at this temperature only a very faint and slight evolution of gas occurred, in fact, evolution was only just perceptible, and after a short time ceased. But 240° , the point at which the mixture shows but a reasonable speed of evolution of nitrous oxide, is one at which the nitrate of ammonium itself has overstepped its equilibrium of stability, and tended to violent evolution. Meantime it was ascertained that nitrate of ammonium begins to evolve nitrous oxide between 170° and 180° , and that the rapidity of evolution of the gas at 215° was fully as great as that from the mixture at 240° or 250° C. The trials were made in the paraffin bath in perfectly similar bulb-tubes, and with thermometers in the bath and in the salts. Thus, to get the mixed salts so to mutually decompose as to yield nitrous oxide with reasonable rapidity it is necessary to acquire a temperature at which nitrate of ammonium cannot exist. There is a kind of critical point for ammonium nitrate, and that point is much below 240° C.; it is even below 200° C. The way of representing the change which takes place on heating the mixture of equivalent weights of nitrate of sodium and sulphate of ammonium for the production of nitrous oxide, is to the best of my belief best represented as follows—

No doubt, when a portion of $(\text{NH}_4)_2\text{SO}_4$ is formed we have present the nascent elements of ammonia and nitric acid, but unite to form nitrate of ammonia at 240° or 250° C. they cannot. We have seen, moreover, that both NO and N_2O_3 , by reducing agents form nitrous oxide, so that were these gases present momentarily in the passing reaction referred to, the change to the final nitrous oxide is perfectly natural and intelligible. This only indicates, I think, the ease and readiness with which the gaseous elements of nitrate of ammonium under a variety of conditions of temperature can adapt themselves in a variety of changes.

NITRATE OF LEAD AND SULPHATE OF AMMONIUM.—By heating nitrate of lead, PbN_2O_6 , alone we adopt the tolerably ancient and classical method for producing nitrogen peroxide, NO_2 , along with oxygen and oxide of lead. On heating a mixture of nitrate of lead with its equivalent of sulphate of ammonium, however, I find that instead of the red fumes of NO_2 the colourless gas N_2O is evolved. This experiment, along with that of heating lead nitrate alone, I would suggest as a pair of instructive lecture experiments to show side by side in illustration of the degree of stability or instability of the N_2O_3 molecule under the influence of heat, alone, and in presence of such a reducing agent as NH_3 .

SODIUM NITRATE AND AMMONIUM OXALATE.—This mixture did not yield nitrous oxide, the decomposition of the ammonium oxalate apparently occurring at a temperature below that at which the necessary decomposition of the sodium nitrate occurred. Such a result might be expected, since oxalic acid decomposes just above 160° .

SODIUM NITRATE AND AMMONIUM PHOSPHATE.—The dry mixture, on heating, evolves nitrous oxide, but not so effectively as the ammonium sulphate mixture.

BARIUM NITRATE AND AMMONIUM SULPHATE, also yield nitrous oxide on heating, but with much more difficulty than lead nitrate and ammonium sulphate.

I desire to express my best thanks to Messrs. S. Ernest Linder and H. Pieton, formerly students of University College, and especially to my late assistant, Mr. Hamilton, for their assistance in carrying out several of the details of this experimental inquiry with me.

I am continuing the investigation of this subject, and more particularly of the intermediate reactions, and hope shortly to publish more details.

SCHÜRMANN'S REACTIONS.

BY WATSON SMITH,

Lecturer in Chemical Technology in University College, London.

This paper deals with reactions which are the outcome of an investigation forming the subject of an Inaugural Dissertation conducted by Ernst Schürmann in the laboratory of Professor Lothar Meyer of Tübingen, the details appearing in Liebig's *Annalen*, **249—250**, 1888—89. 326—350.

For some time past in a somewhat desultory way I have been examining sundry of these reactions to see if any, and how many, are capable of any more practical application. In this inquiry I have been greatly aided by my late assistant Mr. Hamilton, as well as more recently by my present assistant Mr. J. C. Chorley. The original title of this investigation is, "Die Verwandtschaft der Schwermetalle zum Schwefel," and it seems that the first man who experimented as to the action of various solutions of metallic salts on the insoluble sulphides of the silver, copper, and iron groups, was E. F. Anthon in the year 1837, the results appearing in the *J. für prakt. Chemie*, **10**, 353. In this direction he investigated the metals Pb, Cd, Cu, Ag, Co, Ni, Mn, and Fe. He caused, for example, silver nitrate to react upon CuS, and realised the following equation:—

Thus he succeeded in arranging the metals referred to, in a series such that the salt of any one of these is capable of decomposing the sulphide of the metal following it, or the sulphide by the saline solution of the metal preceding it. His arrangement was Ag, Cu, Pb, Cd, Fe, Ni, Co, and Mn. Schürmann extended the investigation to the following metals, Sb, As, Bi, Sn, Zn, Al, Fe, Co, Cu, Mn, Ni, Pd, Hg, Ag, Ti, Bi, Zn, and Sn.

As regards the salts used, the sulphates of Cu, Cd, Zn, Ni, Fe, and Mn, the nitrates of Pb, Co, Bi, Ag, and Ti, and the chlorides of Sn, Pd, and Hg, were used. Besides these, tartar emetic for Sb, and arsenious acid were employed.

In the experiments, so as to effect fairer comparison, equivalent weights of such salts, &c., were taken, as produced no precipitates in the solutions. One or two specially striking reactions are worthy of note in founding the table to be given. These are: (1.) That, between lead nitrate and two equivalents of sulphide of zinc, lead sulphide and zinc nitrate being very quickly formed, so that in less than two hours the whole of the lead will be in the precipitate and one equivalent of Zn in solution; also (2.) Those between arsenic trisulphide and tartar emetic, stannous chloride and zinc sulphate, which latter completely decompose the arsenic trisulphide.

I ought perhaps to mention that the sulphides experimented upon in this research were not natural sulphides, but sulphides obtained by precipitation. The total results are collected together in a table in which the salts marked with an asterisk only acted upon the adjacent sulphides in sealed tubes under pressure.

Sulphides.	Completely decomposed.	Partially decomposed.	Not decomposed.
Ag_2S	$\text{Hg}(\text{NO}_3)_2$	..	CuSO_4
As_2S_3	HgCl_2 CuSO_4	FeSO_4	..
..	$\text{C}_4\text{H}_4\text{O}_6\text{SbK}^*$ $\text{Pb}(\text{NO}_3)_2^*$ ZnSO_4^* NiSO_4^*	..	..
Bi_2S_3	CuSO_4	..	CdSO_4 $\text{Pb}(\text{NO}_3)_2$ $\text{C}_4\text{H}_4\text{O}_6\text{SbK}$
CdS	CuSO_4	$[\text{SnCl}_2]$	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ZnSO_4 NiSO_4 $\text{C}_4\text{H}_4\text{O}_6\text{SbK}$

the sulphur of the sulphides for the metals of the salts presented to them. Though I had in my experiments noted what Schürmann might have regarded as differences of affinity of the sulphur (*vide* my results as given where Pb, Cu, Zn, and Sb, as chlorides, though sufficiently far removed in Schürmann's list from the metals whose sulphides they are set to decompose, exert but little action), yet I had not at first the intention of applying any general criticism to Schürmann's standpoint, but of limiting myself to the bare experimental facts elicited for the sole purpose of application, technologically, to the treatment of mineral sulphides. My friend Dr. C. R. A. Wright, however, thinks the opportunity should not be lost of demonstrating a certain fundamental fallacy which lurks in Schürmann's generalisation, and which leads him to attempt definite scientific classification of the metals referred to. It were, perhaps, another thing had such classification been put forward as a rough technical guide with reference to the results of the special reactions examined, but I thoroughly agree with Dr. Wright that, since the attempt has gone further than this, correction should be applied. Dr. Alder Wright's views are as follows:—

The interesting cases of double decomposition between insoluble sulphides and soluble salts described by Schürmann are apparently due as much to the difference in affinity of the two metals present for the *acid radical of the soluble salt*, as to the difference in their affinities for sulphur; and hence the experiments hardly warrant any classification of metals based on their relative affinities for sulphur as thus deduced. For instance, when lead sulphide and copper nitrate solutions act on one another, copper sulphide and lead nitrate are formed; thus—

But it does not therefore follow that copper has a higher affinity for sulphur than lead; in point of fact the reverse is the case, for according to Julius Thomsen's thermochemical affinity values, the heat of formation of copper sulphide is *less* than of lead sulphide, *viz.* (using Thomsen's notation).

	Calories.
Pb, S.....	20,430
Cu, S.....	9,760
Difference.....	10,670

If therefore lead could react on copper sulphide at the ordinary temperature, it is to be expected that lead sulphide would be found and copper liberated; at any rate this change should be brought about more readily than the converse change, since the former would be accompanied by a considerable heat evolution (10,670 calories), and the latter would require an equal heat absorption.

The heat of formation of lead nitrate solution (from lead, oxygen, and dilute nitric acid) is considerably greater than the heat of formation of copper nitrate solution (from copper, oxygen, and dilute nitric acid); hence a Daniell cell may readily be obtained by placing lead in lead nitrate solution, and copper in copper nitrate solution,* the energy exhibited by the current being due to the displacement of copper from nitrate by lead, just as in the ordinary Daniell it is gained by the displacement of copper from sulphate by zinc. Thomsen's values are—

	Calories.
Pb, O, 2 HNO ₃ aq.....	68,070
Cu, O, 2 HNO ₃ aq.....	52,410
Difference.....	15,660

Hence it results that when lead sulphide and copper nitrate solution act on one another producing copper sulphide and lead nitrate, the action as a whole is accompanied by heat evolution to the extent of 15,660—10,670 = 4,990 calories. Hence the reaction takes place, notwithstanding that the affinity of copper for sulphur is *less* than that of lead for sulphur.

* I have also used thin, clean sheet lead, and still better spongy lead, to precipitate small quantities of copper from solutions of ammonium acetate slightly acid with acetic acid.—W. S.

Since the heat of solutions of metallic oxides in dilute nitric, hydrochloric, sulphuric, or acetic acids, &c., in many cases differ but little, it follows that in such cases the difference in heat of formation of a given pair of salts containing different metals, but the same acid radical is practically the same as the difference between the heats of formation of the oxides of the two metals. Hence the question as to whether the sulphide of a metal A will or will not be decomposed by a soluble salt of another metal B, will in such cases depend on whether the sum of the heats of formation of the oxide of A, and the sulphide of B is or is not greater than the corresponding sum in the case of the oxide of B and sulphide of A.

DISCUSSION.

The CHAIRMAN said that, for himself, he was not quite convinced by the argument used as to the course of the reaction with the sodium nitrate and ammonium sulphate. It seemed to him that the argument from temperature still left it ambiguous as to whether nitrate of ammonium was not formed and immediately decomposed, the fact that it could not exist at such temperatures being no argument to that end. He had nevertheless a strong suspicion about these reactions that were said to occur in two stages. He had always held the opinion that they were simultaneous.

Mr. OSCAR GUTTMANN said that it might be of interest to hear, in addition to Professor Watson Smith's highly interesting experiments, that a friend of his had prepared nitrate of ammonium by mixing solutions of nitrate of soda and sulphate of ammonium, and exposing the mixture to a temperature of -15°C . He had seen a sample of this nitrate of ammonium, about a year ago, after it had been lying open on a writing table for several days. He saw the same sample again about four weeks ago, and it was upon both occasions perfectly dry. His friend preferred this way of making nitrate of ammonium to that of absorbing ammonia gas by nitric acid, as he thereby avoided the impurities contained in the nitrate of soda; and it was to these impurities that he attributed the hygroscopic qualities of nitrate of ammonia, whilst the sample mentioned above was evidently free from that defect. There was still some doubt whether this process could be worked on a large scale, as the investigations were not yet completed.

Mr. C. F. CROSS remarked that the author had omitted mention of Ackworth and Armstrong's researches on the reduction of nitric acid by metals (Chem. Soc. J. 1877, 32, 54—90), in which these authors showed that nitrous oxide was formed to the extent of from 1 to 85 per cent. of the total gaseous products ($\text{NO}, \text{N}_2\text{O}, \text{N}$) according to the conditions of the action.

The equation proposed to account for the production of N_2O under the conditions described in the paper did not attempt any explanation of the reaction. It appeared probable that in the molecular re-arrangement which took place ammonia was oxidised to hydroxylamine concurrently with the reduction of the nitric to the nitrous group, and it might be possible to prove the occurrence of this reaction as the intermediate stage of the decomposition. Hydroxylamine salts and nitrites reacted quantitatively in aqueous solution according to the equation—

and the decomposition appeared to be realisable under a wide range of conditions.

Mr. CRESSWELL asked whether anything had been done with Schürmann's reactions in respect of the two metals, magnesium and aluminium, the symbols of which he did not see on the board. The main reaction of the Schaffner and Helbig process depended entirely upon the want of affinity of magnesium for sulphur. A patent had recently been taken out—or rather an investigation had taken place—as to the possibility of manufacturing aluminium from aluminium sulphide because of the amenity of that body to treatment by electrolysis.

Mr. WATSON SMITH, in reply to the observations made about the nitrous oxide process, said that it appeared to him to be a matter of logic,—that if only partial fusion, amounting to mere softening, could take place at certain temperatures very high up in the scale, and if no proper fusion took place, then there was no real chemical contact. He could not understand in such a case that a chemical change would entirely occur: it might, however, do so to a certain extent. It appeared to him to be an extremely interesting thing that the aqueous solution of these two salts should decompose at the low temperature referred to. From the dry mixture at 240° nitrous oxide came off somewhat slowly; but if nitrate of ammonia were there it would come off vigorously, tending to explosion. But that was not the case. In point of fact, if nitrate of ammonium were heated by itself at 215°, the evolution was as rapid as from the mixture heated to 240°. With regard to the hydroxylamine reaction suggested by Mr. Cross, he did not think that hydroxylamine itself would resist that temperature. If these things did not exist at the temperature given, he could not see that such a change would take place as one could reasonably show by an equation. It would certainly be a mixture of the elements of the substance; but he did not regard that as the substance itself, especially when one considered Berthelot's investigations on the seven different reactions possible on heating nitrate of ammonium. Referring to Mr. Cresswell's question, he believed that Schürmann had omitted aluminium and magnesium because they did not form sulphides under the same conditions as the other metals which he had included.

The results are as follow:—

JUTE.			
—	I.	II.	Mean.
Carbon	46.18	47.12	45.65
Hydrogen.....	5.83	6.33	6.08
Oxygen	47.99	48.27	48.27

COTTON-WOOL.						
—	A. and C.			B.		
	I.	II.	Mean.	I.	II.	Mean.
Carbon.....	42.66	42.16	42.41	42.73	42.47	42.70
Hydrogen	6.25	6.16	6.20	6.33	6.07	6.20
Oxygen	51.09	51.63	51.39	50.74	51.56	51.10

The jute contained 11.35 per cent. of moisture; samples A and C, 5.34; and sample B, 5.83 per cent. The moisture was estimated by drying over sulphuric acid for four weeks in a vacuum.

Although these bodies cannot be regarded as pure chemical individuals, it is interesting to compare the results of certain definite compounds with the results of their analysis. Those which most nearly approach the above composition are:—

—	C.	H.	O.
Pentosane or xylene ($C_5H_8O_2$) ..	45.45	6.06	48.48
Cellulose ($C_6H_{10}O_2$)	44.44	6.17	49.38
Grape-sugar, $C_6H_{12}O_6$	40.00	6.66	53.33
Starch (probably) $C_6H_{10}O_5$..	43.63	6.26	50.10

These samples were distilled in the manner described in our first paper (this Journal, 1892, p. 395). As before, the gas was collected and analysed; and the distillate was separated into three portions, viz., weak acetic acid, crude methyl alcohol and tar.

The results are as follow:—

THE DESTRUCTIVE DISTILLATION OF WOOD.

BY JNO. C. CHORLEY AND WM. RAMSAY, F.R.S.

LAST May we brought before the Society the results of some experiments on the distillation of wood. We have followed up these researches by investigating the behaviour of compounds which have a greater claim to be considered definite. These are jute and cotton-wool.

The sample of jute was purified by boiling it in a dilute solution of caustic soda; the cotton-wool was of two qualities; the samples A and C consisted of crude wadding, while the sample B was purified wool, and is sold under the name of medicated cotton.

These substances were analysed without having been dried; they were afterwards dried and the analyses calculated on the dry material.

—	Jute.			Cotton-Wool.			
	I.	II.	AI.	A2.	B1.	B2.	C.
Weight in grms.	71	73	45	60	67	45	50
Charcoal, per cent.	28.71	32.87	33.33	30.00	31.33	3.44	33.00
Distillate	57.70	43.15	53.33	59.00	43.32	51.11	46.00
Carbon dioxide	Lost	12.33	6.66	9.23	5.22	7.77	11.00
Other gases.....	..	11.65	6.68	10.47	17.13	6.68	10.00
Vol. of gas, cc.	3,000	2,500	2,000	2,700	1,500	1,000	3,500
Vol. of gas from 100 grms.....	4,220	3,420	4,000	4,500	2,240	2,200	7,000
Composition of gas per cent.:							
Carbon monoxide	78.80	85.20	70.02	85.71	51.14	52.46	76.20
Oxygen.....	3.01	1.73	3.60	2.80	8.50	4.73	3.34
Residual gas.....	18.19	12.95	10.42	11.46	37.36	43.11	20.46
Tar, per cent.	14.78	0.85	..	8.33	0.70	13.33	12.03
Acetic acid	0.40	1.40	..	2.44	1.75	2.11	1.31
Methyl spirit	..	10.08	..	..	3.04	10.24	7.07