LXXXI.—*Rehydration of Metallic Oxides.*

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THE anhydrous basic metallic oxides, prepared by heating the precipitated hydrates, have been long recognised as hygroscopic; that they should take up water from a moist atmosphere in a definite molecular ratio, though perhaps to be predicted, is a point which appears never to have been made the subject of an experimental investigation. By exposing a number of these oxides, after depriving them, wholly or partially, of their water of hydration, to an atmosphere saturated with aqueous vapour at ordinary temperatures, I have found that rehydration occurs, attended in most cases by contraction of the reacting molecules, and therefore probably with evolution of heat, up to a definite limit of a molecular character. I take this opportunity of laying before the Society a brief account of the results which I have thus far obtained, reserving a fuller publication of the numbers which they express and other details, until I shall have completed a more extended series.

Cobalt I.—*α.* The hydrated sesquioxide was prepared by oxidising the precipitated protoxide, suspended in potash, by a current of chlorine gas. After drying at 100°, till its weight was constant, it lost on

carefully heating to a temperature below red heat, 14.69 per cent. ($2\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ contains 14.02 per cent. H_2O). The oxide, dried at 100° , was placed over water under a bell-jar, and the percentage gain of water was estimated as under:—

After a lapse of 2 days ..	29.7	per cent.	($\text{Co}_2\text{O}_3 \cdot 4\text{H}_2\text{O} = 30.3$)
„ 4 „ ..	33.3	„	
„ 6 „ ..	34.4	„	
„ 10 „ ..	35.0	„	($\text{Co}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 35.1$)
„ 17 „ ..	34.2	„	

There is thus evidence of the attainment of a limit, about which there is a tendency to slight variation.

(β .) The anhydrous oxide, from the above determinations, was then exposed to similar conditions, and the following numbers observed:—

After a lapse of 3 days ..	17.1	per cent.	($\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O} = 17.8$)
„ 7 „ ..	20.3	„	
„ 17 „ ..	25.5	„	
„ 21 „ ..	25.44	„	($\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O} = 26.99$)
„ 24 „ ..	24.6	„	

The limit is approximately $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

(γ .) The oxide was returned a second time, and the following observed:—

After a lapse of 7 days ..	17.4	per cent.	($\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O} = 17.8$)
„ 15 „ ..	21.03	„	
„ 22 „ ..	21.9	„	
„ 30 „ ..	21.4	„	($2\text{Co}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 21.3$)
„ 39 „ ..	20.6	„	

II. Anhydrous Co_3O_4 , prepared from cobaltous nitrate by ignition, gave the following results:—*

	(a.) Per cent.	(b.) Per cent.	
After a lapse of 4 days ..	6.27	—	
„ 7 „ ..	—	7.49	
„ 9 „ ..	—	7.72	
„ 10 „ ..	10.18	—	
„ 14 „ ..	9.2	9.15	
„ 16 „ ..	9.96	—	
„ 24 „ ..	—	10.28	($2\text{Co}_3\text{O}_4 \cdot 3\text{H}_2\text{O} = 10.09$)

I give the numbers observed in the above instances as a typical selection, but I refrain altogether from any discussion of them at the present time, and also from giving those relating to the volumes of the rehydrates.

Chromium.†—(α .) Precipitated oxide dried at 100° ($\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ obs.),

* Rammelsberg.

† Compare *Miller's Chemistry*, 2, 603 (4th edition).

became constant on exposure to rehydrating conditions, at $\text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$. Observations were made upon this *rehydrate*, which is a perfectly free powder, dry to the touch, to determine the retentive capacity of the rehydrates for combined water. For this purpose the percentage of water was determined after exposure to the comparatively dry atmosphere of the balance case, with the following results:—

Observed under rehydrating conditions, and expressing the limit $\text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ (calc. 45.1 per cent.)				Then exposed in balance case.	
After	4 days	44.8 per cent.		1 hour	43.87 per cent.
„	6 „	44.8 „		18 hours ..	43.9 „
„	11 „	44.43 „		66 „ ..	43.89 „
„	17 „	45.1 „			

(β .) The sesquioxide after ignition approximated to the limit of rehydration, $\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

Aluminium.—(α .) Oxide precipitated by boiling the solution of the ordinary hydrate in excess of ammonia; after dehydration at a low red heat, it became, on exposure to rehydration, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. This same limit was observed in three several instances.

(β .) The ordinary precipitated oxide, after ignition, underwent definite rehydration to $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. After strong blowpipe ignition, the rehydration became irregular in character, approximating to the limit, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Iron.—(α .) Precipitated oxide dried at 100° ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ obs.), approximated to the limit $\text{Fe}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and (β) after ignition to $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

The rehydration of the above oxides is in all cases attended by contraction.

Copper.—Cupric oxide was investigated in three different forms:—

(α .) Oxide prepared by igniting the metal in oxygen. After six days' exposure the oxide lost 0.36 per cent. on ignition; it may therefore be regarded as permanently anhydrous.

(β .) From ignition of cupric nitrate. This takes up 2—4 per cent., but exhibits irregularity; the more usual limit is $8\text{CuO} \cdot \text{H}_2\text{O}$.

(γ .) From sulphate by precipitation. After drying at 100° ($4\text{CuO} \cdot \text{H}_2\text{O}$ obs.) it took up water, on exposure, in a manner which points to rehydration per saltum,* thus in 24 hours 18.8 per cent. ($\text{CuO} \cdot \text{H}_2\text{O} = 18.4$), and in 48 hours 25 per cent. ($2\text{CuO} \cdot 3\text{H}_2\text{O} = 25.3$); it then approximated slowly to the limit $\text{CuO} \cdot 2\text{H}_2\text{O}$. After ignition

* The solution of the dynamical part of the problem I hope to effect by means of a specially constructed balance, the pointer recording the motions of the beam on a travelling surface.

it exhibited a much more tardy rehydration, becoming $\text{CuO} \cdot \text{H}_2\text{O}$ after 37 days' exposure.

The rehydration of this oxide appears to be attended by no change of volume, so that from the observed specific gravity the percentage of water in a rehydrate may be directly calculated.

The *rehydration of anhydrous salts* also appears to be a molecular phenomenon, similar in character to that of the oxides. I subjoin the numbers observed in the case of anhydrous copper sulphate:—

	Per cent.	
After 18 hours' exposure	16·51	
„ 66 „	24·29	
„ 90 „	29·45	
„ 114 „	34·21	
„ 138 „	35·6	
„ 162 „	35·85	} $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 36·07 \text{ p. c.}$
„ 210 „	36·10	
„ 258 „	35·99	

The above instances suffice to explain the nature of this investigation, and the general character of the results.