$$(Tl^{3+} - Tl^{1+}, 1.2 \text{ v.}; \ Ce^{4+} - Ce^{3+}, 1.5 \text{ v.})$$

It is therefore surprising to find that when ceric sulfate and thallous sulfate in N sulfuric acid are mixed, there is virtually no reaction, even on boiling. At 25° the half period is longer, perhaps much longer, than a thousand hours. The observed potential difference indicates the possibility of reaction and performance of work *when separated,* but when together reaction fails to take place. Mellor's Treatise (Vol. V, p. 662) cites the existence of a double salt of thallous ceric sulfates, $2Tl_2SO_4 \cdot Ce(SO_4)_2$. The most probable explanation of this unreactivity is that oxidation of thallous ion requires the loss of *two* electrons (Tl^{2+} being unknown) while ceric ion can accept only *one* (Ce^{2+} being unknown).

The addition of $MnSO_4$ (0.001 M) to a mixture of ceric and thallous sulfates (0.01 g. atomic in N H_2SO_4 at 25°) so catalyzes the reaction that the half period is about one hour. The probable mechanism of the catalysis follows from the facts that (a) ceric sulfate rapidly oxidizes Mn^{++} to Mn^{3+} and then to Mn^{4+} (MnO_2), and (b) MnO_2 oxidizes Tl^{+} to Tl^{3+}. Platinum black, also, rather more rapidly catalyzes the reaction. The halide ions show slight catalytic activity.

These and other reactions, including oxidations involving oxygen, and their catalysis are being studied from the point of view of the hypothesis stated. There are many apparent contradictions, some of which already appear capable of resolution; whether it will be possible to establish the hypothesis as a general rule, future work will decide.

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EXCHANGE ADSORPTION AND ITS INFLUENCE UPON THE SOLUBILITY OF PRECIPITATES WITH IONIC LATTICES IN ELECTROLYTE SOLUTIONS

Sir:

In a previous communication [I. M. Kolthoff and Charles Rosenblum, THIS JOURNAL, **55**, 851 (1933)] it was reported that in the adsorption of the sodium salt of Ponceau 4R only dye ions were adsorbed, no sodium ions being removed from the solutions. Other experiments have shown that this "exchange" adsorption at the water–solid interface of pure ionic precipitates may occur quite generally. Finely divided calcium oxalate monohydrate was precipitated and purified by intermittent shaking and washing for several months. In the determination of the adsorption of alkali iodates, sulfates and sodium hydroxide, it was found that only the anions were adsorbed, or at least ten times more strongly than the alkali ions. On shaking with very dilute barium and manganese chloride solutions only the cations were adsorbed. Therefore cation as well as anion exchange occurs

$$\begin{array}{lcl}
\text{CaOx} + SO_4^{=} & \longrightarrow & CaSO_4 + \text{Ox}^{=} \\
\text{Solid} \quad \text{Solution} & & \text{Interface} \quad \text{Solution} \\
\text{CaOx} + Ba^{++} & \longrightarrow & \text{BaOx} + Ca^{++}
\end{array}$$

An important conclusion which can be drawn from the occurrence of exchange adsorption is that the solubility of an ionic precipitate in an electrolyte solution is a function of the amount of solid present or, more precisely, of the amount of surface exposed by the solid in those cases in which cation or anion exchange takes place. Experimentally this was shown to be true. The solubility of calcium oxalate monohydrate was determined by shaking small and large quantities of precipitate with various solutions until equilibrium was attained; the saturated solutions were analyzed for oxalate or calcium by micro methods.

With small quantities of solid present, the normal solubilities were found ($[Ca^{++}] = [Ox^{=}]$ in saturated solution). Some data are given herewith.

$[Ca^{++}]$ AND $[Ox^{=}]$ IN SATURATED SOLUTIONS OF $CaOx \cdot H_2O$ AT 25°

Electrolyte	Concn., *M*	Normal solubility in millimoles per liter		Solubility with 12 to 15 g. of CaOx per 250 cc.	
		Ox	Ca	Ox	Ca
Water		0.067	0.067	0.067	0.067
$(NH_4)_2SO_4$	0.01	.112	.115	*.31*	.05
NH_4IO_3	.01	(.090)	.090	(.13)	.058
NaOH	.01	.126	(.126)	*.30*	(.052)
$BaCl_2$	.001	.078	(.078)	.03	(*.21*)

The saturated solutions of calcium oxalate contain an excess of oxalate ions in the experiments with alkali sulfates, iodates and sodium hydroxide, but an excess of calcium ions with barium and manganese chloride, the absolute values being a function of the amount of solid present.

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DIELECTRIC POLARIZATION IN SOLIDS

Sir:

In a study of the relation between dielectric properties and chemical constitution, in progress at Bell Laboratories for several years, some observations of interest in connection with recent communications on rotation of molecules or groups in crystalline solids [Hitchcock and Smyth, THIS JOURNAL, **55**, 1296 (1933)] deserve reporting. A transition in the solid state accompanied by a change of heat capacity and dielectric constant, ϵ, as predicted by Pauling for HCl has been observed for camphor, borneol and isoborneol.

d-Camphor shows a change of ϵ between −37 and −32° larger than that reported for HCl or H_2S. *d*-*l*-Camphor shows a change of the same magni-