CHEMISTRY

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1961

SovietRxiv

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Abstract

Full Text

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ON THALLIUM POLYCHROMATES

(Presented by Academician I. V. Tananaev, 14 VII 1961)

Thallium chromates are among the least soluble compounds of this metal; therefore they are of great importance for the separation of thallium from solutions both in technological processes and in analytical chemistry. Systematic investigations of thallium chromates have not previously been carried out. There are only isolated, sometimes contradictory, indications of the formation of thallium chromate, bichromate, and trichromate ($^{1-6}$). However, the compositions of all possible thallium isopolychromates, the conditions of their formation, and their physicochemical properties are not reliably known.

Fig. 1. *A* –phase diagram of the system Tl_2CrO_4–CrO_3–H_2O at 25°. *B* –solubility isotherm in the region of microconcentrations of the components

To determine the composition of thallium polychromates and their solubility, we investigated heterogeneous equilibria in the system Tl_2CrO_4–CrO_3–H_2O at 25°. The obtained phase diagram of this system (Fig. 1) is characterized by the formation of incongruently soluble thallium bichromate and solid solutions between thallium chromate and bichromate. No other polychromates of monovalent thallium are formed in the system.

To verify the literature data on the existence of thallium trichromate ($^{1-4}$), as well as the suggestion of the formation of thallium polychromates in acidic solutions (^{7}), we isolated crystals, in accordance with the literature indications ($^{1-4}$), from cooled solutions of thallium bichromate preliminarily dissolved in sulfuric or nitric acids. The composition of the crystals obtained (Fig. 3b) corresponds not to thallium trichromate, as was previously believed, but to thallium bichromate:

$Tl_2Cr_2O_7$.	Found, %:	Tl 65.40; 65.19;	Cr 16.62; 16.64;	Tl : Cr = 1.00 : 1.00; 1.00 : 1.00	
	Calculated, %:	Tl 65.43;	Cr 16.65;	Tl : Cr = 1 : 1	

No other thallium polychromates are precipitated from acidic solutions either. Investigation of heterogeneous equilibria in the systems $Tl_2Cr_2O_7$–$Na_2Cr_2O_7$–H_2O, $Tl_2Cr_2O_7$–$K_2Cr_2O_7$–H_2O, and $Tl_2Cr_2O_7$–$(NH_4)_2Cr_2O_7$–H_2O at 25° showed the absence of chemical compounds and solid solutions between the components.

The branch of the solubility isotherm in the system Tl_2CrO_4–CrO_3–H_2O corresponding to the crystallization of solid solutions based on thallium chromate is characterized by a very low concentration of chromic anhydride (Fig. 1B). The second branch of the same isotherm, corresponding to the crystallization of thallium dichromate, extends over a considerable range of chromic anhydride concentrations (Figs. 1A, 2A). The extent of the solubility isotherms in systems formed by thallium dichromate and sodium, potassium, or ammonium dichromate is determined by the solubilities of the latter in water (Figs. 2B–D). The solubility of thallium dichromate in solutions of chromic anhydride, as well as in solutions of sodium, potassium, and ammonium dichromates (and, apparently, lithium, rubidium, and cesium dichromates), decreases to practically complete absence in the thallium solution. Only in liquid phases with comparatively high concentrations of chromic anhydride, and also of alkali-metal and ammonium dichromates, does the solubility of thallium dichromate begin to increase somewhat (Fig. 2).

Fig. 2. Solubility isotherms of the systems:
A –$Tl_2Cr_2O_7$–CrO_3–H_2O,
B –$Tl_2Cr_2O_7$–$Na_2Cr_2O_7$–H_2O,
C –$Tl_2Cr_2O_7$–$(NH_4)_2Cr_2O_7$–H_2O;
D –$Tl_2Cr_2O_7$–$K_2Cr_2O_7$–H_2O at 25°

State diagrams of the systems studied are a necessary physicochemical basis for the process of precipitating thallium from solutions in the form of dichromate (8-10). It should be pointed out that when thallium dichromate is precipitated with potassium and ammonium dichromates (as well as with rubidium and cesium dichromates), coprecipitation of the components is observed, caused by an adsorption phenomenon arising during the formation of the precipitate. Precipitation of thallium dichromate from acidic solutions on heating in the presence of relatively small amounts of potassium and ammonium (rubidium and cesium) may not be accompanied by coprecipitation (11).

The conditions, found from the state diagrams of the systems studied, for the quantitative precipitation of thallium in the form of dichromate are of practical importance not only for use in quantitative analysis (8-11), but also in hydrometallurgical processes for the production of thallium. Application in technology of the method of quantitative precipitation of thallium, which in this case is simultaneously also a method for its quantitative separation from accompanying elements (8,10), makes it possible to obtain the maximum possible yield of the principal component and, at the same time, in the purest possible state.

In solutions of chromic anhydride of relatively high concentration, and also in

Fig. 3

Figure 2: Fig. 3

concentrated solutions of sodium dichromate (the most soluble of the dichromates considered), the appearance in the liquid phase of monovalent thallium, owing to dissolution of thallium dichromate, is accompanied by a mutual oxidation-reduction reaction between monovalent thallium and hexavalent chromium. Therefore the liquid phases in the system $Tl_2Cr_2O_7$—$Na_2Cr_2O_7$—H_2O, corresponding to the crystallization

$Na_2Cr_2O_7 \cdot 2H_2O$, as well as the crystallization of $Tl_2Cr_2O_7$ in the region of high concentrations of sodium dichromate (Fig. 2), contain, along with monovalent thallium, an insignificant amount of trivalent thallium (and, consequently, an equivalent amount of trivalent chromium). In solutions of chromic anhydride the oxidation-reduction reaction between monovalent thallium and hexavalent chromium proceeds more intensively

Fig. 3. Microphotographs of crystals (72×): *a* —$Tl_2Cr_2O_7$, precipitated by chromic anhydride. —$Tl_2Cr_2O_7$, separated upon cooling of acidic solutions supersaturated for the given temperature. , —$Tl[TlCr_2O_8]$

and at high concentrations a change is observed in the composition not only of the liquid phases, but also of the solid phases. At the same time, the interaction between thallium dichromate and chromic anhydride naturally cannot be considered within the scope of the study of a ternary system.

In the process of heterogeneous interaction of thallium dichromate with solutions of chromic anhydride of concentration above ~ 30 wt.% (at 25°), the solid phase undergoes a change: the formation of a new chemical compound is observed—an earlier unknown thallium polychromate. Thallium enters into the composition of this polychromate in different valence states—as monovalent and trivalent. The results of analyses of the obtained thallium polychromate (upon attainment of the equilibrium state between the liquid and solid phases) agree well with those calculated for $Tl[TlCr_2O_8]$:

Found, %: Tl(I) 31.64; 31.42; Tl(III) 32.02; 31.44; Cr(VI) 16.22; 15.70
$Tl(I) : Tl(III) : Cr(VI) = 1.00 : 1.01 : 2.01$; $1.00 : 1.00 : 1.96$

$Tl[TlCr_2O_8]$. Calculated, %: Tl(I) 31.89; Tl(III) 31.89; Cr(VI) 16.23;
$Tl(I) : Tl(III) : Cr(VI) = 1 : 1 : 2$

The formation of the complex anion $[TlCr_2O_8]^{1-}$ during incomplete oxidation of thallium in thallium bichromate apparently occurs through the formation of new bonds between trivalent thallium and oxygen.

The polychromate of monovalent and trivalent thallium is obtained in the form of needle-like crystals of various sizes with well-formed faces (Fig. 3 ,). In water it is only slightly soluble; in organic solvents, in particular acetone and ethyl alcohol, it is practically insoluble.

The isopolychromates of monovalent thallium are therefore limited to the existence of thallium bichromate. However, the tendency characteristic of thallium to form complex compounds in whose composition it is simultaneously present in different valence states is also manifested in thallium chromates, as indicated by the formation of the polychromate of monovalent and trivalent thallium.

The investigation of the previously unknown thallium polychromate is continuing.

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Received
6 VII 1961

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