sharpening produced at first an increase in ϵ_{max} (or log ϵ_{max}) but as the temperature was further lowered a reduction in band strength occurred—less or absent in the case of non-planar dyes. Non-ionized merocyanine dyes show a greater or less displacement of the spectrum with change of temperature, depending upon the polarity of the solvent. A notably sharp coupling of solvent and soluble (dye) molecules is indicated by this displacement.

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[7] Rarely lower; the lower values $\nu_0 - \Delta\nu$ seem to be generally prohibited in absorption. The "extra" band of merocyanines in the gas state or in non-polar solvents[2] may be an exception.

[CONTRIBUTION FROM THE EASTERN EXPERIMENT STATION, U. S. BUREAU OF MINES]

The System Potassium Carbonate–Sodium Carbonate–Water at 100 and 150°[1]

BY GUY ERVIN, JR., A. L. GIORGI AND C. E. MCCARTHY

Introduction

A study of the solubility relations in aqueous solutions of the carbonates of sodium and potassium was undertaken at this Laboratory in connection with a laboratory and pilot-plant investigation[1a] of a process for the production of potassium carbonate from wyomingite, a leucite-bearing rock found in Wyoming. The process involves a base-exchange step by which a solution containing a mixture of sodium and potassium carbonate is obtained. For the separation of the carbonates it is proposed to evaporate at 100°, producing the monohydrate, $Na_2CO_3 \cdot H_2O$, followed by the anhydrous double salt, $K_2CO_3 \cdot Na_2CO_3$. The resulting solution is cooled to 25°, crystallizing out potassium carbonate sesquihydrate, $K_2CO_3 \cdot 3/2H_2O$. The mother liquor from the crystallization step is recirculated to the double-salt step, and the double salt is recirculated to the original solution, thus effecting a continuous process with no material discarded. An accurate knowledge of solubility is essential to operation of the process.

Two previous studies of this system in the high-temperature range have been made in Russia[2] in connection with a similar technological problem on the treatment of solutions obtained by alkaline leaching of nepheline. At 50° and lower the system has been adequately studied by Hill and Miller.[3] The authors' results at 100° are in essential agreement with those of Makarow and Schulgina. However, those authors present data at 120, 140, and 145° which indicate that the double-salt field becomes smaller with increasing temperature and ceases to exist at 145°; upon the basis of this result they propose evaporation at 145°, thus simplifying the process by eliminating the need for recycling the double salt. In the present study at 150° conclusive evidence was obtained to prove that the double salt exists at this temperature and has actually a slightly larger field than at 100°, which is in accord with theory. Findlay (The Phase Rule, 8th Ed., p. 237) states: " . . . the general rule can be given, that if the water of crystallization of the two constituent salts together is greater than that of the double salt, the latter will be produced from the former on raising the temperature." This is a direct result of van't Hoff's law of mobile equilibrium, which is a particular case of the theorem of Le Chatelier.

Experimental Procedure

The sodium carbonate and potassium carbonate used were Baker C. P. reagents. Qualitative tests showed the absence of impurities. For the majority of the runs the

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

[1a] Unpublished work, Bureau of Mines, U. S. Department of the Interior, College Park, Md.

[2] Makarow and Schulgina, *Bull. Acad. Sci. U. S. S. R. Classe sci. chim.*, 511 (1940); Vasiliev, *Trans. State Inst. Applied Chem.*, **22**, 110 (1935).

[3] Hill and Miller, THIS JOURNAL, **49**, 669 (1927).

initial complexes were made by mixing standardized solutions of these compounds plus $Na_2CO_3 \cdot H_2O$ or $K_2CO_3 \cdot 3/2H_2O$ or both. Sodium carbonate monohydrate was prepared by recrystallizing anhydrous sodium carbonate, while $K_2CO_3 \cdot 3/2H_2O$ was purchased as such. In some cases the anhydrous compounds stored in the oven at 120° were used directly.

The equipment was the same as that employed by Schroeder, Berk, and Gabriel,[4] who have described it fully. Briefly, it consisted of a set of steel solubility bombs of about 250-milliliter capacity. The top of each was fitted with an internal solution sampler tube, and the bottom contained a wire screen and drain plug. A sample of solution was taken, and the solid was separated from the residual solution while maintaining the operating temperature. The air thermostat was arranged so that these operations could be performed without opening the door of the thermostat.

The bombs were thoroughly tested for leaks at 150° using sodium carbonate solution. The temperature of the bomb itself was determined by means of a thermocouple and potentiometer; the hot junction of the thermocouple was wrapped around one of the bomb studs. The temperature of the 100° runs was $101.1 \pm 0.1°$, and the 150° runs were at $150.0 \pm 0.1°$.

A separate set of runs was made at 100° in ordinary chemical glassware. A 1-liter, three-neck flask was fitted with a mercury-seal stirrer, a thermometer, and a sampling pipet and was mounted in an oil thermostat. Samples of solution were obtained by pipetting a portion of the clear supernatant solution into a weighing bottle, finding the weight and making up to volume for analysis. Solid samples were obtained by pipetting a slurry onto a preheated sintered-glass filtering crucible, to which suction was applied.

The chemical compositions were determined by an acid titration to the methyl orange end-point in conjunction with a direct sodium determination[5] by the triple acetate method. Potassium was determined by difference. When the weight ratio of potassium carbonate to sodium carbonate exceeded 10:1, potassium was removed as the perchlorate before the sodium determination.[6] The acid titration is accurate to ±0.1% and the sodium determination to ±0.5% when prior removal of potassium is unnecessary. When potassium is removed, however, the accuracy is only ±10%. Since this occurred when the sodium was less than 5% in solution, the error was never greater than 0.5 of a percentage unit of sodium carbonate and averaged much less than this.

Tests for equilibrium consisted of obtaining check results on duplicate mixtures run for widely different lengths of time. In the case of the glass apparatus, solution samples were taken at twelve-hour intervals until three successive analyses checked within 0.5%. The time allowed for equilibrium was at least thirty-eight hours at 100° and at least twenty-two hours at 150°. Working at 50° or lower Hill and Miller[3] allowed eighteen to twenty-four hours for equilibrium with a simple salt and forty-eight hours for equilibrium with a double salt or solid solution. Makarow[2] and Schulgina allowed thirty hours at 100°, five to six hours at 120°, and three to three and one-half hours at 140 to 145°. It is known that the proportion of solid in the mixture should be low if equilibrium is to be reached in a reasonable time. In this work the solid was below 10% of the mixture at 100° and below 25% at 150°.

Identification of Solid Phases.—The solids were removed from the bombs, dried in air or in a desiccator over anhydrous potassium carbonate, and submitted for microscopic examination and in some cases for X-ray analysis. The optical properties of Na_2CO_3 and $Na_2CO_3 \cdot H_2O$ were found in the literature,[7] while those of $K_2CO_3 \cdot Na_2CO_3$ and $K_2CO_3 \cdot 3/2H_2O$ were obtained at this station. $K_2CO_3 \cdot Na_2CO_3$ is hexagonal, $N_\epsilon = 1.422 \pm 0.003$, $N_\omega = 1.531 \pm 0.003$, crystals equi-dimensional or slightly elongate, $K_2CO_3 \cdot 3/2H_2O$ is monoclinic or triclinic, $N_\alpha = 1.474 \pm 0.003$, $N_\beta = 1.483$ (approx.), $N_\gamma = 1.510 \pm 0.003$, $2V(+) = 66°$ (computed), extinction inclined 15 to 20°. The examination effected a positive identification of all solid phases. One difficulty was encountered. In that part of the double-salt field nearest the $K_2CO_3 \cdot 3/2H_2O$ field, $K_2CO_3 \cdot 3/2H_2O$ was always found associated with $K_2CO_3 \cdot Na_2CO_3$. The cause was crystallization from the retained mother liquor which was always present in high proportion because of the extreme fineness of the double salt. Taking this into consideration, the point nearest the $K_2CO_3 \cdot 3/2H_2O$ field which showed double salt should be the invariant point, $K_2CO_3 \cdot 3/2H_2O$–$K_2CO_3 \cdot Na_2CO_3$. The invariant point as located by chemical evidence checked with this point at both temperatures.

As a further check on the identity of the solid phases, X-ray patterns were obtained on a few samples. These included the double salt at the two extremities of its field at 150° and one sample from each phase area at both temperatures. Patterns for all the compounds occurring in the system at these temperatures were found in the literature.[8] The patterns always agreed with the microscopic identifications.

Accuracy.—Sources of error included lack of equilibrium, weighing errors, and errors in the chemical analyses. The sampler tubes each weighed about a kilogram, and weighings were accurate to the nearest tenth of a gram. No runs were accepted in which the sample weighed less than 10 g. so that the weight of sample was accurate to at least 1%. The sample usually weighed 25 to 30 g. The error in the chemical analyses was less than this, except for the low sodium concentrations.

A measure of the over-all accuracy of the results was obtained by algebraic extrapolation of the tie lines.[9] The composition of the solution, of the initial complex, and of the solid phase should all fall on the same straight line. Using the solid-phase composition as given by the microscope and the composition of the initial complex, a tie line is obtained, and the deviation of the solution composition from this line may be calculated. By means of this calculation, the average deviations were found to be ±0.5% potassium carbonate and ±0.3% sodium carbonate. These deviations show the combined effect of all the errors involved. At the invariant points, where such an extrapolation is not possible, duplicate determinations were averaged, and the average deviation from the mean was calculated. The average deviations were again ±0.5% potassium carbonate and ±0.3% sodium carbonate. Five determinations were made at each invariant point on the 100° isotherm, four determinations at the invariant point ($K_2CO_3 \cdot 3/2H_2O$–$K_2CO_3 \cdot Na_2CO_3$ at 150°), and one at the other 150° invariant.

The wet residues were also analyzed in some cases but were considerably less accurate than the other determinations. Nevertheless, they furnish further chemical evidence for the correctness of the results. The variation was usually no more than 1-2 percentage units.

Experimental Results and Discussion

The 100° Isotherm.—The chemical compositions are given in Table I. The solid phase in equilibrium with each solution is indicated in the last column. The table includes three sets of data: runs made in the glass apparatus, runs made in the solubility bombs, and a preliminary set of runs made in the bombs, in which equilibrium was attained in the solution but not in the solid. In the preliminary set, the initial complexes were made up by adding the anhydrous salts to

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[4] Schroeder, Berk and Gabriel, THIS JOURNAL, **59**, 1783 (1937).

[5] Barber and Kolthoff, *ibid.*, **50**, 1625 (1928).

[6] Barber and Kolthoff, *ibid.*, **51**, 3233 (1929).

[7] Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, New York, N. Y., 1931.

[8] Hanawalt, Rinn and Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).

[9] Hill and Ricci, THIS JOURNAL, **53**, 4306 (1931).

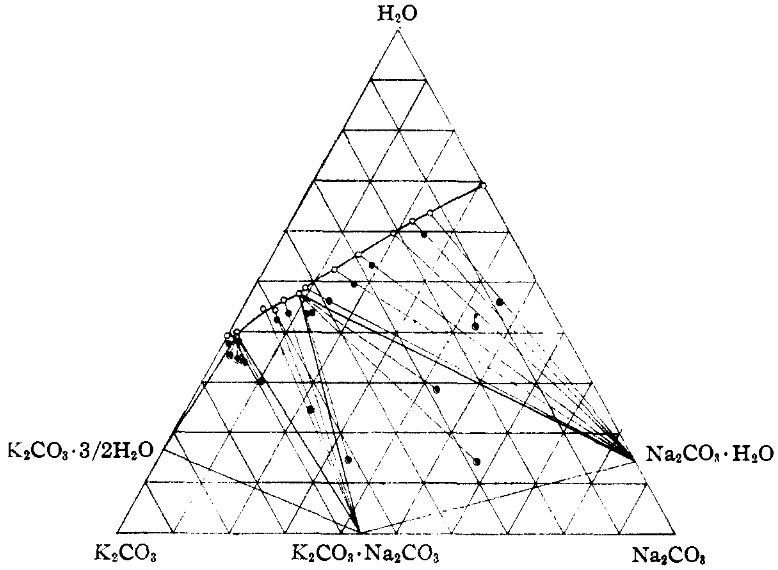

Fig. 1.—The 100° isotherm: O, solutions; ●, initial complexes; ◉, wet residues.

the bombs followed by the proper amount of water. Caking of the anhydrous salts prevented true equilibrium in the times allowed, as indicated by microscopic examination of the solids and by the divergence of the tie lines. The agreement with the subsequent experiments, in which the complexes were formed by mixing solutions and hydrated salts, indicates that equilibrium with respect to the solution was reached, and the results are included as a substantiation of the solubility curve. The type of run is designated in the first column as G for glass, B for bomb, and P for preliminary. The compositions of the mixtures given in the fourth and fifth columns are wet residues for the runs marked G and initial complexes for those marked B; they are not reported for those marked P because these mixtures were not at equilibrium.

The data of Table I are plotted in Fig. 1, omitting the preliminary set of runs. In drawing the tie lines the composition of the solid was taken as a fixed point and the best straight line drawn through that composition and the compositions of the mixture and solution. The isotherm has three branches, corresponding to $K_2CO_3·3/2H_2O$, $K_2CO_3·Na_2CO_3$, and $Na_2CO_3·H_2O$ as solid phases. The monohydrate has the largest field, and $K_2CO_3·3/2H_2O$ has a very small field in accord with its high solubility. The anhydrous double salt is seen to be incongruently soluble, reacting with water to give $Na_2CO_3·H_2O$ and a solution richer in potassium carbonate than the double salt.

The agreement of the authors' data with those of Makarow and Schulgina at 100° is fairly close. They report a composition of 45.8% K_2CO_3 and 8.5% Na_2CO_3 for the monohydrate-double salt invariant which compares with the present result of 44.0% K_2CO_3 and 8.6% Na_2CO_3. Their compositions at the invariant, $K_2CO_3·3/2H_2O$–$K_2CO_3·Na_2CO_3$ are 58.6% K_2CO_3 and 2.0% Na_2CO_3 as compared with 59.2% K_2CO_3 and 1.5% Na_2CO_3 from the authors' data.

The 150° Isotherm.—The data are shown in Table II and plotted in Fig. 2. The only change from the 100° isotherm is the replacement of $Na_2CO_3·H_2O$ by anhydrous Na_2CO_3. The location of the invariant point Na_2CO_3–$K_2CO_3·Na_2CO_3$ is very close to the $Na_2CO_3·H_2O$–$K_2CO_3·NaCO_3$ invariant at 100°. The $K_2CO_3·3/2H_2O$–$K_2CO_3·Na_2CO_3$ invariant is at a considerably higher potassium carbonate concentration so that the field has widened somewhat. The double salt is still incongruently soluble.

As stated in the introduction, results at 150° are directly contradictory to those of Makarow and Schulgina. The use of steel containers, adequate time for equilibrium, and positive identification of the solid phases by means of the microscope and the X-ray attest to the validity of the authors' results. Although no consistent explanation can be given for the disagreement with the results of Makarow and Schulgina, there

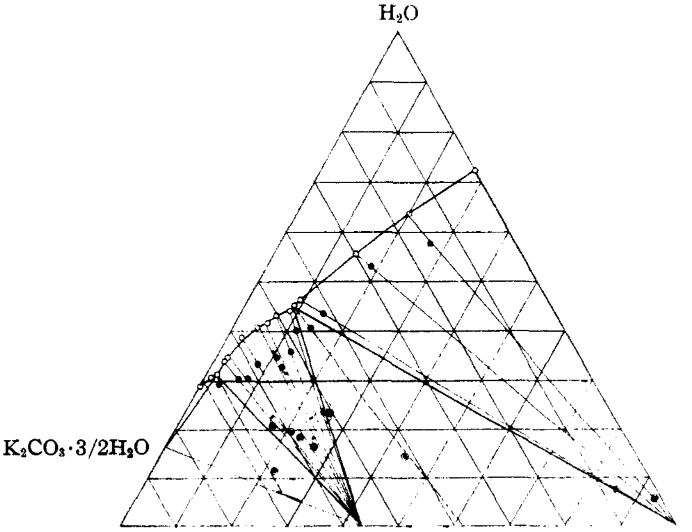

Fig. 2.—The 150° isotherm: O, solutions; ●, initial complexes; ◉, wet residues.

TABLE I

THE 100° ISOTHERM

Type of run	Compositions in weight per cent. Solution		Initial Complex or wet residue		Solid phase
	K_2CO_3	Na_2CO_3	K_2CO_3	Na_2CO_3	
..	60.9	0.0	..	..	$K_2CO_3\cdot 3/2H_2O$
B	58.9	1.3	61.5	1.0	$K_2CO_3\cdot 3/2H_2O$
G	59.4	1.5	62.3	2.5	$K_2CO_3\cdot 3/2H_2O$ + $K_2CO_3\cdot Na_2CO_3$
G	59.4	1.5	61.5	4.1	
G	59.4	1.5	60.6	5.5	
G	59.2	1.5	59.5	10.5	
B	58.4	1.6	59.3	2.6	
P	57.0	2.2	..	..	$K_2CO_3\cdot Na_2CO_3$
P	57.0	2.7	..	..	$K_2CO_3\cdot Na_2CO_3$
P	52.0	4.7	..	..	$K_2CO_3\cdot Na_2CO_3$
G	51.9	3.8	53.1	22.5	$K_3CO_3\cdot Na_2CO_3$
P	51.8	4.4	..	..	$K_2CO_3\cdot Na_2CO_3$
B	49.9	6.0	50.6	7.1	$K_2CO_3\cdot Na_2CO_3$
P	49.8	5.3	..	..	$K_2CO_3\cdot Na_2CO_3$
B	47.2	6.6	47.7	8.7	$K_2CO_3\cdot Na_2CO_3$
P	45.4	7.5	..	..	$K_2CO_3\cdot Na_2CO_3$
P	44.6	8.4	..	..	$K_2CO_3\cdot Na_2CO_3$
P	44.6	8.4	..	..	$K_2CO_3\cdot Na_2CO_3$
G	44.7	8.3	51.3	34.2	$K_2CO_3\cdot Na_2CO_3$ + $Na_2CO_3\cdot H_2O$
G	44.6	8.4	28.4	43.0	
B	43.9	9.0	44.6	12.0	
B	44.2	8.3	43.3	13.0	
G	42.3	9.0	28.4	57.4	
B	42.2	9.1	39.1	14.8	$Na_2CO_3\cdot H_2O$
P	41.4	9.3	..	..	$Na_2CO_3\cdot H_2O$
P	40.5	10.1	..	..	$Na_2CO_3\cdot H_2O$
G	37.7	10.3	19.4	63.8	$Na_2CO_3\cdot H_2O$
B	35.1	12.4	33.0	17.5	$Na_2CO_3\cdot H_2O$
P	29.7	14.8	..	..	$Na_2CO_3\cdot H_2O$
B	29.4	15.3	28.0	18.8	$Na_2CO_3\cdot H_2O$
P	28.6	16.1	..	..	$Na_2CO\cdot\cdot H_2O$
P	27.0	15.2	..	..	$Na_2CO\ \cdot H_2O$
G	20.8	19.7	15.4	43.4	$Na_2CO_3\cdot H_2O$
P	17.0	20.0	..	..	$Na_2CO_3\cdot H_2O$
B	16.2	21.8	15.9	25.0	$Na_2CO_3\cdot H_2O$
G	12.2	24.1	8.5	45.5	$Na_2CO_3\cdot H_2O$
..	0.0	30.9	..	..	$Na_2CO_3\cdot H_2O$

are several factors which might have caused error in their work. These are the short times used for equilibrium, the use of glass containers with the resultant large contamination by silicon dioxide at the high temperatures, and the lack of optical examination of the solid phases.

TABLE II

THE 150° ISOTHERM

Compositions in weight per cent. Solution		Initial complex		Wet residue		Solid phase
K_2CO_3	Na_2CO_3	K_2CO_3	Na_2CO_3	K_2CO_3	Na_2CO_3	
71.0	0.0	..	..	..	..	$K_2CO_3\cdot 3/2H_2O$
68.2	1.0	..	..	..	..	$K_2CO_3\cdot 3/2H_2O$
67.1	2.4	67.6	3.1	73.8	4.4	$K_2CO_3\cdot 3/2H_2O+$ $K_2CO_3\cdot Na_2CO_3$
65.7	1.7	66.9	3.9	..	..	
67.5	1.1	67.6	3.1	66.6	22.0	
67.6	2.1	67.6	3.1	..	..	
64.4	1.6	63.7	6.1	59.5	21.0	$K_2CO_3\cdot Na_2CO_3$
63.3	2.0	61.8	7.8	62.1	17.0	$K_2CO_3\cdot Na_2CO_3$
58.7	2.7	58.6	8.1	58 4	23.3	$K_2CO_3\cdot Na_2CO_3$
55.0	4.2	54.4	10.9	57.0	26.8	$K_2CO_3\cdot Na_2CO_3$
52.7	5.7	54.4	12.7	51.4	24.9	$K_2CO_3\cdot Na_2CO_3$
50.2	6.6	51.3	12.8	..	..	$K_2CO_3\cdot Na_2CO_3$
47.5	8.4	48.1	11.8	50.5	26.0	$K_2CO_3\cdot Na_2CO_3$
46.4	8.6	45.2	14.0	41.7	44.0	$K_2CO_3\cdot Na_2CO_3+$ Na_2CO_3
44.3	9.2	41.7	14.9	..	..	Na_2CO_3
29.6	14 8	28.3	18.6	7.2	85.4	Na_2CO_3
16.1	20.1	15.2	27.0	1.3	93.4	Na_2CO_3
0.0	27.7	..	..	..	..	Na_2CO_3

No attempt was made in this study to determine the solubilities of the individual salts in water with accuracy. The values used are those reported in the literature,[10,11] which were checked within a few tenths of a per cent. The value for the solubility of potassium carbonate in water at 150° was obtained by extrapolation of the data of Mulder which extend up to 130°.

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Summary

1. The system K_2CO_3–Na_2CO_3–H_2O has been investigated at 100° and 150°, employing the usual chemical methods and in addition identifying the solid phases by means of microscopic examination and X-ray patterns.
2. At 100° the isotherm has three branches: that of $K_2CO_3\cdot 3/2H_2O$, $K_2CO_3\cdot Na_2CO_3$, and $Na_2CO_3\cdot H_2O$.
3. The 150° isotherm also has three branches corresponding to $K_2CO_3\cdot 3/2H_2O$, $K_2CO_3\cdot Na_2CO_3$, and Na_2CO_3. The field of the double salt is slightly more extensive here than at 100°. The continued existence of the anhydrous double salt on increasing the temperature is in accord with the theorem of Le Chatelier.
4. The double salt is incongruently soluble in the temperature range studied and decomposes in contact with water to give solid $Na_2CO_3\cdot H_2O$ or Na_2CO_3 plus a solution relatively richer in potassium carbonate.

COLLEGE PARK, MD. RECEIVED NOVEMBER 22, 1943

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(10) Waldeck, Lynn and Hill, THIS JOURNAL, **54**, 928 (1932).

(11) Mulder, "Scheikundige Verhandelingen en Onderzochingen," Vol. 3, pt. 2, Rotterdam, 1864.