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Sodium Dichromate Monohydrate

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Abstract

When crystals of sodium dichromate dihydrate are heated at 1 atm pressure, the phase change

$$Na_2Cr_2O_7,2H_2O \rightarrow Na_2Cr_2O_7,H_2O + \text{saturated solution}$$

occurs at 82·8°C with the absorption of 17·6±0·95 kJ per mole of dihydrate. A second phase change

$$Na_2Cr_2O_7,H_2O \rightarrow Na_2Cr_2O_7 + \text{saturated solution}$$

occurs at 91·1°C with the absorption of a further 12·4±1·5 kJ per mole of dihydrate.

There have been many investigations of the phase equilibria (see ref.[1], which also cites eight references to the more reliable previous studies) and the solubility relationships[2] in the system $Na_2Cr_2O_7+H_2O$. It has not been noted previously that the solid phase in equilibrium with the saturated aqueous solution in the temperature range 82·8–91·1°C is a monohydrate.

Differential Scanning Calorimetry

Samples from four different batches, A–D, of commercial sodium dichromate dihydrate were dried by heating at 75°C for 2 days and then for 1 day at 125°C. The molar ratios, $H_2O : Na_2Cr_2O_7$, deduced were: A, 2·0052±0·0008; B, 1·9915±0·0001; C, 1·9892±0·0001; D, 1·9621±0·0001. Drying to constant weight by direct heating at 125°C is difficult since small amounts of water are retained in the hard cake of material that results from the two phase changes below 100°C.

All samples of the dihydrate, when heated in a Perkin–Elmer 1B differential scanning calorimeter (d.s.c.) with helium as the coolant and carrier gas, showed two endotherms below 100°C. The curve *1* of Fig. 1 shows the two endotherms recorded with sample B in a volatile-sample pan with a perforated lid, while curve *2* shows the simultaneous record from the katharometer monitoring the exit gas. The curve *3* shows the endotherms in a similar experiment when the perforation was covered by a 2-mg ball bearing (1/32 in.). In this case no displacement of water vapour by helium was indicated by the katharometer. The endothermic changes therefore occur in a condensed system and, during each, two solid phases are in equilibrium

[1] Hartford, W. H., *Ind. Eng. Chem.*, 1949, **41**, 1993.
[2] Seidell, A., 'Solubilities of Inorganic and Metal Organic Compounds' (4th Edn revised by W. F. Linke) Vol. 2, p. 1027 (American Chemical Society: Washington 1965).

with a saturated solution. There are not two solid phases of the dihydrate at the first transition since the saturated solution at 80°C has a molar ratio, $H_2O : Na_2Cr_2O_7$, greater than two,[1,2] nor two solid phases of the anhydrous salt at the second transition since the salt formed by complete dehydration in air at 70°C shows no further phase change below 200°C.

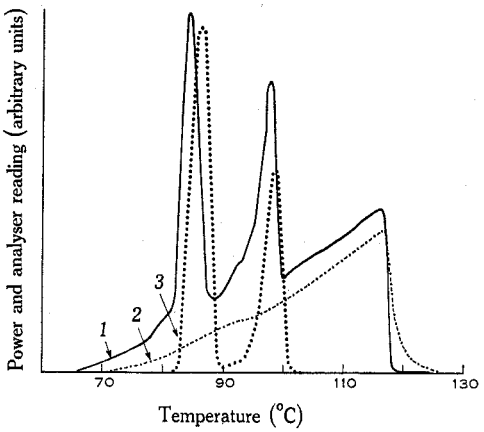

Fig. 1. D.s.c. endotherms.
1, $Na_2Cr_2O_7,2H_2O$ in volatile-sample pan with perforated lid, heated in He atmosphere at 2 K min^{-1};
2, effluent analyser reading corresponding to *1*;
3, $Na_2Cr_2O_7,2H_2O$ in volatile-sample pan but with perforation in lid covered by 2-mg ball bearing, heated at 2 K min^{-1}.

Preparation of $Na_2Cr_2O_7,H_2O$

(A) A sample of $Na_2Cr_2O_7,2H_2O$ was placed in a tube which had a sintered glass disc (porosity 0) sealed across it towards the lower end. The whole was enclosed in a tightly stoppered outer tube and heated in an oven at 80–82°C for several days. Saturated solution drained from the crystals which were removed and pressed between filter papers to remove as much as possible of the adhering mother liquor. The residual liquid formed some dihydrate as impurity. The best preparation contained 1·022, 1·029 mole of water per mole of dichromate and gave the d.s.c. scan shown as *2* in Fig. 2.

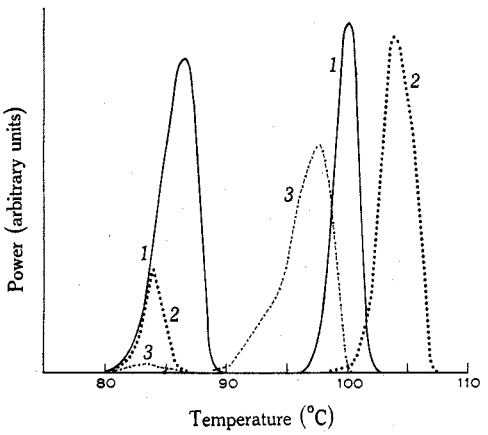

Fig. 2. D.s.c. endotherms.
1, $Na_2Cr_2O_7,2H_2O$ in volatile-sample pan with perforation in lid covered by 2-mg ball bearing, heated at 1 K min^{-1};
2, $Na_2Cr_2O_7,H_2O$ containing a little $Na_2Cr_2O_7,2H_2O$ prepared by partial melting method, heated at 1 K min^{-1};
3, $Na_2Cr_2O_7,H_2O$ containing trace of $Na_2Cr_2O_7,2H_2O$ prepared by treating $Na_2Cr_2O_7,2H_2O$ with $Na_2Cr_2O_7$ at 65°C for 2 days, heated at 1 K min^{-1}.

A finely ground sample of the monohydrate, covered with a thin film of polythene (commercial 'Gladwrap'), gave an X-ray diffraction pattern with the strongest peaks at 2θ values of 9·47°, 10·26°, 14·80°, 18·29°, 22·18°, 26·25°, 31·19°, 34·19°.

(B) An equimolar mixture of $Na_2Cr_2O_7,2H_2O$ and $Na_2Cr_2O_7$ was finely ground and heated in a sealed container at 65°C for 2 days. As indicated by curve *3* of Fig. 2 the product showed only a trace of the first endotherm but a strong second endotherm. It also gave the X-ray diffraction pattern of the monohydrate.

The infrared absorption spectra of the two preparations showed the typical pattern for the dichromate ion,[3] with absorptions at 960, 940, 904, 882 cm^{-1} and the absorption characteristic of the scissor deformation vibration of H_2O at 1620 cm^{-1}. The substance is therefore a true monohydrate and not the sodium bichromate ($NaHCrO_4$) which would have the same analytical composition.

Heats of Phase Changes

A sample of zone refined naphthalene (ΔH_f 18·98 kJ mol^{-1}) and a National Bureau of Standards sample of acetanilide, which was shown by the d.s.c. method to have a molar purity greater than 99·9% (ΔH_f 22·01 kJ mol^{-1}), were used to determine the area per kilojoule on the d.s.c. charts. While the total energy absorbed in the two endotherms during the heating of the dihydrate was consistent for all samples A–D at 30·05 kJ mol^{-1}, with a standard deviation of 0·44 kJ mol^{-1} for 17 determinations, there was a considerable variation in the relative areas of the two constituent endotherms. This was due, particularly with sample A, to the intrusion of the metastable transition

$$Na_2Cr_2O_7,2H_2O \rightarrow Na_2Cr_2O_7 + \text{saturated solution} \qquad \text{(i)}$$

which Hartford[4] has shown to occur at 84·6°C. True equilibrium is difficult to obtain in the small, unstirred and unseeded samples used in differential scanning calorimetry.[5] The most reproducible results were obtained with sample D, which, according to its water content, contained sufficient monohydrate to provide seeding nuclei. Eight determinations with this sample, after correction for the reduced content of dihydrate, gave the values 17·85 (σ 0·47) kJ mol^{-1} of dihydrate for the process

$$Na_2Cr_2O_7,2H_2O \rightarrow Na_2Cr_2O_7,H_2O + \text{saturated solution} \qquad \text{(ii)}$$

and 12·35 (σ 0·73) kJ mol^{-1} of dihydrate for the process

$$Na_2Cr_2O_7,H_2O \rightarrow Na_2Cr_2O_7 + \text{saturated solution} \qquad \text{(iii)}$$

Temperature of Phase Changes

There was a similar variation in the temperatures for the phase transitions obtained with the differential scanning calorimeter (Figs 1 and 2). Reproducible values (±0·1°C) were obtained from cooling curves for samples of approximately 100 g of the dihydrate, heated to 100°C in a Dewar flask and allowed to cool with stirring and appropriate seeding. These were 82·8°C for process (ii) and 91·1°C for process (iii).

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[3] Campbell, J. A., *Spectrochim. Acta*, 1965, **21**, 1333.
[4] Hartford, W. H., *J. Amer. Chem. Soc.*, 1941, **63**, 1473.
[5] Brennan, J. S., Brown, N. M. D., and Swinton, F. L., *J. Chem. Soc., Faraday Trans. 1*, 1974, 1965.