

species such as CoBr_3^{3-} and CoBr_6^{4-} at 160 °C,¹⁵ most certainly originate from melts with an approximate Co(II) distribution of CoBr_4^{2-} (~40%), CoBr_3^- (~35%), CoBr_2 (~20%), and CoBr^+ (~5%) (Figure 5).

Attempts to quantitatively study the fluoride complexes were made by recording spectra of melts with small amounts of CoBr_2 (producing essentially Co^{2+} and Br^- in the melt) and KF added up to the solubility limit of LiF (0.03 mol kg⁻¹). No spectral changes at all could be observed, however, after addition of fluoride (melts A-C in Table I). This might be due either to the presence of fluoride complexes with an absorbance in the 550-nm region very similar to that of $\text{Co}(\text{NO}_3)_4^{2-}$ (cf. ref 35) or to the fact that no fluoride complexes are formed in detectable amounts. In order to discriminate between these two possibilities, we recorded the spectra of melts D and E (Table I) with an approximate fivefold excess of bromide over fluoride. These spectra were identical with those which could be calculated for fluoride-free melts with the same concentrations of cobalt and bromide. Hence, it is concluded that fluoride acts as a considerably weaker ligand than bromide. This conclusion qualitatively agrees with previous observations from conductivity³⁶ and cryoscopy³⁷ studies.

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The sequence of decreasing stability of cobalt(II) halide complexes in molten $(\text{K,Li})\text{NO}_3$, $\text{Cl}^- > \text{Br}^- \gg \text{F}^-$, is in contrast to the characteristic class a acceptor sequence $\text{F}^- > \text{Cl}^- > \text{Br}^-$ for aqueous solution chemistry of Co(II).²⁻⁴ The reason for this difference is probably to be found in a strong interaction of Li^+ with F^- in the melts. Preliminary measurements³⁸ indicate that β_1 for LiF in water is about 1.5 M⁻¹ which compares with $\beta_1 = 2.5 \text{ M}^{-1}$ for CoF^+ .² If this closeness in affinity for F^- persists in nitrate melts, the large excess of Li^+ over Co(II) effectively reduces the tendency for Co-F complexation.

Correspondingly, there should be a similar although not so pronounced competition between Li^+ and Co(II) for Cl^- . This means that the difference in chloride and bromide affinity for cobalt is actually larger than that indicated by the difference in the corresponding stability constants.

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Registry No. CoCl_4^{2-} , 14337-08-7; CoBr_4^{2-} , 14493-02-8.

Supplementary Material Available: Tables V and VI, the compositions of Co,K,Li- NO_3 ,Cl and Co,K,Li- NO_3 ,Br melts of which spectra have been recorded (2 pages). Ordering information is given on any current masthead page.

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Solid Solutions $(\text{Ag,Na})_2\text{CrO}_4$ and Silver Chromate Complexes in $(\text{K,Na})\text{NO}_3$ Melts. A Potentiometric, Spectrophotometric, and Solubility Study

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The complex formation between Ag(I) and CrO_4^{2-} in molten 1:1 $(\text{K,Na})\text{NO}_3$ has been studied mainly by emf and solubility measurements. Stability constants β for the rather weak complexes AgCrO_4^- , Ag_2CrO_4 , and $\text{Ag}(\text{CrO}_4)_2^{3-}$ have been determined. The emf measurements were performed at five temperatures between 523 and 623 K. The temperature dependence of β_{11} is interpreted in terms of ΔH°_1 and ΔS°_1 for the formal process $\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{AgCrO}_4^-$, which is favored to about the same extent by ΔH°_1 and $-\Delta S^\circ_1$ contributions to ΔG°_1 at 553 K. The solubility of a range of solid solutions $(\text{Ag,Na})_2\text{CrO}_4$ has been measured at the reference temperature 553 K in melts with Ag^+ in excess over CrO_4^{2-} and *vice versa*. Stability constants obtained from these measurements agree with those from potentiometric data. The activity of Ag_2CrO_4 in the solids has been determined. A phase transition from solid solutions of Ag_2CrO_4 (I) to a Na-rich phase (II) with $x_{\text{Na}} = 0.53 \pm 0.05$ was detected by thermodynamic methods and X-ray powder diffraction techniques. Phase I is close to thermodynamically ideal whereas phase II exhibits large positive deviations from ideality. Absorption spectra of CrO_4^{2-} in melts with various cationic compositions show a remarkable shift of the low-energy band toward lower energies upon association with Ag^+ . This is attributed to the occurrence of a considerable d- π back-donation from Ag(I) to CrO_4^{2-} .

Introduction

In previous papers we have reported on the complexation of NO_2^- and IO_3^- with Ag(I) in the molten "standard solvent" equimolar $(\text{K,Na})\text{NO}_3$. Although the thermodynamic stability of complexes formed in those systems is comparably low, the silver ion may be considered as a good "probe" metal ion for comparing the complexing ability of various oxoanions, since the Ag(I) activity can be determined conveniently by emf measurements with silver electrodes. A number of emf studies

of Ag(I) association with divalent oxoanions in various molten alkali nitrates have also appeared in the literature,³⁻⁷ but the spread in the data—with respect to temperature, solvent composition, and complex stabilities—is unfortunately too large in most cases to make a meaningful comparison of, e.g., enthalpy and entropy effects on the association in different

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systems possible. It is also, in general, desirable to use more than one experimental method to study the complexation in order to avoid misinterpretation of data.

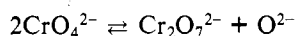
The complex formation between CrO_4^{2-} and Ag(I) has been studied in various molten alkali nitrates by Sacchetto and co-workers,⁶ using emf measurements. Only the 1:1 complex AgCrO_4^- was considered, but the data of what was said to be a preliminary set of measurements in equimolar $(\text{K,Na})\text{NO}_3$ are too scattered to be used in a discussion of the thermodynamics of the association process, which can be schematically written as



In a similar study Alvarez-Funes and Hill determined the stability of AgCrO_4^- in molten KNO_3 .⁷

In the present paper a more thorough investigation of the association and solubility equilibria in the system $\text{Ag, (K,Na)-CrO}_4, \text{NO}_3$ is presented. The aim of the study is to examine which associated silver chromate species exists in $(\text{K,Na})\text{NO}_3$ melts—with special emphasis on the thermodynamics of process 1—and to elucidate the heterogeneous equilibria between solid chromate phases and melts, since solid solution formation with Ag(I) compounds has turned out to be of great importance in other systems.^{2,8} The main information on these topics is obtained from potentiometry and solubility measurements, but a number of visible absorption spectra of CrO_4^{2-} in different cationic environments have also been recorded at 553 K. The spectral results will be considered in the discussion section of this paper.

The condensation of CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$ in molten equimolar $(\text{K,Na})\text{NO}_3$ has been investigated by Kust.⁹ The equilibrium constant for the reaction



is really very low, 1.4×10^{-8} at 553 K, but acid Ag^+ ions might be expected to shift the equilibrium to the right. No indication of such an interfering reaction has been found by us, however, in the present study.

Experimental Section

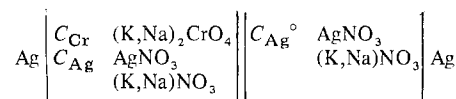
Silver nitrate, sodium nitrate, and potassium nitrate (Merck p.a.) were pretreated and stored as described previously.¹⁰ Alkali metal chromate was added as an equimolar mixture of sodium chromate (Baker analyzed reagent) and potassium chromate (Merck p.a.). These salts were dried separately, ground together, and then dried again at 120 °C for several days prior to use. Silver chromate (Merck p.a.) was used without any further purification. In some cases, silver chromate was precipitated directly in the melt from added alkali chromate and silver nitrate.

Furnaces, temperature control, and measurement and the construction of the cell for emf measurements have been described elsewhere.^{1,10,11}

Solubility Measurements. Systems with approximately 3 g of Ag_2CrO_4 , 75 g of $(\text{K,Na})\text{NO}_3$, and varying amounts of AgNO_3 or $(\text{K,Na})_2\text{CrO}_4$ were agitated at 553 K for at least 50 h in Pyrex glass tubes. Some systems contained amounts of Ag_2CrO_4 varying between 0.3 and 10 g. Maximum concentrations were 0.25 mol kg^{-1} $(\text{K,Na})_2\text{CrO}_4$ and 0.5 mol kg^{-1} AgNO_3 . (The solubility of alkali chromate in 1:1 $(\text{K,Na})\text{NO}_3$ at 553 K was determined to be 0.26 ± 0.01 mol kg^{-1} .) Samples from the nitrate phase were analyzed for silver and chromate. Silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions after elimination of chromate by precipitation as BaCrO_4 . The total chromate concentration, C_{Cr} , was determined spectrophotometrically in samples dissolved in water from the CrO_4^{2-} absorption at 370 nm for systems with $C_{\text{Cr}} > 2 \times 10^{-4}$ mol kg^{-1} in the melt. At lower concentrations the more sensitive method employing diphenyl

carbazide was used.¹² In the latter case silver had to be removed from the aqueous solution by precipitation with bromide before the addition of diphenyl carbazide. For systems containing more than 2 g of Ag_2CrO_4 , the equilibrium composition of the solid phase was calculated from the difference between added and found amounts of various ions in the nitrate melt.

Potentiometric Measurements. The following cell was used:



C_{Ag} and C_{Ag}° denote total concentrations of Ag(I) in test and reference melts, respectively. The cell was usually set up with 250 g of $(\text{K,Na})\text{NO}_3$ and 0.0025 mol kg^{-1} AgNO_3 in both cell compartments and left with vigorous stirring for about 18 h. Successive additions of $(\text{K,Na})_2\text{CrO}_4$ were then made, and the emf, E , was measured repeatedly at constant temperature over four different electrode combinations after each addition by means of a Digiscan 10 PRC data-logging unit from Mess + System Technik, München. The E values were measured to ± 0.05 mV. Stable readings were as a rule obtained within 30 min after each addition of chromate. In order to decide whether or not polynuclear species are present in melts with an excess of CrO_4^{2-} over Ag^+ , some series were run with $C_{\text{Ag}} = 0.0065$ mol kg^{-1} at 280 °C as well. Eight different melt compositions were as a rule studied in each series; the maximum concentration of chromate was 0.16 mol kg^{-1} . All series of measurements were duplicated at least once. Data were recorded at five different temperatures in the range 250–350 °C.

Absorption Spectra. The equipment used has been described elsewhere.¹³ The spectra were recorded at 553 K in 10-mm fused silica cells with pure $(\text{K,Na})\text{NO}_3$ solvent as reference. The densities of the composite melts were determined by interpolation under the assumption that partial molar volumes of the constituents are independent of composition. Data from previous publications on NaNO_3 , KNO_3 and binaries $\text{NaNO}_3\text{-AgNO}_3$ and $\text{KNO}_3\text{-AgNO}_3$ were used.^{14–16} The possible errors introduced by this procedure are probably much smaller than the estimated uncertainty ($\sim 5\%$) in the measured absorbances.

Results from Potentiometric Measurements

Stability constants, defined by

$$\beta_{mn} = \frac{[\text{Ag}_m(\text{CrO}_4)_n]^{m-n}}{[\text{Ag}^+]^m [\text{CrO}_4^{2-}]^n} \quad (2)$$

are determined. Since junction potentials are negligible in these dilute ionic melts

$$\Delta E = \frac{RT}{F} \ln (C_{\text{Ag}}/[\text{Ag}^+]) \quad (3)$$

where ΔE is E at the chromate concentration considered minus E at $C_{\text{Cr}} = 0$ in the left-hand compartment of the cell. Combination of eq 2 and 3 with the stoichiometric requirement

$$C_{\text{Ag}} = [\text{Ag}^+] + \sum_m \sum_n m [\text{Ag}_m(\text{CrO}_4)_n]^{m-2n} \quad (4)$$

yields

$$\exp\left(\frac{F(\Delta E)}{RT}\right) = 1 + \sum_m \sum_n m \beta_{mn} [\text{Ag}^+]^{m-1} [\text{CrO}_4^{2-}]^n \quad (5)$$

It appeared that the left-hand member of eq 5 could be accurately described by a second-degree polynomial in $[\text{CrO}_4^{2-}]$ independent of the Ag(I) content of the melts. Hence the complexes AgCrO_4^- and $\text{Ag}(\text{CrO}_4)_2^{3-}$ are the only species that

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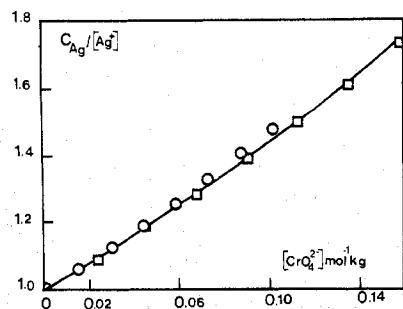


Figure 1. $C_{Ag}/[Ag^+]$ vs. $[CrO_4^{2-}]$ from two emf titrations in 1:1 (K,Na)NO₃ at 553 K: $C_{Ag} = 0.0065 \text{ mol kg}^{-1}$ (○) and $C_{Ag} = 0.0026 \text{ mol kg}^{-1}$ (□). The full-drawn curve is calculated from the stability constants of Table I.

Table I. The Overall Stability Constants β_{11} and β_{12} for $Ag^+ - CrO_4^{2-}$ Complexes in Molten 1:1 (K,Na)NO₃ from Emf Measurements^a

T/K	$\beta_{11}/\text{mol}^{-1} \text{ kg}$	$\beta_{12}/\text{mol}^{-2} \text{ kg}^2$
524	4.0 ± 0.2	7.9 ± 1.8
538	3.9 ± 0.1	6.0 ± 0.7
553	4.1 ± 0.1	3.6 ± 1.1
588	3.5 ± 0.2	5.0 ± 1.3
622	3.30 ± 0.05	2.3 ± 0.7

^a The limits of error are 95% confidence limits.

have to be considered in melts having chromate in excess over silver. This is exemplified by Figure 1, displaying results from two series of measurements at 280 °C.

The final treatment of data was made by use of a computer program yielding the best fitting parameters β_{mn} from eq 5 by minimizing the sum of squared errors $(\Delta E_{\text{obsd}} - \Delta E_{\text{calcd}})^2$. Table I gives stability constants from the emf measurements at five temperatures.

The thermodynamic parameters ΔH°_1 and ΔS°_1 for process 1 have been estimated from a study of $\Delta G^\circ_1 = -RT \ln \beta_{11}$ as a function of temperature. The standard state chosen relates to ionic fractions of unity. ΔG°_1 is a good linear function of T so ΔH°_1 and ΔS°_1 have been estimated by linear regression with a weight scheme analogous to the one described in a previous paper.¹ The resulting parameters are $\Delta H^\circ_1 = -6.0 \pm 1.6 \text{ kJ mol}^{-1}$ and $\Delta S^\circ_1 = 20 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$. Stated errors are one estimated standard deviation.

Data for the second step of complexation are not accurate enough to make a similar estimate of ΔH°_2 and ΔS°_2 possible.

Results from Solubility Measurements

The Solid Phase. When the composition of the solid phases was determined after equilibration, it appeared that they contained stoichiometrically an excess of chromate relative to silver in most cases. In order to find out whether the counterions to this excess chromate were Na⁺, K⁺, or both, systems with pure KNO₃ and pure NaNO₃ as solvents were prepared. Silver chromate (0.012 mol) was equilibrated with KNO₃ (0.88 mol) or NaNO₃ (0.88 mol) at 350 °C. Analyses showed that the mole fraction of Ag₂CrO₄, x_1 , in the solid phase was 0.92 in the sodium system, whereas no indication of any dissolution of K₂CrO₄ into the Ag₂CrO₄ phase could be detected in the potassium system. These findings gave the conclusion that sodium chromate from the (K,Na)NO₃ based melts is dissolved into the solid silver chromate.

Figure 2 gives the composition of the solid as a function of C_{Cr} in the nitrate melt. The mole fraction x_2 of Na₂CrO₄ in the (Ag,Na)₂CrO₄ solid rises as C_{Cr} increases, and around $C_{Cr} = 0.118 \text{ mol kg}^{-1}$ there is a steep increase in x_2 up to $x_2 = 0.53 \pm 0.05$, which suggests a phase transition from what can be described as an Ag₂CrO₄ based solid solution I to a Na-rich

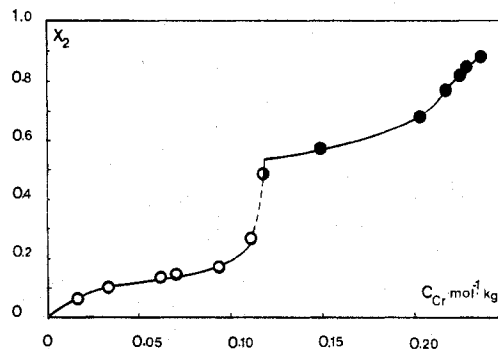


Figure 2. The fraction x_2 of Na₂CrO₄ in the solid phase as a function of C_{Cr} in the melt. Symbols: phase I (○); phase II (●). The half-filled symbol represents a formal value for a probable mixture of I and II at the transition point.

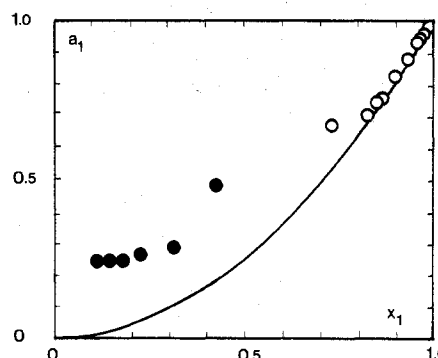


Figure 3. The activity a_1 of Ag₂CrO₄ as a function of x_1 in the solids. Symbols: phase I (○); phase II (●). The curve represents $a_1 = x_1^2$.

solid phase II with the lower composition limit $x_2 = 0.53$. As this value is determined by extrapolation, it is given with rather wide limits of error. As can be seen from Figure 2 there is again a smooth increase in x_2 for phase II as C_{Cr} is increased.

X-ray powder diffraction studies were made at room temperature on solids with $x_2 = 0.17$, 0.49, and 0.85, as well as on pure Ag₂CrO₄ and Na₂CrO₄. The diffraction pattern for phase I with $x_2 = 0.17$ was very similar to that of pure Ag₂CrO₄ and could be indexed on the basis of the same symmetry as Ag₂CrO₄ with very slight changes in the edge lengths. For phase II with $x_2 = 0.85$ the diffraction pattern was significantly different from those of Ag₂CrO₄ and Na₂CrO₄ which are both orthorhombic.^{17,18} It could, however, be properly indexed on the basis of a monoclinic symmetry with the cell parameters $a = 14.583$ (2) Å, $b = 5.024$ (1) Å, $c = 7.406$ (1) Å, and $\beta = 97.19$ (3)°.

For the powder with the formal composition $x_2 = 0.49$, we could observe significant diffraction lines from both phase I and II, which confirms the previous assumption that the transition I \rightleftharpoons II takes place when the total equilibrium concentration C_{Cr} is $0.118 \text{ mol kg}^{-1}$.

The activity a_1 of Ag₂CrO₄ in the solid phase has to be known in order that solubility data may be used for the determination of complex ion stabilities. a_1 is computed from

$$a_{1j} = \exp \left[\int_{\ln R_0}^{\ln R_j} (x_2/x_1) d \ln R \right] \quad (6)$$

where $R = (y^2[CrO_4^{2-}])^{-1}$ and $y = [Na^+]/([Na^+] + [K^+] + [Ag^+])$.^{8,19} The index j is used to denote different quantities referring to the same actual system and R_0 refers to a system

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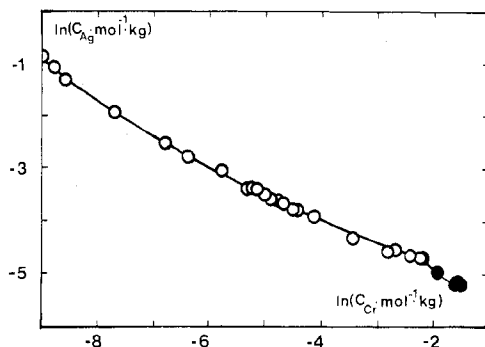
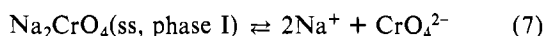


Figure 4. Solubility curve for $(\text{Ag,Na})_2\text{CrO}_4$ in 1:1 $(\text{K,Na})\text{NO}_3$ at 553 K. Open symbols represent melts in equilibrium with phase I; filled symbols represent melts in equilibrium with phase II.

with $x_1 = 1$ and $a_1 = 1$, i.e., the standard state chosen for Ag_2CrO_4 . Hence, the activity of Ag_2CrO_4 in phase II also relates to pure Ag_2CrO_4 . Figure 3 gives a_1 as a function of x_1 in the two solid phases.

In phase I a_1 is well described by the ideal Temkin relation $a_1 = x_1^2$ for $0.8 \leq x_1 \leq 1$, and the solid solutions can thus be regarded as random mixtures of Ag^+ and Na^+ on cation positions in the Ag_2CrO_4 lattice in this composition range. This implies that the activity of Na_2CrO_4 , a_2 , in phase I is given fairly well by $a_2 = x_2^2$. For the heterogeneous reaction



with the species of the right-hand member present in the nitrate melt, an equilibrium constant K_{Na}^{I} may be defined as

$$K_{\text{Na}}^{\text{I}} = [\text{CrO}_4^{2-}]y^2a_2^{-1} \quad (8)$$

The solubility data for the range $0.016 \leq C_{\text{Cr}} \text{ mol}^{-1} \text{ kg} \leq 0.094$ (corresponding to $0.07 \leq x_2 \leq 0.17$) have thus been utilized together with a set of $[\text{CrO}_4^{2-}]$ from the stability constant calculation (next section) and the relation $a_2 = x_2^2$ to yield a value of $K_{\text{Na}}^{\text{I}} = (0.83 \pm 0.08) \text{ mol kg}^{-1}$.

The a_1 data obtained for phase II exhibit substantial deviations from ideal and normal regular solution behavior (cf. Figure 3). Figure 3 shows that a_1 tends to a constant value around 0.25 if x_1 for phase II is extrapolated into the range $0 \leq x_1 \leq 0.1$. Since $x_1 = 0$ demands $a_1 = 0$, this behavior suggests that at least one more solid-phase transition has to take place in that composition range. This prediction is also supported by the fact that the X-ray powder diffraction patterns of phase II ($x_1 = 0.15$) and Na_2CrO_4 are quite different.

Complexation in the Range $2C_{\text{Cr}} > C_{\text{Ag}}$. Figure 4 surveys the experimental material.

A general expression for the solubility "product" of Ag_2CrO_4 is

$$K_s = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]/a_1 \quad (9)$$

By combination of eq 9 with eq 2 and 4, we obtain

$$C_{\text{Ag}}[\text{CrO}_4^{2-}]^{1/2}a_1^{-1/2} = K_s^{1/2} \left(1 + \sum_m \sum_n m\beta_{mn} [\text{Ag}^+]^{m-1} [\text{CrO}_4^{2-}]^n \right) \quad (10)$$

Inspection of the solubility curve shows that no species with more negative charge than 3- are formed. Since emf measurements clearly show the absence of polynuclear complexes in this composition range, all data were treated according to eq 10, assuming AgCrO_4^- and $\text{Ag}(\text{CrO}_4)_2^{3-}$ only. A second-degree polynomial in $[\text{CrO}_4^{2-}]$ that describes the experimental data $C_{\text{Ag}}[\text{CrO}_4^{2-}]^{1/2}a_1^{-1/2}$ can easily be found by iteration. $K_s^{1/2}$, $K_s^{1/2}\beta_{11}$, and $K_s^{1/2}\beta_{12}$ at 553 K are thus determined by a least-squares fit. K_s and the stability constants are collected in Table II.

Table II. Stability Constants and K_s for Ag_2CrO_4 in 1:1 $(\text{K,Na})\text{NO}_3$ at 553 K Determined by Different Experimental Methods^a

$10^6 K_s / \text{mol}^3 \text{ kg}^{-3}$	$\beta_{11} / \text{mol}^{-1} \text{ kg}$	$\beta_{12} / \text{mol}^{-2} \text{ kg}^2$	$\beta_{21} / \text{mol}^{-2} \text{ kg}^2$	method
6.4 ± 0.4	3.6 ± 1.2		8 ± 3	sol $C_{\text{Ag}} > 2C_{\text{Cr}}$
6.4 ± 1.0	4.2 ± 2.6	4 ± 10		sol $2C_{\text{Cr}} > C_{\text{Ag}}$
	4.1 ± 0.1	3.6 ± 1.1		emf

^a The errors are 95% confidence limits.

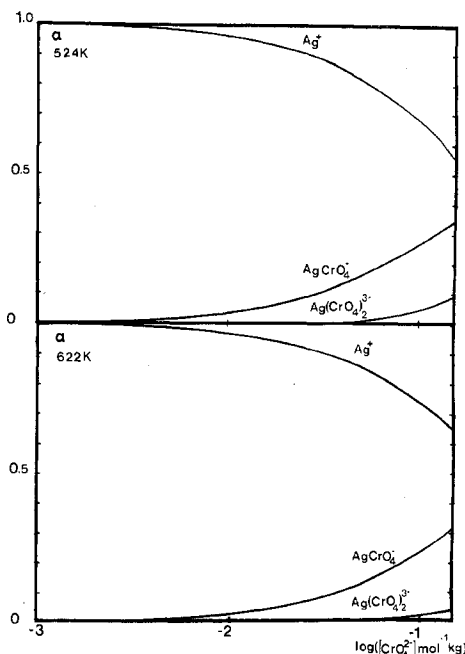


Figure 5. The fraction α of Ag(I) present in different species in molten 1:1 $(\text{K,Na})\text{NO}_3$ at 524 and 622 K as a function of the chromate concentration in the limit $C_{\text{Ag}} \rightarrow 0$. The graphs are calculated from the constants of Table I.

Complexation in the Range $C_{\text{Ag}} > 2C_{\text{Cr}}$. In analogy with eq 10, we have

$$C_{\text{Cr}}[\text{Ag}^+]^2a_1^{-1} = K_s \left(1 + \sum_m \sum_n n\beta_{mn} [\text{Ag}^+]^m [\text{CrO}_4^{2-}]^{n-1} \right) \quad (11)$$

From the shape of the solubility curve it is clear that a neutral complex has to be taken into account in a proper description model. Any complex of the composition $\text{Ag}_{2n}(\text{CrO}_4)_n$ may be considered, but we have made the reasonable assumption that the simplest species with the formal composition Ag_2CrO_4 is formed.

It should be mentioned that for even higher values of C_{Ag} than those displayed in Figure 4, the solubility, C_{Cr} , tends to increase with increasing C_{Ag} . This might be taken as an indication of the presence of complexes with $(m - 2n) > 0$, but we have refrained from any quantitative treatment of data for these melts which are extremely concentrated in AgNO_3 .

For the range covered by Figure 4, the experimental data $C_{\text{Cr}}[\text{Ag}^+]^2a_1^{-1}$ are well described by a second-degree polynomial in $[\text{Ag}^+]$. An iterative least-squares calculation process yields K_s , $K_s\beta_{11}$, and $K_s\beta_{21}$ at 553 K. The results are found in Table II.

Discussion

As might be expected the tendency of Ag^+ to associate with CrO_4^{2-} is rather weak in molten alkali nitrate. Figure 5 shows the relative amounts α of the different silver-containing species as a function of $[\text{CrO}_4^{2-}]$ in melts having CrO_4^{2-} in excess over Ag(I) at 524 and at 622 K. Ag^+ and AgCrO_4^- are the dom-

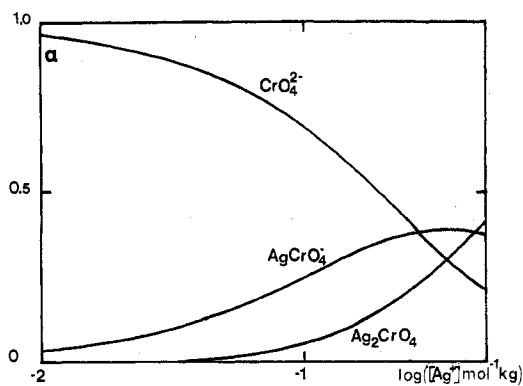


Figure 6. The fraction α of CrO_4^{2-} present in different species in molten 1:1 (K,Na)NO₃ at 553 K as a function of $[\text{Ag}^+]$ in the limit $C_{\text{Cr}} \rightarrow 0$. The graphs are calculated by use of the values $\beta_{11} = 3.6 \text{ mol}^{-1} \text{ kg}$ and $\beta_{21} = 8 \text{ mol}^{-2} \text{ kg}^2$ (cf. Table II).

inating species, and $\text{Ag}(\text{CrO}_4)_2^{3-}$ contributes at most to only 9% of C_{Ag} at the lower temperature, 524 K, and is practically negligible at 622 K in the concentration range covered by our measurements. Figure 6 gives an analogous overview of the stepwise attachment of Ag^+ to one CrO_4^{2-} ion at 553 K. As can be seen from the distribution curves, the second complex Ag_2CrO_4 is present in amounts quite comparable to those of AgCrO_4^- in melts of high Ag^+ contents. The maximum fraction $[\text{AgCrO}_4^-]/C_{\text{Cr}}$ amounts to about 0.4 in such melts.

Table II displays a comparison between stability constants and K_s determined by different methods at 553 K. Although the results agree within the estimated limits of uncertainty, it is quite evident that potentiometric data yield the most precise estimate of β_{11} . The large uncertainty in β_{12} from solubility data is an obvious consequence of the low stability of $\text{Ag}(\text{CrO}_4)_2^{3-}$ in combination with the complications brought about by the $\text{Na}^+ - \text{Ag}^+$ liquid-solid ion exchange in systems with melts of high CrO_4^{2-} contents. Due to the selective solubility of Na_2CrO_4 in the solid phase the K:Na ratio of the melts was at most shifted from 1:1 to 1.18:1. The difference in cationic composition might influence the complexation to a slight extent, but such a systematic effect is obviously hidden within the wide limits of random errors.

Our value of $K_s = 6.4 \times 10^{-6} \text{ mol}^3 \text{ kg}^{-3}$, which is obtained from both branches ($C_{\text{Ag}} > 2C_{\text{Cr}}$ and $2C_{\text{Cr}} > C_{\text{Ag}}$) of the solubility isotherm, compares badly with previous determinations. Brookes and Flengas²⁰ obtained $K_s = 1.3 \times 10^{-7} \text{ mol}^3 \text{ kg}^{-3}$ in 1:1 (K,Na)NO₃ at 553 K spectrophotometrically, and Flengas and Rideal²¹ roughly estimated K_s to be $1.0 \times 10^{-6} \text{ mol}^3 \text{ kg}^{-3}$ in the same solvent at 523 K from emf titration data. These discrepancies are most probably due to the fact that the formation of solid solutions $(\text{Ag,Na})_2\text{CrO}_4$ was disregarded in ref 20 and 21.

Visual observations of chromate-containing melts showed that the yellow CrO_4^{2-} color tended to get paler if Ag^+ were present in high concentrations. A number of absorption spectra of chromate in different cation environments were therefore recorded at 553 K. Our primary aim was to see if any support for the interpretation of thermodynamic data in terms of complex formation with Ag^+ could be found in the spectra. Figure 7 compares three instructive absorption spectra. Spectrum 1 is due to absorption (A_1) by pure (K,Na)₂CrO₄ in (K,Na)NO₃ ($C_{\text{Cr}} = 1.2 \times 10^{-4} \text{ mol kg}^{-1}$ or $2.3 \times 10^{-4} \text{ M}$). Spectrum 2 gives the absorbance A_2 from a melt with the same chromate concentration, $1.2 \times 10^{-4} \text{ mol kg}^{-1}$, and a large excess of Ag^+ added as AgNO_3 ($C_{\text{Ag}} = 0.20 \text{ mol kg}^{-1}$ or 0.39 M). For the sake of comparison the absorbance A_3 of a chro-

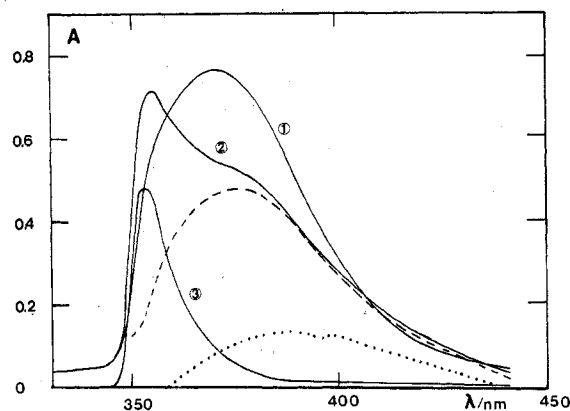


Figure 7. The absorbance A for solutions of 1, $1.2 \times 10^{-4} \text{ mol kg}^{-1}$ (K,Na)₂CrO₄ (A_1); 2, $1.2 \times 10^{-4} \text{ mol kg}^{-1}$ (K,Na)₂CrO₄ + 0.20 mol kg^{-1} AgNO_3 (A_2); and 3, 0.20 mol kg^{-1} AgNO_3 (A_3) in molten 1:1 (K,Na)NO₃ at 553 K in 10.00-mm cell. The spectra are recorded vs. pure solvent. Difference curves: $A_2 - A_3$ (dashed) and $A_2 - A_3 - 0.50A_1$ (dotted).

Table III. Characteristics of the Low-Energy Absorption Band of CrO_4^{2-} in Aqueous Solution and Ionic Melts

medium	T/K	$\lambda_{\text{max}}/\text{nm}$	$10^{-3} \times \epsilon_{\text{max}}/\text{M}^{-1} \text{ cm}^{-1}$	ref
H ₂ O	298	370	4.10	23
KNO ₃	635	371	3.38	24
(K,Na)NO ₃ , 1:1	553	371	3.60	20
(K,Na)NO ₃ , 1:1	553	371	3.30	this work
(K,Li)NO ₃ , eut	433	369	3.62	25, 26
(K,Li)Cl, eut	643	371	3.08	24

mate-free AgNO_3 solution, 0.20 mol kg^{-1} , is also displayed in Figure 7.

The low-energy band of charge-transfer character of CrO_4^{2-} in an alkali metal ion environment is found at the wavelength $\lambda_{\text{max}} = 371 \text{ nm}$ with a molar absorption coefficient $\epsilon_{\text{max}} = 3.30 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in good agreement with the observations by Brookes and Flengas.²⁰ Spectrum 3 shows that the presence of AgNO_3 in the alkali nitrate melt causes a relatively strong absorption in the 355-nm region, close to the UV absorption edge of the (K,Na)NO₃ solvent itself. (Changes in refractive index are estimated to affect the absorbance to less than 1%.) This absorption peak also appears in spectrum 2 of course, but since C_{Ag} is the same in melts 2 and 3 and since $C_{\text{Cr}} \ll C_{\text{Ag}}$ in melt 2, the absorbance due to chromate species only can be derived simply as $A_2 - A_3$. This is the dashed curve of Figure 7.

A_1 and the dashed curve $A_2 - A_3$ are directly comparable, since C_{Cr} is the same and the calculated mass densities only differ by an amount of 2%. Previously published data show that changes in cation environments in ionic melts influence this absorption band, which has been ascribed to the $t_1 \rightarrow e$ transition²² in CrO_4^{2-} , to a very small extent. This is clear from the data collected in Table III. Smith and Boston²⁴ have also observed that the spectral profiles of this band in pure LiNO₃ and CsNO₃ closely follow that for KNO₃. The effect of the presence of Ag^+ in the (K,Na)NO₃ melt (less than 2% of the total cation content) is thus remarkably large in view of these general observations. It can be seen from Figure 6 that our solubility data predict a distribution of chromate in melt 2 as

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6×10^{-5} mol kg^{-1} CrO_4^{2-} , 4×10^{-5} mol kg^{-1} AgCrO_4^- , and 2×10^{-5} mol kg^{-1} Ag_2CrO_4 . The absorbance contribution from only AgCrO_4^- and Ag_2CrO_4 can therefore be deduced by subtraction of $0.50A_1$ from $A_2 - A_3$. The result is represented by the dotted spectrum of Figure 7: a broad field of absorption in the 360–440-nm region with an indication of two maxima around 385 and 400 nm.

The dotted spectrum could of course be tentatively regarded as consisting of two partially overlapping bands with individual maxima at about 380 and 400 nm due to AgCrO_4^- and Ag_2CrO_4 , respectively. At the present state such an assignment would be of a too speculative nature, but the matter certainly deserves a more quantitative and exhaustive experimental study than this preliminary one. Qualitatively, however, the shift toward lower energies upon Ag^+ association is rather interesting. A significant cation–oxygen σ bonding, utilizing the oxygen lone-pair electrons, should rather be expected to change the absorption band toward higher energies. Such spectral changes have been observed upon, e.g., protonation of CrO_4^{2-} to HCrO_4^- with λ_{max} shifted from 370 to 351 nm.^{27,28} Therefore it seems probable that the change toward lower energies for the Ag-coordinated CrO_4^{2-} ion in nitrate melts is a result of an additional d– π back-donation of electrons from silver to chromate. The spectral observations discussed here thus furnish strong evidence for the existence of complexes with a chemical interaction between Ag(I) and CrO_4^{2-} which is fundamentally different from the alkali metal– CrO_4^{2-} interactions in the nitrate melts.

The quasi-lattice theory²⁹ has been used by Sacchetto and co-workers⁶ in an attempt to rationalize data for Ag(I) association with CrO_4^{2-} in nitrate melts. Our results, however, clearly demonstrate the inapplicability of the quasi-lattice

formalism for systems of this kind, containing polyvalent polyatomic ions. The apparent pair association energy ΔA_1 of the model tends to be strongly temperature dependent. A coordination number of 5 yields $d\Delta A_1/dT = -9 \pm 2$ J mol^{-1} K^{-1} , which—for reasons discussed in a previous paper on iodate complexation²—is incompatible with both internal entropy and mixed-solvent effects.⁶

Our analysis of the thermodynamics for the formation of AgCrO_4^- , schematically described by process 1, shows that the association reaction is favored to approximately the same extent by its exothermic character and by the gain in entropy at 553 K. This pattern is somewhat different from that of the $\text{Ag}^+ - \text{IO}_3^-$ association in the same solvent, which is driven by a large entropy gain only.² The minute ΔH°_1 for the IO_3^- association was found to be about the expected one if contributions from changes in electrostatic interactions between hard-sphere model ions were considered only. An analogous model calculation for the CrO_4^{2-} association should probably consider the uncomplexed CrO_4^{2-} as selectively Na^+ -solvated. A hard-sphere interchange with Ag^+ would then yield a positive contribution to ΔH°_1 . The absolute magnitude of such an electrostatic contribution is very much depending on the choice of effective radius for CrO_4^{2-} , but one is inclined to believe that the covalent character of the $\text{Ag}^+ - \text{CrO}_4^{2-}$ bonding—as evidenced by the spectral changes—most probably causes a larger energy gain than -6 kJ mol^{-1} , which is the overall enthalpy change.

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Registry No. Ag_2CrO_4 , 7784-01-2; Na_2CrO_4 , 7775-11-3; KNO_3 , 7757-79-1; NaNO_3 , 7631-99-4; Ag , 7440-22-4.

Supplementary Material Available: Tables IV and V, giving all experimental data from solubility and emf measurements (8 pages). Ordering information is given on any current masthead page.

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Synthesis of Neodymium and Samarium Monoxides under High Pressure

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Under high pressure the neodymium and samarium sesquioxides react with the pure metals, which is not the case at ordinary pressure. The new compounds, recovered at normal pressure probably in a metastable state, have a face centered cubic structure and their cell parameters are respectively 4.994 and 4.943 Å. Chemical analyses do not show major contamination by hydrogen, carbon, or nitrogen. The lattice constant of the neodymium compound is equal to the value calculated for the monoxide on the assumption that the metal is in the trivalent state; for samarium it is slightly larger. Samarium appears to be in a valence state slightly lower than 3. No reaction is observed for thulium although a large range of pressures and temperatures were investigated (10–80 kbar, 500–1200 °C).

Introduction

Until recently bulk preparations of the rare earth monoxides, except for europium monoxide, could not be obtained despite numerous attempts using various techniques (oxidation of the metal, reduction of the sesquioxide by different agents, reactions in open or closed systems). It is now well established^{1,2} that the compounds^{3–5} made with the EuO structure (NaCl

type) were in fact compounds containing large quantities of hydrogen, carbon, or nitrogen. Reported preparations of SmO thin films⁶ with the unlikely zinc blende structure have been demonstrated to be hydride phases.⁷ However, recently Léger et al.⁸ showed that application of high pressures allowed the synthesis of ytterbium monoxide. Whereas the calculated

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