

REACTIONS OF SILICA WITH ALKALI CHROMATES

JAN HLAVÁČ, KATEŘINA MARUŠKOVÁ

*Department of Glass and Ceramics,
Institute of Chemical Technology, Technická 5, 166 28 Prague*

Received 31. 7. 1995

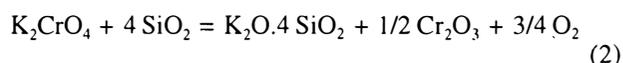
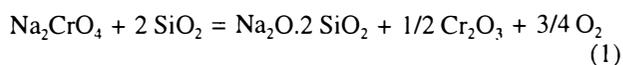
On the basis of experience gained with melting glasses containing chromates in the batch, the authors assume that alkali chromates react at high temperatures in air spontaneously with silica, forming Cr_2O_3 and alkali silicate, and liberating oxygen. The assumption was experimentally verified on mixtures of SiO_2 with sodium and potassium chromates, at 2:1 and 4:1 ratios, using DTA, GTA, X-ray diffraction and gas chromatography of the gaseous reaction products. It has been proved by GTA that the reaction of SiO_2 with Na_2CrO_4 takes place over the range of 1073 to 1120 °C, and that with K_2CrO_4 at 1220 to 1360 °C.

INTRODUCTION

Immobilization of radioactive wastes by vitrification (i.e. by fusion into a glass matrix) can also be applied to wastes containing alkali chromates; however, in that case the chromates have first to be reduced to chromic oxide so as not to produce a separated phase. With current types of silicate and borosilicate glasses, the reduction proceeds spontaneously, yielding tabular crystals of Cr_2O_3 which remains fixed in the vitreous matrix without impairing its chemical and mechanical integrity. The phenomenon has long been utilized in traditional glass-making in the manufacture of paste jewellery glass called chrome aventurine [1].

The cause of this spontaneous reaction of chromates has not yet been fully explained; it occurs in the temperature region where chromates as such are still completely stable. Sodium and potassium chromates melt at about 790 °C and 968 °C respectively [2] and their vaporization starts at about 1300 °C. When polyvalent oxides are present in the glass, the cause of the reduction is obvious. Practical experience shows that in the course of glass melting chromates donate oxygen to all other polyvalent oxides present at their lower oxidation levels. They react very readily in particular with FeO, As_2O_3 , and others [3]. However, the reduction takes place even when melting glasses free of any components capable of being oxidized. The chemical nature of glass manifests itself so that the reduction of chromates is promoted above all by the acidic components of glass, SiO_2 and B_2O_3 , whereas the basic components increase the solubility of Cr^{VI} in glass [4]. These effects of chemical composition of glass can be expressed by means of quantified basicity parameters [5].

In order to explain the spontaneous reduction in the absence of reducing agents, the present authors expressed the assumption^{*)} that the reduction proceeds as a result of a reaction with SiO_2 , according to the following equations which include stable alkali silicates as products:



The present study was aimed at verifying this assumption.

Thermodynamic analysis

Calculation of the change in standard Gibbs energy for the given reactions was carried out with the use of tabular thermodynamic data [6] according to the equation

$$\Delta G_r^0 = \Delta G_{f(\text{prod})}^0 - \Delta G_{f(\text{reactants})}^0 \quad (3)$$

where ΔG_r^0 is the change in standard Gibbs energy during the reaction, ΔG_f^0 is the Gibbs energy of formation.

The results are plotted in Figure 1 together with the calculated pressure of oxygen liberated during the reaction. The following relationships were used in the latter calculation:

^{*)} The ratio of reacting components has been chosen with the highest possible SiO_2 content with regard to the stability of the silicate products (the stability being indicated by the respective phase diagrams), and with respect to the availability of the thermodynamic data.

$$\Delta G_r^0 = -RT \ln K$$

$$\ln K = 0.75 \ln p_{\text{O}_2} / p^0$$

where K is the equilibrium constant, p^0 is the atmospheric pressure of 101.325 kPa, i.e. 1 atm.

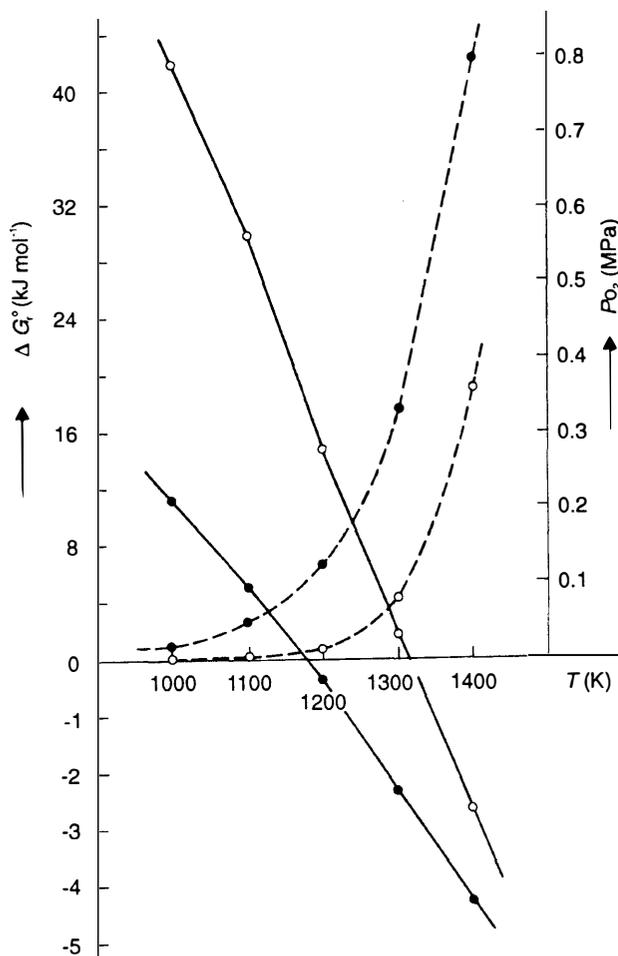


Figure 1. Calculation of Gibbs energy and partial oxygen pressure for reactions (1) and (2)

— G_r^0 , ● reaction (1); - - - p_{O_2} , ○ reaction (2)

The calculations showed that from the standpoint of thermodynamics, the reaction of alkali chromates with silica dioxide is viable at temperatures above 1180 K for sodium chromate, and above 1315 K for potassium chromate.

EXPERIMENTAL PART

The reaction was studied by several methods which are mutually complementary. Use was made of a mixture of silica sol (stabilized with NH_3 , containing 29.27 % SiO_2) and aqueous solutions of sodium and potassium chromates.

The reaction mixture was prepared by pipetting the appropriate amounts of both liquids into teflon crucibles so as to achieve a molar ratio of 2:1 for reaction (1), and one of 4:1 for reaction (2). The mixture was then heated in an oven at 150 °C. The resulting dry powder was ground in an agate mortar and used in the experiments either directly or after compacting, by a pressure of 50 to 100 MPa, into pellets 2 mm in thickness and 0.25 g in weight. Prior to high-temperature exposure, the pellets were pre-annealed for three hours at 600 °C; this treatment has changed their colour to light yellow. A permanent colour transition from yellow over orange to the final green takes place with reaction (1) by 30-minute exposure to temperatures above 1050 °C. At 1160 °C, the mixture containing potassium chromate still remained orange with a minute greenish hue.

The powdered mixtures were subject to DTA and GTA measurements, and determination of oxygen by gas chromatography. The pellets were used in experiments concerned with determining the loss in weight following isothermal exposure to various temperatures. The reaction products were studied by X-ray phase analysis.

Differential thermal analysis

The measurements were made on an apparatus constructed at the Central Laboratory of the Institute. Sample weight was 70 mg, temperature was measured with a Pt/PtRh10 thermocouple, and a heating rate of 7.5 °C min^{-1} was used. The powdered samples were pre-annealed for 4 h at 500 °C. The results for sodium chromate are plotted in Figure 2. The curve of chromate alone exhibits two characteristic endothermic peaks at 428 °C and 800 °C. Both temperatures correspond well with data from the literature, according to which the former temperature is that of a polymorphous inversion (413 °C), and the latter that of melting temperature, specified at 780 °C and 792 °C respectively [2]. The SiO_2 gel obviously keeps its amorphous form. The DTA curve of the mixture shows three endothermic effects, of which the first two correspond to polymorphous inversion and chromate melting, and the third one is assumed to indicate reaction (1), with a peak minimum at 1055 °C. Figure 3 presents the results for potassium chromate, which also has two endothermic effects at 675 °C and 972 °C. The temperature of 675 °C corresponds to a change in modification, involving a change from the lemon yellow colour to a red one, and the other temperature is that of melting. Temperature ranges from 940 °C to 984 °C are reported in the literature, the most frequent value being 968 °C. The curve of the mixture has a course similar to that of the sodium chromate mixture. The first two effects correspond to a polymorphous inversion and to the melting of potassium chromate, while the effect of reaction (2) is not apparent.

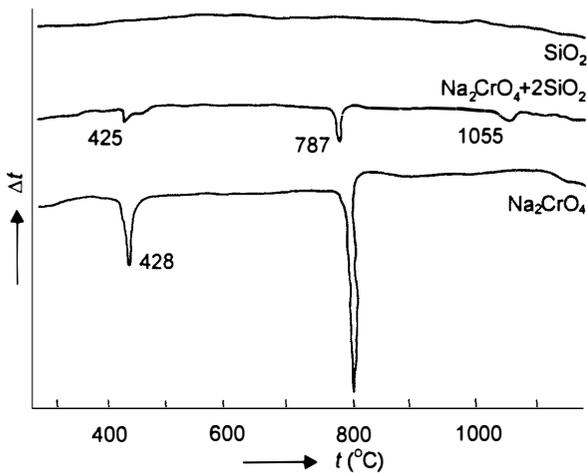


Figure 2. DTA record for the system $\text{Na}_2\text{CrO}_4\text{-SiO}_2$

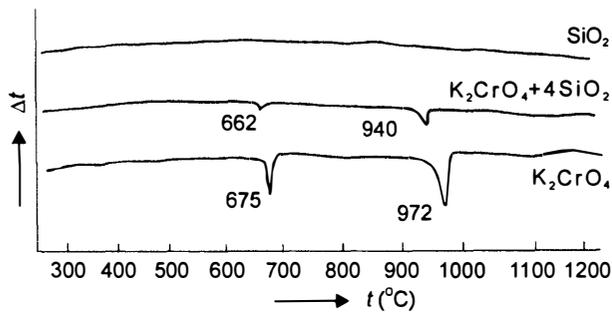


Figure 3. DTA record for the system $\text{K}_2\text{CrO}_4\text{-SiO}_2$

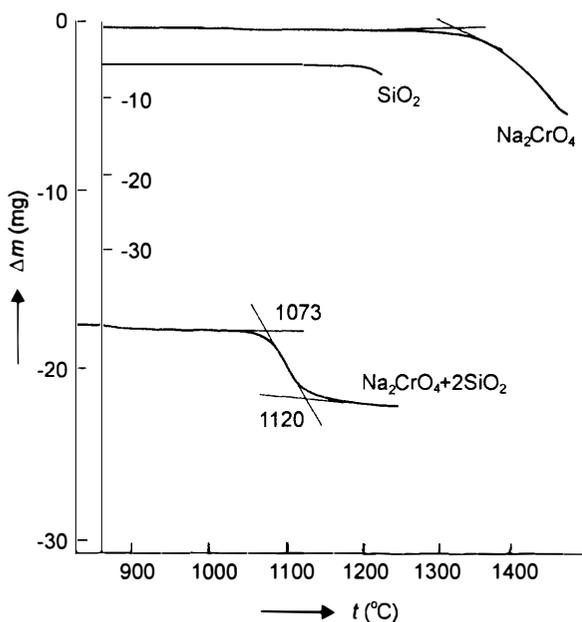


Figure 4. GTA record for the system $\text{Na}_2\text{CrO}_4\text{-SiO}_2$

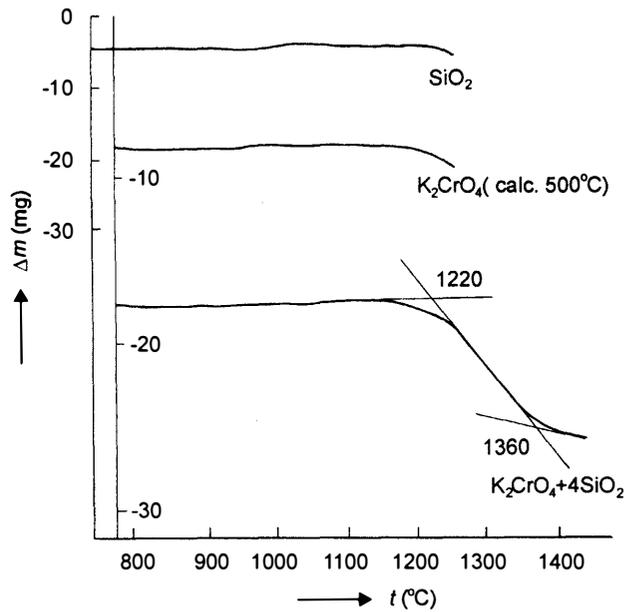


Figure 5. GTA record for the system $\text{K}_2\text{CrO}_4\text{-SiO}_2$

Gravimetric thermal analysis

The curves were obtained from Derivatograf Q-1500 D. The sample weight was 100 mg and the heating rate employed was $7.5\text{ }^\circ\text{C min}^{-1}$. The results are plotted in Figures 4 and 5. The temperature of reaction (1) is indicated over the interval of $1073 - 1120\text{ }^\circ\text{C}$, and that of reaction (2) over the interval $1220 - 1360\text{ }^\circ\text{C}$, which is in agreement with the data obtained from DTA. To assess a possible effect of compacting the powder, GTA was carried out on powdered mixtures as well as on compacted pellets of sodium chromate and silica, in this case at the 1:4 molar ratio. The difference in the reaction temperatures (cf. Figure 6) is very small, so that it may be concluded that the oxygen escaping from the reaction mixture represents no significant limiting factor. During thermal exposure of a powdered sample in a Pt boat the powder showed a higher degree of reacting at the points of contact with the boat, and moreover, the reaction product was difficult to remove from the boat. Because of the finding shown in Figure 6, pellets suspended on a Pt wire device were used in the isothermal exposures.

Gas chromatography

The method was used to assess the assumption that the loss in weight according to reactions (1) and (2) is caused by liberated oxygen. Use was made of the apparatus employed in analyses of gases escaping in the course of glass melting. The samples 1 g in weight were

placed in a silica glass flask which was heated at a rate of $6\text{ }^{\circ}\text{C min}^{-1}$ and through which an inert gas (He) was passed at a controlled rate, carrying the released gas into the carrier gas circuit of the gas chromatograph. Figure 7 shows the total amount of oxygen liberated during reaction (1), as calculated from the concentration data. In comparison with the GTA and DTA curves, the curve representing the rate of oxygen release is shifted towards lower temperatures (with its onset at about $900\text{ }^{\circ}\text{C}$), pro-

bably as a result of the low partial pressure of oxygen. The liberation of oxygen takes place in two steps which cannot be explained without a more detailed study.

X-ray diffraction

The X-ray phase analysis was carried out on the DRON-UM-1 diffractometer, using CrK-alpha radiation. Analysis of a sample $\text{Na}_2\text{CrO}_4+2\text{SiO}_2$ that had been exposed at $1150\text{ }^{\circ}\text{C}$ for six days revealed the presence of crystalline Cr_2O_3 - eskolaite. A comparison of the experimentally established and tabular values of interplanar distances d is given in Table I. Apart from eskolaite also sodium chromium silicate (ureyite) was found in the reaction product after short time exposure at lower temperatures (to be published later).

Table I. Tabular and experimentally established values of interplanar distances d [\AA], evidence for the presence of crystalline Cr_2O_3 - eskolaite

Tabular values of d (\AA)	Measured values of d (\AA)
3.633	3.627
2.666	2.666
2.480	2.478
2.176	2.175
1.815	1.813

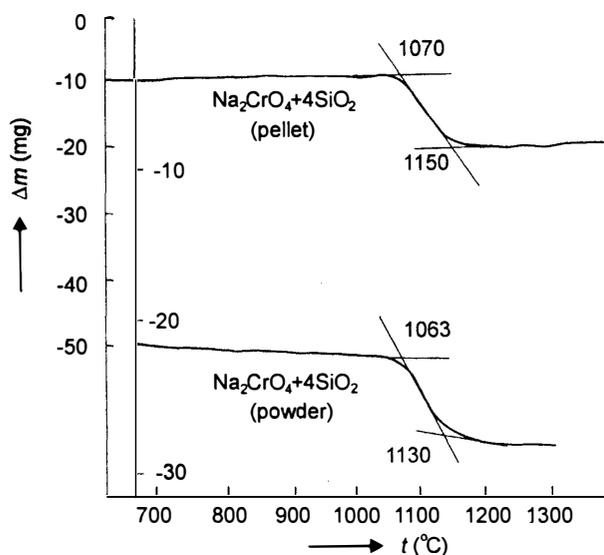


Figure 6. GTA record for the system $\text{Na}_2\text{CrO}_4+4\text{SiO}_2$ in pellet form and in powder form

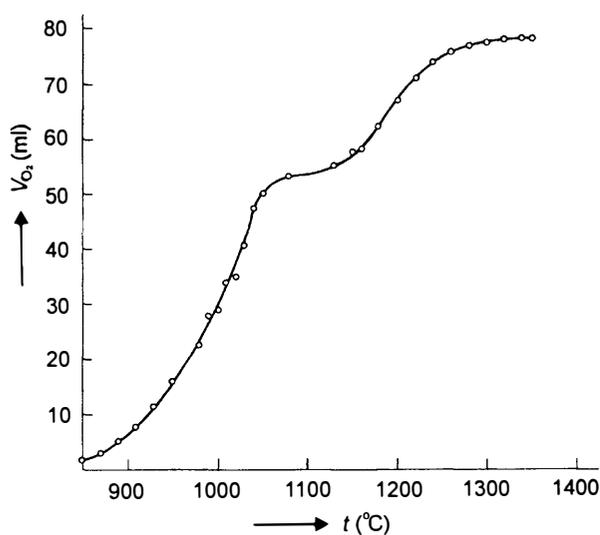


Figure 7. The amount of O_2 released during reaction (1), as recorded by gas chromatography

CONCLUSION

It has been proved that the assumed reaction actually takes place, indirectly by DTA and GTA, and directly by determining the escaping oxygen and by identifying chromic oxide (eskolaite) in the product by X-ray phase analysis. However, the reaction mechanism is more complex than that presumed by the simple equations 1 and 2 (see X-Ray diffraction). The reaction starts at atmospheric pressure at a well measurable rate about $100\text{ }^{\circ}\text{C}$ above the temperature at which standard Gibbs energy for the respective reactions acquires negative values. The compaction degree of the samples had no substantial effect on the reaction temperature, and it may be therefore assumed that it will not influence significantly the kinetics of the reaction proceeding at temperatures above the melting points of the chromates, as well as above those of the silicate products.

Acknowledgement

The authors wish to thank Dr. J. Kloužek, for making available the gas chromatograph and providing expert advice, to Mgr. J. Ederová for carrying out the thermal analyses, and to Dr. J. Maixner for X-ray analysis.

References

1. Volf M.B.: *Chemical Approach to Glass*, Elsevier, Amsterdam-Oxford-New York-Tokyo 1984.
2. *Gmelins Handbuch der Anorganischen Chemie*, 8. Auflage, Chrom. Teil B, System No. 52, Springer Verlag, Weinheim 1962.
3. Schreiber H.D. et al.: *Phys.Chem.Gl.* 27, 152 (1986).
4. Weyl W.A.: *Coloured Glasses*, The Society of Glass Technology, Sheffield 1951, p. 141, etc.
5. Uhlmann D.R., Kreidl N.J.: *Optical Properties of Glass*, American Ceramic Society 1991, pp. 159-184.
6. Barin I., Knacke O.: *Thermochemical Properties of Inorganic Substances*, Verlag Stahleisen, Düsseldorf 1973.

Translated by K. Němeček

REAKCE OXIDU KŘEMIČITÉHO
S ALKALICKÝMI CHROMANY

JAN HLAVÁČ, KATEŘINA MARUŠKOVÁ

*Ústav skla a keramiky, Vysoká škola chemicko-technologická,
Technická 5, 166 28 Praha*

Na základě zkušeností s tavením skel s obsahem chromanů ve vsázce byl vysloven předpoklad, že alkalické chromany reagují za vysokých teplot na vzduchu s oxidem křemičitým za tvorby Cr_2O_3 , alkalického křemičitanu a za uvolňování kyslíku. Reakce tohoto typu nebyly zatím v literatuře popsány. Výpočet pomocí tabelovaných dat ukázal, že jsou termodynamicky schůdné.

Experimentálně byly tyto reakce sledovány ve směsích SiO_2 s chromanem sodným a draselným v molárním poměru 2:1 a 4:1. Směsi byly připraveny ze solu SiO_2 a vodných roztoků chromanů vysušením. Poměr SiO_2 a chromanu byl zvolen s ohledem na stabilitu vznikajících křemičitanů a na dostupnost termodynamických dat. K prokázání průběhu reakce byly zvoleny metody DTA a GTA, z nichž první zaznamenala endotermní efekty, druhá pak současný úbytek hmotnosti, objevující se pouze ve směsi, nikoliv u samotných složek. Plynovou chromatografií bylo prokázáno uvolňování plynného kyslíku v tomtéž rozmezí teplot. Rtg fázová analýza ukázala při nejvyšších teplotách vznik krystalického Cr_2O_3 - eskolaitu s dobře vyvinutou strukturou. Předpokládané reakce tedy skutečně probíhají, a to podle GTA v oblasti teplot 1073 až 1120 °C v případě Na_2CrO_4 a v rozmezí 1220 až 1360 °C v případě K_2CrO_4 . Obě tato teplotní rozmezí leží nad body tání obou chromanů i vznikajících křemičitanů.