XXXIV.—*The Relation between the Absorption Spectra of Metallic Ions and their Valency.*

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ALTHOUGH many observers have studied the absorption of light by solutions of inorganic compounds, no systematic attempt has been made as yet to connect the absorption spectra of such compounds with their chemical and physical properties. The selective absorption of the solutions of certain metals, such as cobalt, has been the subject of extensive investigation, whereas comparatively little attention has been paid to general absorption.

Hartley's work on the metallic nitrates (Trans., 1902, **81**, 556; 1903, **83**, 221) has shown that increase of atomic weight of the metal causes increase in general absorption, just as in the case of organic substances where increase in molecular weight is accom-

panied by increase in absorption. This was explained as due to the greater weight of the molecule slowing the oscillatory motion and causing absorption of rays of greater wave-length.

Drossbach (*Ber.*, 1902, **35**, 91) also maintained that solutions of the heavy metals strongly absorbed the ultra-violet rays. That atomic weight is only a factor of slight importance in causing light absorption by solutions of metals is seen when thorium is contrasted with iron. Thorium (at. wt.=232) is about four times as heavy as iron, and is non-absorptive, whilst iron (at. wt.=56) is markedly absorptive.

The present investigation has been confined to the absorption of light by metals in aqueous solution, and it has been found that a relation exists between the absorption of light and the valency of the metal. The absorption spectra of the salts examined may be divided into two classes: *absorptive* and *non-absorptive*. By *non-absorptive* is meant a normal solution, 10 mm. of which transmits all rays of wave-length greater than λ 2350. Rays of wave-length 2160 are transmitted by 10 mm. water, and it will be seen that solutions of most of the *non-absorptive* metals are equally transparent. Since the distinction between the two classes is not sharply marked, the wave-length 2350 has been selected as dividing the metals into two groups in accordance with their chemical properties.

The metals which yield *non-absorptive* salts are:

Li, Na, K, Rb, Cs, Gl, Mg, Ca, Ba, Sr, Zn, Cd, Th, Al, Zr.

The metals, solutions of the salts of which are *absorptive*, fall into two classes, according as they give visibly-coloured solutions, such as:

Cu, Au, Ti, Ce, V, Cr, Ur, Mn, Fe, Co, Ni, Pd, Pt,

or give colourless solutions that absorb the ultra-violet rays:

Ag, Hg, Tl, Sn, Pb, Sb, Bi.

If the chemical properties of these metals are considered, it will be seen that the metals of the *non-absorptive* group are characterised by constant valency, whilst those of the *absorptive* group are of varying valency. A metal is here regarded as of constant valency when it yields only one series of salts, the valency being determined, not by the oxides of the metals, but by its fluorides or chlorides. Oxides have been used as the means of deciding the valency of metals, but the objection, that in the case of the higher oxides the oxide may be either an "ozonide," in which the oxygen is doubly linked to the metal, or an "antozonide," in which the oxygen atoms are partly joined to one another, is only in part met by the chemical means at our disposal for distinguishing between these two types of oxides. For that reason the existence of a second series of salts has been accepted as evidence of variation in valency.

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The relations between valency and absorption are rendered evident when the metals are compared according to their arrangement in the periodic classification.

After each salt is placed the wave-length up to which 10 mm. of an *N*-solution, or an equivalent length of a more dilute solution, transmit the rays of the iron arc.

Group I.

LiCl transmits to λ 2160		NH ₄ Cl transmits to λ 2160
NaCl " " λ 2170		CuSO ₄ " " λ 3150
KCl " " λ 2160		AgF " " λ 2560
RbCl " " λ 2160		AuCl ₃ " " λ 5250
CsCl " " λ 2210		

The alkali metals yield only one fluoride, MF, and are typical of constant valency. They are quite transparent.

Copper and gold both yield two well-defined series of salts corresponding with Cu₂Cl₂, CuCl₂ and AuCl, AuCl₃. They both show strong absorption. In addition to the ordinary salts of silver, similar to AgCl, the compounds Ag₂F, Ag₂Cl, Ag₂Br, and Ag₄O are described (Abegg's "Handbuch der Anorganische Chemie," Vol. II., 1, 1908), in which silver forms a series of salts of general formula Ag₂X. The absorption of silver salts is in agreement with this.

Group II.

LiSO ₄ transmits to λ 2190		BaCl ₂ transmits to λ 2170
MgSO ₄ " " λ 2170		ZnSO ₄ " " λ 2170
CaCl ₂ " " λ 2170		CdSO ₄ " " λ 2230
SrCl ₂ " " λ 2160		HgCl ₂ " " λ 2660

Glucinum, magnesium, and the members of the A sub-group give one series of salts, corresponding with MCl₂. Zinc and cadmium are also of constant valency. These elements are all non-absorptive.

Mercury differs from the other members of this group, as it forms two well-defined series of salts. Its solution shows a considerable amount of absorption.

Group III.

Al ₂ (SO ₄) ₃ , (NH ₄) ₂ SO ₄ transmits to λ 2280		TlCl ₃ transmits to λ 3400
AlCl ₃ " " λ 2350 (but lines weakened from λ 2500)		

Aluminium and thallium are the only members of this group that have been examined as yet. Aluminium is a metal of constant valency, whereas thallium forms both thallic (TlCl) and thallic (TlCl₃) compounds, a distinction which is reflected in their absorption spectra.

The difference in absorption between the simple and the double salt of aluminium may be due to a certain degree of residual affinity

in ordinary compounds of aluminium which is completely saturated in the double salt.

Group IV.

ZrOCl ₂ transmits to λ 2330		SnCl ₄ transmits to λ 2740
Ce(SO ₄) ₂ ,, ,, λ 5400		Pb(C ₂ H ₃ O ₂) ₂ ,, ,, λ 2850
Th(SO ₄) ₂ ,, ,, λ 2280		

In the A sub-group titanium and cerium both give tervalent compounds, MCl₃, in addition to the quadrivalent compound, MCl₄, typical of the group. A solution of titanous chloride is deep violet, whilst solutions of ceric salts are also coloured.

Zirconium, which is intermediate between titanium and cerium, and thorium are of constant valency and are non-absorptive.

Tin and lead both give chlorides corresponding with MCl₂ and MCl₄, and both absorb light.

Group V.

AsCl ₃ transmits to λ 2710		BiCl ₃ transmits to λ 3700
SbCl ₃ ,, ,, λ 3750		

Vanadium forms the chlorides VCl₂ and VCl₃, and its solutions are strongly coloured.

Arsenic and antimony both absorb the ultra-violet rays, and they yield the compounds AsCl₃, AsF₅ and SbCl₃, SbCl₅.

Bismuth forms the chlorides BiCl₂ and BiCl₃, and not only are its solutions absorbent, but the solution examined showed a deep band in the ultra-violet in Bi/1000 solution.

Group VI.—As the maximum valency allowed by the periodic law increases, the tendency towards variation in valency also increases. Chromium yields the fluorides CrF₂ and CrF₃, and uranium possesses three chlorides, UCl₃, UCl₄, UCl₅. Both these metals absorb light strongly in solution.

Group VII.—Manganese sulphate transmits to λ 2300.

In addition to the numerous oxides of manganese, the dichloride, MnCl₂, and the trichloride, MnCl₃, are known. Solutions of manganese salts are strongly coloured. Manganous salts, although of a slight pink colour in solution, are remarkably non-absorptive in the violet- and ultra-violet regions.

Group VIII.—Ferrous sulphate transmits to λ 2800.

Iron, cobalt, palladium, and platinum give coloured solutions, and they all form more than one series of salts.

Nickel, whilst giving strongly-coloured solutions, does not form any salts analogous to the ferric salts; yet evidence of its power to vary in valency is found in the complex cyanides which it yields.

A consideration of the results tabulated above will show that the metals, which vary in valency, give solutions characterised by their power of absorbing ultra-violet light. It has not been possible to determine whether this property is perfectly general, but about thirty-five of the commoner metals have been examined, and they are all in harmony with the rule. Apparently the metals of the rare earths may behave exceptionally; for example, the salts of neodymium are coloured, although only one chloride, NdCl_3 , is described. Admitting these exceptions, the great majority of the metals are in agreement with the rule, and the close relationship between valency and optical properties is manifest.

If the metals are arranged in order of electro-potential, as determined by the *E.M.F.* developed between metals and solutions of their salts at a given dilution, they form a series with the more electro-positive metals at one end and the less electro-positive at the other. Decrease in electro-positiveness—→

If a line is drawn between cadmium and thallium it divides the metals into two groups: (a) those to the left, the more electropositive metals, are the metals of constant valency, and the salts of which are non-absorptive; (b) those to the right, the less electropositive metals, are the metals that vary in valency, and the salts of which absorb ultra-violet light. Manganese, a metal which changes in valency, is abnormally placed between aluminium and zinc, but it is interesting to note that, whilst manganic salts are coloured, solutions of manganous salts (for example, manganous sulphate) are remarkably diactinic.

The absorption of light by the non-metallic elements, and the effect of oxidation on the absorption of light of both metallic and non-metallic elements, are at present being studied.

EXPERIMENTAL.

Most of the salts have been examined in normal solutions, but a few comparatively insoluble ones have been examined in more dilute solutions.

The salts employed were obtained from Kahlbaum in the majority of cases, and they were subsequently purified by repeated crystallisation. Chlorides, fluorides, and sulphates have been used almost throughout, as these acidic radicles are non-absorptive.

The aluminium chloride was obtained from the solution of ammonium alum previously employed, and was photographed in a solution containing an excess of hydrochloric acid. Thallium trichloride was prepared by forming an aqueous suspension of 2.3945 grams of thallous chloride, into which chlorine was passed until all the thallous salt was dissolved. The solution was then evaporated to remove excess of chlorine, and made up with water to 100 c.c.

Solutions of the arsenic, antimony, and bismuth salts were obtained by the addition of sufficient hydrochloric acid to give a clear solution. The solutions were photographed by means of a Hilger's quartz spectrograph, an exposure of twenty seconds of the iron arc being given.

In the case of absorptive solutions the dilution is given at which the solution becomes transparent.

Salt.	Weight. Grams in c.c.	Dilution.	Thickness of layer. Cms.	Rays transmitted to λ .
LiCl	9 in 200	1.06N	20	2330
NaCl	5.850 in 100	"Na/1	2	2160
KCl	7.456 in 100	"K/1	20	2240
RbCl	6.0455 in 50	"Rb/1	1	2170
CsCl	0.8418 in 50	"Cs/10	10	2260
NH ₄ Cl	5.351 in 100	"NH ₄ /1	1	2160
CuSO ₄ .5H ₂ O	2.4973 in 100	"Cu/10	10	2170
AgF	1.2688 in 100	"Cu/1000	20	2160
AuCl ₃ .HCl.4H ₂ O	2.0605 in 50	"Ag/10	2	3150
GlSO ₄ .4H ₂ O	8.8620 in 50	"Ag/100	2	2930
MgSO ₄ .7H ₂ O	24.656 in 100	"Au/10	1	2260
CaCl ₂ .6H ₂ O	70 in 100	"Au/10,000	18	2560
		"Gl/1	2	2460
		"Mg/1	1	2330
		"Ca	10	2330
		"	1	5000
		"	1	2330
		"	10	2340
		"	1	2190
		"	20	2250
		"	1	2170
		"	20	2330
		"	2	2170

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Salt.	Weight. Grams in c.c.	Dilution.	Thickness of layer. Cms.	Rays transmitted to λ .
$\text{SrCl}_2, 6\text{H}_2\text{O}$	26.59 in 100	Sr/1	20	2330
			1	2160
$\text{BaCl}_2, 2\text{H}_2\text{O}$	24.433 in 100	Ba/1	19	2340
			1	2170
$\text{ZnSO}_4, 7\text{H}_2\text{O}$	14.375 in 50	Zn/1	10	2260
			1	2170
$\text{CdSO}_4, 8/3\text{H}_2\text{O}$	12.826 in 50	Cd/1	10	2330
			1	2230
HgCl_2	1.3546 in 50	Hg/10	10	2660
			1	2530
		Hg/1000	1	2300
$\text{Al}_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4, 24\text{H}_2\text{O}$	9.070 in 100	Al/5	10	2280
			1	2170
AlCl_3	—	Al/10	10	2350
				(weakened from 2500)
			1	2200
TiCl_3	—	Ti/10	20	3400
			2	3200
		Ti/10,000	1	2260
$\text{ZrOCl}_2, 9\text{H}_2\text{O}$	3.3968 in 100	Zr/10	18	2340
			2	2250
$\text{Ce}(\text{SO}_4)_2, 4\text{H}_2\text{O}$	4.0445 in 100	Ce/10	20	5400
			2	4850
		Ce/10,000	1	2180
$\text{Th}(\text{SO}_4)_2, 4\text{H}_2\text{O}$	2.5 in 250	Th/50	50	2280
			25	2210
SnCl_4	13.04 in 50	Sn/1	10	2920
			1	2740
		Sn/1000	1	2330
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{H}_2\text{O}$	37.922 in 100	Pb/1	20	3000
			2	2850
		Pb/1000	1	2340
AsCl_3	from 0.9896 As_2O_3 in 100	As/10	20	2710
			2	2350
SbOCl	1.7166 in 100	Sb/10	20	3750
			1	3520
		Sb/1000	1	2380
BiOCl	2.5946 in 100	Bi/10	20	3700
			2	3610
		Bi/10,000	1	2280
$\text{MnSO}_4, 7\text{H}_2\text{O}$	27.72 in 100	Mn/1	20	2330
			1	2300
$\text{FeSO}_4, 7\text{H}_2\text{O}$	2.7806 in 100	Fe/10	20	3250
			2	2580
		Fe/100	1	2180

Conclusions.

(1) The metallic elements may be divided into two groups: those of constant valency, the salts of which in aqueous solution transmit the ultra-violet rays, and those of varying valency, the salts of which in aqueous solution absorb ultra-violet light.

(2) If the metals are arranged according to their electrode-

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potential, the more electro-positive metals are found to be of constant valency and non-absorptive.

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