XXIII.—*The Absorption Spectra of Metallic Nitrates.*
Part II.

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THE descriptions and measurements of spectra observed in five series of solutions of metallic nitrates examined in various ways are contained in Part I (Trans., 1902, **81**, 571), accompanied by a tabular statement which shows where complete absorption occurs of all rays beyond wave-length 340 in solutions containing either gram-molecules of different nitrates or definite fractions of these proportions in a litre

of solution. The measurements were recorded in oscillation-frequencies as well as wave-lengths.*

In the 6th series, a more intimate knowledge was sought of the bands characteristic of NO_3 which are observed in solutions of the various nitrates when diluted in the proportion of one gram-molecule in 20 litres, and at intermediate stages down to 100 litres. Some notable differences were observed, particularly in the curves drawn from the spectra of salts with high molecular weights.

The coloured nitrates of cobalt and nickel were examined because they each show two absorption bands, one belonging to the metal and the other to the NO_3 ion; they were compared with cupric nitrate which, under precisely similar conditions, shows no absorption band whatever.

Preparation of the Nitrate Solutions.

This series of solutions was made in such a manner that the spectra observed would all be strictly comparable with those of the nitrates of the monad metals and with ethyl nitrate. Specially prepared pure carbonates were each digested with 100 c.c. of double normal nitric acid for a period of from two to five days, after which each solution was made up to 200 c.c. with distilled water. The solutions were for the most part quite neutral, others very nearly so. After their spectra had been photographed, they were analysed with great care, the actual quantity of base in each solution being very accurately determined. The following were the figures thus obtained, expressed as grams of nitrate contained in a litre of solution:

	Found.	Calculated.		Found.	Calculated.
$\frac{\text{Ca}(\text{NO}_3)_2}{2}$	20.5	20.0	$\frac{\text{Zn}(\text{NO}_3)_2}{2}$	31.2	32.7
$\frac{\text{Sr}(\text{NO}_3)_2}{2}$	43.3	43.8	$\frac{\text{Mn}(\text{NO}_3)_2}{2}$...	26.87	27.5
$\frac{\text{Pb}(\text{NO}_3)_2}{2}$	102.1	103.4	$\frac{\text{Ni}(\text{NO}_3)_2}{2}$	96.83	95.35
$\frac{\text{Cd}(\text{NO}_3)_2}{2}$	53.7	56.0			

When double normal nitric acid is saturated with bismuth carbonate, the addition of water would, if the compound $\text{Bi}(\text{NO}_3)_3$ is formed, result in the solution containing $\text{BiO}\cdot\text{NO}_3$ and free nitric acid. The

* There is a misprint relating to sodium; " $1/\lambda$ 3938" should read $1/\lambda$ 2938. The absorption spectrum due to thorium nitrate is made to appear very intense, as if 1/100th of a gram-molecule in a litre absorbed all rays beyond $1/\lambda$ 2883 when 200 mm. of the solution are examined. The fraction should be 1/4th of a gram-molecule, and in the case of erbium it should be 1/6th of a gram-molecule.

quantity found in the bismuth nitrate solution corresponded to 28.6 grams of $\text{BiO} \cdot \text{NO}_3$ per litre, but that calculated for $\text{Bi}(\text{NO}_3)_3$ was 224.5 grams. This wide discrepancy shows that the substance in solution must have been the oxy-nitrate. The extraordinary absorption shown by the nitrate solution, considering the small quantity of the salt present and the wide departure from the characteristic nitric acid curve which the spectra photographed from the bismuth nitrate solution exhibit, are facts of great interest.

The large atomic mass of bismuth is a factor which may be taken into consideration, and, in this respect, the absorption spectra of the nitrate solution may be compared with those of lead and cadmium nitrates.

The solutions of cobalt, nickel, and copper nitrates, which were neutral to litmus, deposited traces of either hydroxide or carbonate which had been held in solution by the metallic nitrate. These deposits were not observed until after the solutions had been kept for some months.

The curves (p. 224) drawn from the measurements show several variations, more especially in the most characteristic part of the curves. The following are the spectrum measurements obtained from normal solutions at different dilutions from 1 in 20 to 1 in 100, the column of liquid being, in each case, 200 mm. in length.

6th Series.—Potassium Nitrate.

Normal solution.

Dilution.	Spectrum continuous to $\frac{1}{\lambda}$.		
1/20	3002		
1/30	3002 very feebly to 3045.		Rays transmitted.
1/40	3065.		$\frac{1}{\lambda}$.
1/50	3065.	Absorption band.	A line at 3638.
		$\frac{1}{\lambda}$.	
1/60	3065.	3149 to 3638.	3638 to 3889.
1/70	3149.	3149 „ 3542.	3542 „ 3889.
1/80	3149.	3323 „ 3492.	3492 „ 3889.

At the last dilution, as the band is weak, lines are seen at 3262 and 3323, but very feebly transmitted.

Scale of oscillation-frequencies.

Scale of oscillation-frequencies.

HNO_3
3rd Series

$\text{Cd}(\text{NO}_3)_2$
6th Series

KNO_3
 $\text{Mg}(\text{NO}_3)_2$
6th Series

$\text{Mn}(\text{NO}_3)_2$
6th Series

$\text{Ca}(\text{NO}_3)_2$
6th Series

$\text{BiO} \cdot \text{NO}_3$
6th Series

$\text{Sr}(\text{NO}_3)_2$
6th Series

$\text{Pb}(\text{NO}_3)_2$
6th Series

6th Series

Cobalt Nitrate

6th Series

Nickel Nitrate

6th Series

Copper Nitrate

Where the curved lines are thin the transmitted spectrum is feeble.

6th Series.—Magnesium Nitrate.

Normal solution.

Dilution.	Spectrum continuous to		
	$^{1/\lambda}$.		
1/20	3010.		
1/30	3010.		Rays feebly transmitted.
1/40	3079.	Absorption band.	$^{1/\lambda}$.
1/50	3079.	$^{1/\lambda}$.	3668 to 3854.
1/60	3086.	3079 to 3668.	3668 „ 3915.
1/70	3165.	3086 „ 3556.	3556 „ 3915.
1/80	3390	3165 „ 3516.	3516 „ 3915.
		Feeble transmission of isolated rays.	3471 „ 3915.

In making the above measurements, the general curve of absorption was drawn on the glass surface of the plate with red ink, so as to avoid errors by reading feeble isolated lines as if they were the termination of rays continuously transmitted.

6th Series.—Magnesium Nitrate.

Normal solution.

Dilution, 1/20 to 1/100. The spectra were at each stage exactly like those of potassium nitrate.

6th Series.—Calcium Nitrate.

Normal solution.

Dilution.	Spectrum continuous to		
	$^{1/\lambda}$.		
1/20	3002.		
1/30	3045.		
1/40	3065.		Rays transmitted.
1/50	3065.	Absorption band.	$^{1/\lambda}$.
1/60	3065 feeble to 3149.	$^{1/\lambda}$.	3840 to 3889.
1/70	3149.	3149 to 3840.	3840 „ 3890.
1/80	3149.	3149 „ 3650.	3650 „ 3890.
1/90	3149 feeble to 3323.	3149 „ 3630.	3630 „ 3890.
		3323 „ 3540.	3540 „ 3890.

6th Series.—Strontium Nitrate.

Normal solution.

Dilution.	Spectrum continuous to		
	¹ / _λ .		
1/20	3002.		
1/30	3002.	Absorption band.	Rays transmitted.
1/40	3002 very feebly to 3066.	¹ / _λ .	¹ / _λ .
1/50	3066.	3066 to 3830.	3830 to 3889.
1/60	3066.	3066 „ 3638.	3638 „ 3889.
			very feeble.
1/70	3066 very feebly to 3149.	3149 „ 3590.	3590 to 3889
			feeble.
1/80	3066 very feebly to 3149.	3149 „ 3542.	3542 to 3889
			feeble.

6th Series.—Cadmium Nitrate.

Normal solution.

Dilution.	Spectrum continuous to		
	¹ / _λ .		
1/20	3002.		
1/30	3002 very feebly to 3028.	Absorption band.	Transmitted very feebly.
1/40	3065.	¹ / _λ .	¹ / _λ .
1/50	3065.	3065 to 3540.	3540 to 3889.
1/60	3065.	3065 „ 3540.	3540 „ 3889.
1/70	3065 feebly 3149.	3149 „ 3540.	3540 „ 3889.
1/80	3065 feebly 3149.	3149 „ 3540.	3540 „ 3889.

6th Series.—Manganese Nitrate.

Normal solution.

Dilution.	Spectrum continuous to		
	¹ / _λ .		
1/20	3002.		
1/30	3002.		
1/40	3066.	Absorption band.	Rays transmitted.
1/50	3066.	¹ / _λ .	¹ / _λ .
1/60	3149.	3149 to 3638.	3638 to 3770.
1/70	3149.	3149 „ 3529.	3529 „ 3889.
1/80	3149 feebly to 3263.	3263 „ 2492.	3492 „ 3889.

6th Series.—Lead Nitrate.

Normal solution.

Dilution.	Spectrum continuous to		
	$^{1/\lambda}$.		
1/20	3021.		
1/30	3021 line at 3065.		
1/40	3065 line at 3082.		
1/50	3086.		
1/60	3093.	Absorption band.	Rays transmitted very feebly.
1/70	3075.		
1/80	3075.		
		$^{1/\lambda}$.	$^{1/\lambda}$.
		3075 to 3550.	3550 to 3915.

There is barely an indication of the absorption band in this nitrate. In this respect, the spectrum curve resembles that of bismuth.

*6th Series.—Bismuth Nitrate.*28.6 grams of $\text{BiO}\cdot\text{NO}_3$ per litre in normal nitric acid solution.

Dilution.	Spectrum continuous to		
	Isolated		
	$^{1/\lambda}$. lines.		
1/20	3017. 3065.		
1/30	3017. 3082.		
1/40	3017. 3082.		
1/50	3017. 3086.		
1/60	3017. 3086—3172.	Absorption band.	Rays transmitted.
1/70	3017. 3086—3172.		
1/80	3172. 3285.		
		$^{1/\lambda}$.	$^{1/\lambda}$.
		3285 to 3537.	3537 to 3674.

6th Series.—Cupric Nitrate.

Normal solution.

The spectrum of this substance is much weakened from $^{1/\lambda}$ 2463 to 2783, and particularly about the region of the yellow rays $^{1/\lambda}$ 1696.

Dilution.	Spectrum continuous to		
	$^{1/\lambda}$. Rays visible.		
1/20	2778. 2860.		
1/30	2778. 2929 very feebly.		
1/40	2778. 2972 feebly.		
1/50	2972. 3050.		
1/60	3058.		
1/70	3058. 3135 feebly.	All rays beyond are absorbed.	
1/80	3065. 3135.		

No absorption band visible in this nitrate.

6th Series.—Cobalt Nitrate.

Normal solution, prepared from the carbonate.

Dilu- tion.	Rays trans- mitted. $1/\lambda$.	First Absorption band. $1/\lambda$.	Rays transmitted. $1/\lambda$.	Second Absorption band. Feeble.	Rays transmitted. $1/\lambda$.
1/20	1665 to 1719	1719 to 2270	2270 to 3006		
1/30	1665 „ 1730	1730 „ 2312	2312 „ 3606		
1/40	1665 „ 1742	1742 „ 2093	2093 „ 3072		
1/50	1665 „ 1811	1811 „ 2030	2030 „ 3072		
1/60	1665 „ 1811	1811 „ 2030	2030 „ 3165	3765 to 3668	3668 to 3780
1/70	1665 „ 1833	1833 „ 2030	2030 „ 3165	3165 „ 3507	3507 „ 3852
1/80	1665 „ 1833	1833 „ 1997 Weak.	1997 „ 3188 Rays feeble to 3343.	3343 „ 3474	3472 „ 2920

Nickel Nitrate.

Normal solution, prepared from the carbonate.

Dilu- tion.	Spectrum continuous to $1/\lambda$.	First Absorption band. $1/\lambda$.	Rays transmitted. $1/\lambda$.	Second Absorption band. $1/\lambda$.	Rays transmitted to $1/\lambda$.
1/20	2279	2279 to 2759	2759 to 2990		
1/30	2327	2327 „ 2710	2710 „ 2990		
1/40	2373	2373 „ 2677	2677 „ 3065		
1/50	2391	2391 „ 2619	2619 „ 3079	3079 to 3650	3903
1/60	2534	2534 „ 2568	2568 „ 3157	3157 „ 3538	3903
1/70	3157			3159 „ 3474	3936
1/80	3180			3180 „ 3474	3942
1/90		Rays transmitted feebly to 3330 and again to 3474.			

7th Series.—It was considered desirable to examine a number of definitely hydrated salts with high molecular weights, and those selected as being most suitable were the nitrates of thorium, erbium, and uranium. These were carefully analysed to determine the base, acid, and combined water, the last constituents being estimated by difference.* Normal solutions were examined in thicknesses varying from 200 mm. to 2 mm., which is equivalent to a dilution of 1/100.

* The analyses of the thorium, erbium, and uranyl nitrates were made by Mr. J. Holms Pollok, B.Sc., Assistant Chemist, Royal College of Science, Dublin, to whom my thanks are due.

7th Series.—*Thorium Nitrate*, $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$ [$\text{Th} = 231.5$].

(a) Normal solution: 26.36 grams in 200 c.c. equivalent to 62 grams of NO_3 per litre.

Thickness.	Spectrum continuous to			
mm.	$1/\lambda$.			
200	From 1696 to 2787.			
100	2877.			
50	2980.			
40	2980.			
35	2980.			
30	3002.		$1/\lambda$.	
20	3002.		3065.	
15	3002.		3065.	
10	3065.			Rays transmitted.
5	3065.		Absorption band.	$1/\lambda$.
4	3065.	Line 3149.	$1/\lambda$.	3556 to 3927.
3	3065.	„ 3149.	Very feeble.	3556 „ 3927.
2	3065.	„ 3149.	3354 to 3510.	3510 „ 3960.

Through 200 mm., the most extreme line photographed is $1/\lambda$ 2883 or λ 3466.

At a thickness of 2 mm., there is a sudden extension of the spectrum, which is accounted for by the existence of a feeble absorption band between 3149 and 3537. The rays, very feebly transmitted where this band may be traced, are 3266, and three others to 3519. Beyond this point, the rays are transmitted somewhat less feebly up to 3960, at which point the spectrum ends.

(b) The normal solution diluted, 1 to 100 volumes.

Thickness.	Spectrum continuous to		
mm.	$1/\lambda$.	Absorption band.	Rays transmitted.
200	3072.	$1/\lambda$.	$1/\lambda$.
100	3072.	3354 to 3537.	3537 to 3960.
50	3072.		3960.
40	4006.		3960.
35	4006.		
30	4006.		
20	4128.		
15	4128.		
10	4128.		
5	4176.		
4	4176.		
3	4220.		
2	4320.		

7th Series.—*Erbium Nitrate*, $\text{Er}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$ [$\text{Er} = 116$].

Normal solution: 32.64 grams in 200 c.c. equivalent to 62 grams of NO_3 per litre.

Thickness.	Spectrum transmitted continuously from $1/\lambda$ 1765 to		
mm.	$1/\lambda$.		
200	2929.		
100	2961.		
50	2961.		
40	3005.		
30	3005.		
25	3021.		
20	3021.		
10	3085.		
5	3085.		
4	3172.		
3	3172.		
2	3295.		
		Absorption band.	Rays transmitted.
		$1/\lambda$.	$1/\lambda$.
		3085 to 3864.	3864 to 3920.
		3172 „ 3568.	3568 „ 3920.
		3172 „ 3474.	3474 „ 3920.
		3295 „ 3363.	3363 „ 3940.

Isochromatic plates were used, and the bands characteristic of erbium, photographed by Liveing in solutions of the nitrate, were easily recognised, but being narrow, owing to the small dispersion, only the centre of each band was measured. They had approximately the following oscillation-frequencies and wave-lengths. These bands disappear when the liquid layer is reduced in thickness to about 25 mm.

Scale numbers. Hundredths of an inch.	$1/\lambda$.	λ .	Liveing's measurements. λ .
39.0	1912	5227	523
47.5	2063	4990	488
66.5	2197	4550	449
87.0	2391	4181	415
97.5	2485	4024	404
108.5	2582	3870	387
114.5	2631	3799	377
127.0	2735	3656	365
143.0	2862	3492	—

Ultra-
violet

7th Series.—*Uranyl Nitrate*, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [$\text{U} = 119.9$].

(a) Normal solution : 25.2 grams in 100 c.c. equivalent to 62 grams of NO_3 per litre.

Thickness.	Spectrum continuous		
mm.	$1/\lambda$.		
200	from 1695 to 1901.		
100	1665 „ 1956.		
50	1665 „ 2040.		
40	2040.		
30	2040.		
25	2040.		
20	2040.		
15	2113.		
10	2133.		
5	2173.		
4	2250.		
3	2326.		
2	Rays continuous to 2797.		
	Absorption band.		
	$1/\lambda$.		
	2133	to 2661	2611 to 2759
	2173	„ 2609	2609 „ 2759
	2250	„ 2595	2595 „ 2797
	2326	„ 2445	2445 „ 2797
	Rays transmitted.		
	very feebly.		

No other bands were distinctly photographed, but there was a weakening of the spectrum at points below $1/\lambda$ 2040 (λ 4686).

(b) A second solution, made by diluting to 1/100th the normal strength.

Thickness.	Rays continuous to	
mm.	$1/\lambda$.	
200	2797.	
100	2991.	
50	3079.	
40	3079.	
30	3079.	
25	3079.	
20	3157.	
15	3343.	
10	3343.	
5	3537.	
4	3537.	
3	3537.	
2	3662.	
	Isolated lines very feeble.	
	$1/\lambda$.	
	3157	
	3157, 3310.	
	3279, 3330.	
	3537, 3662.	
	3537, 3662.	
	3780.	
	3903.	
	3903.	
	3903.	

The beautiful photographs of the erbium nitrate spectra under varying conditions, published by Liveing, cannot be surpassed, but unfortunately they do not extend beyond $1/\lambda$ 2905, at which point the NO_3 band only commences (*Trans. Camb. Phil. Soc.*, 1900, 18, 298).

It was thought that thorium salts might show the existence of a band or bands due to the metal, but on converting the nitrate into

chloride by repeatedly evaporating it to dryness with strong hydrochloric acid it was found that this was not the case, the absorption being quite continuous at all dilutions.

Where the curved lines are thin it indicates that the spectrum is feebly transmitted.

The thorium, erbium, and uranyl nitrates exhibit wide differences. The first two differ, but the NO_3 band is not widely displaced, and therefore it might be considered as probable that with thorium nitrate, a salt which in solution deposits a basic compound after the lapse of three or four months, the dissociation is not of the same kind but hydrolytic. There is, however, no proof of this. The uranyl nitrate exhibits the NO_3 band in quite a different position, and here it is evident, either that the salt is not dissociated at all, or that it is dissociated into complex ions, in one of which the NO_3 group is associated with uranium, and in consequence its rate of vibration is greatly retarded, as might be expected from the greater atomic mass of the uranium. Lastly, it may be remarked that cobalt and nickel nitrates each exhibit two bands, one belonging to the cation, and one to the anion.

The cation in each case shows a band in the chloride, bromide, and iodide, which has a different character in each halogen salt. Their measurements are, however, not recorded in the present communication.

The Absorption Spectra of Ethyl Nitrate and Nitric Acid.

It was necessary, in order to complete these observations, to examine, independently of Soret and Rilliet's results, the spectrum of ethyl nitrate as photographed through different thicknesses of the pure compound and also through alcoholic solutions of graduated dilution. Nitric acid, both strong and dilute, was also examined.

The ethyl nitrate was very carefully prepared, and nearly the whole of the liquid boiled at 87° under 30.0 inches pressure. It was kept in the dark until submitted to spectroscopic examination. After moistening a quantity of about 10 c.c. with water and shaking with test papers, it was found to be perfectly neutral.

Nitric Acid, Strong and Dilute, Compared with Potassium and Sodium Nitrates.

Very pure nitric acid of sp. gr. 1.431 was examined in a cell having a thickness of 2 mm. and afterwards placed in a cell 100 mm. thick and filled up with water. The very curious fact was noticed that the dilute solution was more strongly absorbent of the ultra-violet rays than the strong acid. This experiment has been modified in various ways and with acids of different specific gravities, but the result has been the same. It is evident that, when diluted with water, the acid undergoes some molecular changes, which will be dealt with in a further communication.

8th Series.—Ethyl Nitrate.

(a) Undiluted.

Thickness.	Spectrum continuous to	Lines transmitted.
mm.	$1/\lambda$.	$1/\lambda$.
10	3065.	3100.
5	3114.	3132 very faint.
4	3157.	
3	3157.	
2	3157.	Undefined to about 3193.

(b) An *N*/10 alcoholic solution (0.91 gram in 100 grams of alcohol, b. p. 78°).

Thickness.	Spectrum continuous to	
mm.	$1/\lambda$.	Lines transmitted. $1/\lambda$.
200	3157.	
100	3193.	3169 and 3300.
50	3399.	3487 very faint.
40	3399.	3487, 3577.
35	3399.	3487, 3577.
30	3399.	3487, 3577.
20	3587.	3656, 3840.
15	3587.	3656, 3901.
10	3587.	3656, 3915.
5	3895.	3901, 3917.
4	4061.	4090 faint.
3	4061.	4090 faint and 4184.
2	4061.	4128 faint and 4184.

There is no indication of an absorption band. The isolated lines, which are more or less weakly transmitted, simply indicate that the transmission of the rays does not terminate abruptly.

It was found desirable to submit pure anhydrous lithium nitrate dissolved in anhydrous alcohol (b. p. 78°) to the same method of examination as that performed on ethyl nitrate in order to make a strict comparison between the behaviour of an organic and an inorganic salt. The results show a marked difference between the constitution of the ethyl nitrate and that of the solution of the metallic salt. Whereas the ethyl nitrate gave no indication of the existence of the NO_3 group in the molecule under any conditions, the lithium nitrate, on the other hand, in the perfectly anhydrous alcoholic solution, showed distinctly the absorption band characteristic of a nitrate, as if, in fact, the salt molecule consisted of two parts, Li and NO_3 .

8th Series.—*Lithium Nitrate.*An *N*/10 solution comparable with that of ethyl nitrate.

Thickness.	Spectrum continuous to			
mm.	$1/\lambda$.		$1/\lambda$.	
100	2920, weak from		2866.	
50	2920, „		2889.	
40	2920, extends feebly to	2969.		
35	2980, weak from	2920.		
30	2980, „	2961.		
15	2980.			
		Absorption band.		Rays transmitted very feebly.
		$1/\lambda$.	$1/\lambda$.	
		3014 to 3050.	3050 to 3822.	
10	3014.	3014 „ 3058.	3058 „ 3881.	
5	3058.	3058 „ 3638.	3638 „ 3881.	
4	3058. Line 3135.	3135 „ 3474.	3474 „ 3881.	
2	3180.	3180 „ 3474.	3474 „ 3931.	

Spectrum weakened from 3135, 3881, and 3931, indications of continuous rays between 3180 and 3474 showing that the absorption band is greatly weakened.

8th Series.—*Nitric Acid.*

Normal solution.

Thickness of liquid.	Continuous spectrum to			
	$1/\lambda$.		$1/\lambda$.	
{ (1) 10 mm.	3045.	An isolated strong line very feebly transmitted... Also "the following" appear extremely feebly, 3638, 3761, 3886.	3825	}
{ (2) 100	3045.		3825	
{ (3) 5 mm.	3045.	A line appearing very feebly at 3135 with the following, 3638, 3761, 3886.....	3825	}
{ (4) 100 mm.	3045.		3825	
{ (5) 4	3045.	Isolated strong lines appearing exceedingly feebly, 3521, 3568, 3638 and Isolated strong lines appearing very feebly, 3521, 3568, 3638 Precisely the same, but the lines apparently rather less feeble.	3880	}
{ (6) 100 mm.	3045.		3886	
{ (7) 2 mm.	3065.	Faint continuous rays visible from 3065 to about 3130. The line at 3130 appears strong. Lines are also seen to be transmitted, but very feebly, at 3184, 3299, 3323, and 3492. From 3492 to 3889, the lines are transmitted more strongly. Hence the absorption band is much weakened.		}
{ (8) 100 mm.				
		This dilute solution gives exactly the same spectrum.		

It is to be noted that Nos. (2), (3), and (4) are exactly alike. Also (5), (6), (7), and (8).

8th Series.—Sodium Nitrate.

Normal solution.

Thickness.	Spectrum continuous to	
mm.	$1/\lambda$.	$1/\lambda$.
{ 10	3045. Isolated line very feebly transmitted	3825
{ 100	3045. Isolated strong lines feebly transmitted, 3638, 3695, 3825, 3886.	
{ 5	3045. Isolated strong lines feebly transmitted, 3638, 3695, 3761, 3825, and 3886.	
{ 100	3045. Strong line very feebly transmitted Isolated strong lines feebly transmitted, 3638, 3695, 3761, 3825, and 3886. Both spectra equally strong.	3135
{ 4	3065. Isolated strong line feebly transmitted Very feeble, 3521, 3638, 3695, 3761, 3782, 3804, 3825, 3854, and 3889.	3135
{ 100	3065. Line about Very feeble, 3521, 3568, 3638, 3695, 3761, 3782, 3825, and 3889. The two spectra are quite alike.	3135
{ 2	3065. Very feeble continuous rays..... Strong line, 3065. Strong line appearing feeble, 3264. Lines appear but weakly to 3927.	3106
{ 100	3065. Absolutely the same to..... The absorption band has almost disappeared.	3927

8th Series.—Potassium Nitrate.

Normal solution.

Thickness.	Spectrum continuous to	
mm.	$1/\lambda$.	
{ 10	3045. Isolated line 3825.	
{ 100	3045. Isolated strong lines appearing feeble, 3638, 3695, 3761, 3825, and 3889.	
{ 5	3045. Isolated strong lines very feebly transmitted, about 3135, 3638, 3695, 3761, 3825, and 3889.	
{ 100	3045. Exactly similar.	
{ 4	3065. A line about 3135 very feebly transmitted, 3500, 3521, 3568, 3598, 3638, 3695, 3761, 3782, 3804, 3825.	
{ 100	3065. Exactly similar, though, if any difference, possibly a little stronger.	
{ 2	3135. Rays transmitted, 3184, 3264, 3296, 3323, 3355, 3453, 3492, 3529, and 3927.	
{ 100	3135. Exactly similar.	

The Absorption Spectra of Sulphuric and Hydrochloric Acids in Normal Solutions.

A normal solution of sulphuric acid transmits, through a column of liquid 200 mm. in length, a spectrum which is continuous to $1/\lambda$ 4413 and but slightly enfeebled from this point to $1/\lambda$ 4555. The same solution through 100 mm. transmits a spectrum which is practically that of water. In the same way, a normal solution of hydrochloric acid transmits a spectrum which, through 200 mm., does not differ essentially from the spectrum of water up to $1/\lambda$ 4555, there being only a slight enfeeblement of the rays from $1/\lambda$ 4460. A thickness of 100 mm. transmits the rays as freely as a similar column of water.

The Effect of Light on Certain of the Solutions.—It has been mentioned that some of the haloid salts of nickel and cobalt, especially in concentrated solutions, are decomposed when protected from access of air but exposed to ordinary daylight, the action taking place where the light is absorbed by the solution. The following notes were made of the changes observed in solutions of the nitrates when they had been put aside after the examination of their spectra. The solutions of nitrates of normal strength had been preserved for two years in colourless, cylindrically-shaped, well-stoppered bottles nearly filled with liquid and standing in a glass case, but not exposed to sunshine.

$\frac{\text{Cu}(\text{NO}_3)_2}{2}$.—Very slight light brown deposit. No iron present.

$\frac{\text{Ni}(\text{NO}_3)_2}{2}$.—A pale green precipitate which rendered the liquid decidedly turbid.

$\frac{\text{Co}(\text{NO}_3)_2}{2}$.—A red solution with a rather copious brown precipitate which adhered to the glass like a skin.

$\frac{\text{Mn}(\text{NO}_3)_2}{2}$.—A brown precipitate, more copious where there were drops of liquid on the glass or where a thin layer of the liquid adhered to the glass.

Bismuth nitrate.—A slight, but dense, granular precipitate was deposited.

$\frac{\text{Th}(\text{NO}_3)_4}{4}$.—A dense, white precipitate which, after shaking rapidly, settled. Thorium chloride behaved in a precisely similar manner.

$\frac{\text{Pb}(\text{NO}_3)_2}{2}$.—Deposited a very slight, but dense, white precipitate.

Uranyl nitrate remained perfectly clear. A pure neutral solution

of manganese sulphate has a pale pink colour; after a few days, it becomes colourless, it next changes to pale yellow, then to a clear brown liquid, which finally becomes turbid.

Discussion of the Results.

The results obtained in the course of various investigations of the absorption spectra of solid salts and saline solutions must be taken into account in any attempt to elucidate the constitution of the latter.

Bunsen (*Pogg. Ann.*, 1866, 128, 100) examined didymium salts in the crystalline state as well as in solution and found that the width of the absorption bands varied with the thickness of the absorbing medium and with the quantity of salt contained in it. Solutions of the chloride, sulphate, and acetate, each containing the same weight of didymium, yielded different spectra, the bands being shifted towards the red end of the spectrum with increase in the molecular weight of the salt.

Not only one or two, but each of the bands near the Fraunhofer lines, D, E, and F, suffered displacement.

H. Becquerel has more recently observed such variations (*Compt. rend.*, 1887, 104, 777, and 1691) both in crystals and in solutions of the salts. His measurements were made with an instrument of smaller dispersion than that employed by Bunsen, and hence the differences in the spectra of solutions of different salts do not appear so remarkable. Muthmann and Stützel, "Beiträge zur Spectral-analyse von Neodym und Praseodym" (*Ber.*, 1899, 32, 2653), recognised great differences between the spectra of solutions of the nitrate, chloride, and carbonate of neodymium. The last compound differs from the other two by possessing a somewhat intense blue colour. The intensity of the absorption was greatly increased; the band in the violet, λ 432—434, was no longer visible, and that in the green was stronger than in the nitrate. There was a marked alteration in the wave-lengths of the absorbed rays, which showed a shifting of the bands towards the red end of the spectrum, the maximum of absorption being altered to the extent of from 7 to 5 millionths of a millimetre in wave-length in the yellow and green rays. The neodymium carbonate showed, in addition, a fine, well-marked dark line in the orange at λ 600·5, which disappeared when the carbonate was converted into salts with mineral acids. A corresponding band of less intensity was visible in the acetate at λ 597·0. The relative intensities of the bands in the praseodymium carbonate, and also the order in which the lines disappear upon dilution, are quite different from those of the nitrate and the chloride. For instance, whilst in the nitrate solution the line of absorption in the blue is the most

persistent, in the carbonate solution that in the yellow, approximately λ 596.5, is the last to disappear.

The authors, assuming that these changes in the spectra are due to the electrolytic dissociation of the salts by dilution, are unable to reconcile with this the fact of the neodymium exhibiting different absorption spectra when the chloride, nitrate, acetate, and carbonate are examined. On the assumption that the salts are completely resolved into ions, the neodymium ions in the solution of each salt should exhibit the several bands unchanged in position, breadth, and intensity, the neodymium being in strictly atomic proportions in each solution. The bands should furthermore weaken to the same extent and disappear in the same order upon further dilution.

Liveing has shown that concentrated solutions of the chlorides and nitrates of didymium and erbium containing equivalent quantities of metal show the same absorption spectra for each element in solutions of different concentrations.

Didymium acetate shows a modified series of bands, which are shifted more towards the red end than those of the nitrate. The tartrate in ammoniacal solution has all its bands more diffuse than the chloride, some being almost diffused away, and all the bands are shifted towards the red. The strong solutions of the nitrates, however, have a general absorption of the more refrangible rays, and in this respect they differ from those of the chloride and acetate of didymium and from that of the chloride of erbium (*Trans. Camb. Phil. Soc.*, 1900, 18, 298).

The reason of this peculiarity of the nitrates has already been explained in Part I of this communication.

Ionisation is supposed to increase with dilution, and the absorption of rays by the ions should increase in intensity by dilution when the total quantity of salts, dissociated and undissociated, through which the rays are transmitted remains the same, but the experiments on dilution recorded by Liveing militate against this view, as he has pointed out. Ionisation is an effect which should be increased by heating and diminished by acidification, but it was proved by Liveing that the effect of heating and of acidifying salts of didymium and erbium did not cause that change in their spectra which might have been anticipated. In fact, the evidence adduced by him goes very far towards precluding the possibility of the bands characteristic of these salts being produced by the metallic ions.

The effect of heat (*Sci. Trans. Roy. Dubl. Soc.*, 1900, 7, [ii], 253) on dilute and on concentrated solutions of didymium salts, and on solutions of praseodymium and neodymium ammonium nitrates, is to broaden the absorption bands without any diminution of intensity; in fact, the spectra are altered just as if a more concentrated solution of the salt were being examined. The broadening effect was on the side

of the absorption bands nearer the red. Furthermore, in the case of neodymium ammonium nitrate, there was an increased general absorption of the more refrangible rays, in fact, a considerable shortening of the spectrum, but no similar effect was seen in the corresponding praseodymium solution.

In a recently published paper (*Sci. Trans. Roy. Dubl. Soc.*, 1901, 7, [ii], 313—320), I have pointed out that certain haloid salts of copper, nickel, and cobalt, which are hygroscopic, form definite liquid hydrates when exposed to the air, and that the hydrates varied in composition with slight alterations in temperature. The observations were carried on during several months, and deductions were drawn as to the nature of these hydrates and the cause of their formation.

Carlo Rossi (*Gazzetta*, 1901, 31, ii, 502—510. Abstr., 1902, 82, 198), has made a comparison of the solubility coefficients of analogous salts expressed in the number of grams of a compound contained in 100 grams of water. Analogous salts are those with one common ion, whilst the other ions are analogous in the sense of the periodic law. From the tabulated results of observations on sixteen salts, it can be calculated that the number of water-molecules required to dissolve one molecule of salt are for barium 32, strontium 16, and calcium 8. Conversely, the numbers of molecules of the salts which saturate the same quantity of water stand in the relation therefore of 1 : 2 : 4 for the elements in the above order. It is also shown that the molecular volumes of saturated solutions of salts of analogous series have the same values at a definite temperature. This author regards such saturated solutions as representing at any definite temperature true chemical compounds, which are liquid and readily dissociated, being destroyed by the very slightest change in temperature. A similar conclusion was inevitable in the case of deliquescent salts.

The evidence that molecules of hydrated salts exist in solutions consists of a large number of well ascertained facts, but the simplest mode of expressing the character of the spectroscopic evidence is as follows. Salts of whatever nature which crystallise in the anhydrous state and do not form hydrates exhibit absorption spectra in saturated solutions made at 16° or 20°, which undergo but little change upon heating to 100°, and the nature of the change is such that it may generally be predicted for each salt. But the saturated solutions of crystalline hydrated salts undergo remarkable changes when heated, and the actual nature of such changes in their absorption spectra cannot be predicted, but they correspond either with the formation of different known hydrates or with the colour of the anhydrous salt. The sole exceptions observed among coloured compounds are certain salts of chromium, in which the nature of the change was explained

and accounted for in the original communication (*Sci. Trans. Roy. Dubl. Soc.*, 1900, 7, [ii], 253). Dietz, Frank, von Wrochum, and Mylius have shown, from a study of the solubilities of various salts, that there are no fewer than five modifications of calcium chromate which all exist in solution within a certain range of temperature, so that at 18° as many as five distinct saturated solutions of calcium chromate may be obtained (*Wiss. Abhandl. Phys.-Tech. Reichsanstalt*, 1900, 3, 425—477; also *Abstr.*, 1897, 72, ii, 316, 442; 1899, 76, ii, 209, 221). Adie (*Trans.*, 1891, 59, 344) examined potassium nitrate at dilutions 1/5 (nearly), 1/7.5, 1/10, 1/20, 1/40, and 1/80 normal, and found that by comparing the observed osmotic pressures in terms of atmospheres P with the number of times this is greater than π (π being calculated on the assumption that the ultimate osmotic pressure is the same as would be exerted by the compression of a gram-molecule of hydrogen into the same space as the solution occupies), a curve is formed which may be divided into four parts. Starting with a saturated solution, dilution diminishes the osmotic pressure until we get to 1/7.5; from there to about 1/10, the pressure is almost normal, at the former point a little less, and at the latter a little more, than normal. This may represent the duration of existence of some complex molecule of the salt or of a definite hydrate.

When the dilution is 1/10 normal, the dissociating action of the solvent may be supposed to begin to take effect on the complex molecule of the salt. This goes on increasing through dilutions 1/20, 1/40, and 1/80, but does not pass beyond the line of complete dissociation into ions, which apparently coincides with this last dilution (*ibid.*, p. 352). It is precisely at these points, namely, 1/20, 1/40, and down to 1/80 normal, that the absorption spectra show the effect of the NO_3 group on the curves of the various nitrate solutions. Judging from the osmotic pressures, sodium nitrate behaves anomalously, for with a dilution of 1/10 normal it is in a condition between a wholly and a half dissociated salt, but at 1/40 it behaves as if entirely undissociated.

In connection with these osmotic pressures, Adie remarks that "as the curves are so nearly continuous, we cannot infer the existence of definite hydrates in the solutions of the salts examined. For this purpose, one must get a larger range of observations, which can be procured by some less lengthy method, such as the lowering of the freezing point."

Six other metallic nitrates were examined at dilutions of 1/20 and 1/40 of a gram-molecule per litre in order to ascertain the influence of the base upon osmotic pressures and dissociation constants. It may be remarked that at 1/20 the osmotic pressures of magnesium,

barium, cobalt, and copper are much greater than those of calcium and strontium, which correspond closely with those of potassium and sodium, but there are differences at 1/40 dilution.

Whatever the cause of this may be it is remarkable that the spectrum curves below 1/40 of the normal solutions of calcium and strontium nitrates differ from those of barium, but closely resemble those of sodium and potassium nitrates.

In some instances, dissociation takes place into free acid and a basic salt. Adie concludes that the action of the solvent is two-fold, and may be expressed as :

(i) "Combination of the molecules of the dissolved substance with the solvent to form complex molecules.

(ii) Separation of the complex molecules of the dissolved substance, under the action of the solvent, into simpler molecules, not necessarily as small as the limiting gaseous molecule."

The observations made independently by very different methods on the same salts, in solutions of similar strengths, lead to nearly the same conclusions as regards their molecular condition.

Organic Substances of a Basic Character.

It has already been pointed out that ethyl nitrate, whether alone or in solution, yields the same spectrum, and there is no evidence whatever that the molecule contains, or is composed of, dissimilar parts. In this respect, the esters of nitric acid are entirely different from solutions of inorganic nitrates. If we turn now to the absorption curves of nitrogenous organic bases and their hydrochlorides, the differences in the mode of vibration of the base, the acid, and the salt are in some instances very striking (Trans., 1885, 47, 685).

The substances examined were :

- (1) Pyridine and pyridine hydrochloride.
- (2) Quinoline and quinoline hydrochloride.
- (3) Tetrahydroquinoline and tetrahydroquinoline hydrochloride.
- (4) *o*-Toluidine and its hydrochloride.
- (5) *p*-Toluidine and its hydrochloride.

The differences between the spectra transmitted by the base and the salt respectively in (1) are but slight. There is a marked difference between the base and the salt in (2), and there are still greater differences in (3), (4), and (5). These differences, which are somewhat diverse in character, could in no case have been predicted, though a similarity is to be remarked between the differences noticed between base and salt in (3), (4), and (5), which the curves illustrating the original paper clearly exhibit. As the substances (1) and (2) are feebly basic, and the salts therefore easily hydrolysed, the absorption

curves of the bases differ but slightly from those of the salts. The absorption curves of the salts of the stronger bases, (3), (4), and (5), differ widely from those of the bases alone. It is to be inferred from this that they are neither completely ionised nor hydrolysed.

The conclusions arrived at and recorded at the time may here be quoted (*loc. cit.*, p. 693).

"Molecules of compounds, that is to say, molecules composed of dissimilar atoms, vibrate as wholes or units, and the fundamental vibrations give rise to secondary vibrations which stand in no visible relation to the chemical constituents of the molecule, whether these be atoms or smaller molecules. Hence it appears that a molecule is a distinct and individual particle which cannot be represented by our usual chemical formulæ, since these symbolise certain chemical reactions and fail to express any relation between physical and chemical properties."

This is true in the case of carbon compounds where substitution has taken place, and it also holds good for various esters and salts of organic bases, but the statement requires some modification when we deal with either alcoholic or aqueous solutions of metallic salts; for it is an incontestable fact that the NO_3 group exhibits its presence in various ways when the nitrates are suitably diluted beyond 1 gram-molecule of substance in 20 litres of water, and yet we cannot affirm that the NO_3 is a free and independent mobile particle under these conditions, because the influence of the base, or of the positive ion, is apparent. This fact is rendered evident as well by Adie's investigations as by the absorption spectra.

There is a remarkable difference between the constitution of ethyl nitrate, on the one hand, whether undiluted or in dilute alcoholic solution, and, on the other hand, that of the equally dilute solutions of inorganic nitrates of various kinds. The $\text{C}_2\text{H}_5\text{NO}_3$ molecule vibrates as a whole, and there is nothing in its spectrum to indicate the existence within the molecule of any parts which can be differentiated. The nature of the differences in the absorption spectra of the inorganic nitrates, in dilutions ranging from NO_3 in 20 litres of solution to NO_3 in 100 litres, is that which may be expressed by saying that in nearly all cases the intramolecular vibrations characteristic of the NO_3 group are clearly exhibited. With dilutions ranging from a normal solution to dilutions of 1/18 and to 1/19 normal, the nature of the absorption is generally that due to molecular vibrations only; that is to say, it is a general absorption due to the motion of the molecules, and the parts of the molecules are not differentiated. Such motion of translation is accelerated by heat, and, consequently, by raising the temperature of the solution the absorption spectrum is intensified, the effect being to give it the appearance of a stronger solution at a lower

temperature, but the spectrum is not otherwise altered. This fact is capable of a simple explanation by the action of heat causing so many more molecules to pass into the path of the rays that the effect is the same as if the solution were more concentrated.

Though evidence of what may be regarded as ionic dissociation is afforded by the absorption spectra of dilute solutions of inorganic nitrates, yet the spectra are not all alike as they would be if there was a complete resolution into NO_3 and metallic ions, and in some instances the evidence is as equally favourable to the view that certain salts are resolved into HNO_3 and a base. The difference between the absorption curves of various nitrates is greatest with nitrates containing cations of greatest atomic mass relatively to the NO_3 ions.

An explanation applicable to all the hitherto observed facts in relation to absorption spectra and the chemical constitution of saline solutions is as follows.

Assuming the salts to be completely ionised at greater dilutions than 1/20 normal, there must still be an attraction of the positive for the negative ion which leads them to move in pairs or groups of a more or less complex character. For instance, in the case of a nitrate represented by MNO_3 , where M is the metal, the rate of motion of the M may be accelerated or retarded by the NO_3 , or *vice versa*, the rates of vibration being determined by the relative masses of the ions. When the mass of the positive ion is $\text{H}=1$, $\text{K}=39.15$, $\text{Ag}=107.93$, $\text{Ti}=204.1$, and so on, we have $\text{NO}_3=62$; but for $\text{Cd}=112$ we have $(\text{NO}_3)_2$, for $\text{Th}=232$, $(\text{NO}_3)_4$, and for $\text{Pb}=206.9$, $(\text{NO}_3)_2$. With bismuth, the result is in all probability $\text{BiO}\cdot\text{NO}_3$, and therefore we have $\text{BiO}=224$ with $\text{NO}_3=62$. The more powerful absorptions in regions of longer wave-lengths which characterise the salts with high molecular weights are thus accounted for. Furthermore, in dealing with magnesium, zinc, calcium, strontium, and barium nitrates, the comparatively slight differences in the absorption curves may be readily understood, while the general similarity in their spectra to the absorption band of the NO_3 ion is owing to the differences in the atomic masses of the metallic ions being too small to have any appreciable effect on the absorption spectra; such, at any rate, as could be measured with instruments of small dispersion. But, as already indicated, it is otherwise in the case of elements the atoms of which are of large mass.

It has been explained that as the intramolecular vibrations are dependent on, and are a consequence of the molecular vibrations in, such compounds as benzene, triphenylmethane, naphthalene, anthracene, &c., and that where the oscillation frequencies of the molecular vibrations are retarded by the increased mass of the molecule, so

in like manner are the oscillation-frequencies of the intramolecular vibrations retarded. Accordingly we have the positive ion, in its attraction for the negative ion, causing acceleration in the rate of vibration of the negative ion when the mass of the atom is smaller than that of the NO_3 , as, for instance, in the case of sodium, potassium, or lithium. Conversely, the NO_3 accelerates the motion of the positive ion when the atomic mass of the latter is greater than that of the NO_3 , but when the atomic mass of the positive ion is sufficiently large the difference is quite appreciable.

Attention has already been directed in Part I, p. 573, to the probable relation of electrolytic dissociation to photographic action in the following words: "there is reason to believe that the action of radiant energy or dilute solutions is of more frequent occurrence than is usually admitted or taken into account," and instances were mentioned. Since then, three remarkable communications by J. Chunder Bose have been published (*Proc. Roy. Soc.*, 1902, 70, 154—193). It is supposed on good grounds "that the effect of radiation is to produce a state of molecular strain." Experimental evidence is adduced which shows that the molecular strain caused by the action of light changes the physico-chemical properties of substances so that it becomes possible to develop a latent image through differences in chemical stability as, for instance, by reducing agents.

It is evident from their spectra that solutions of metallic nitrates, in dilutions corresponding to one gram-molecule of nitric acid in 20 to 100 litres of water, are in a condition of molecular strain, inasmuch as we possess evidence of their internal molecular vibrations in parts which have not been actually separated.

Conclusion.

The ultimate conclusion drawn from this work is that the operations of dissolving a salt and diluting the solution do not cause a separation of the compound into ions, but only a dissociation of such a character that the molecule is shown to consist of two parts—the movements of the one being influenced by those of the other, so that the molecule of the salt is, in fact, not completely resolved into ions, but is in a condition of molecular tension. The application of external energy, such as light or electricity, may, however, readily cause a separation such as may be brought about by electrolysis or by static electricity and, in some instances, by photographic action.

In the case of esters such as ethyl nitrate, the conditions are seen to be entirely different because the molecule is manifestly neither dissociated nor in a state of molecular tension, there being no evidence of NO_3 having entered into the composition of the compound, even

when the substance has been dissolved and diluted until the ethyl nitrate no longer causes absorption of any of the rays of the spectrum which the solvent is capable of transmitting.