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*A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE*

# The Thermal Dehydration and Recrystallization of Chromic Hydrate

by

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# DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lit by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara, we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

# The Thermal Dehydration and Recrystallization of Chromic Hydrate

R.E. SOWDEN

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## ABSTRACT

Chromic hydrate, $Cr_2O_3 . xH_2O$, precipitated from aqueous chromic chloride solution with (i) ammonia and (ii) light magnesia, was characterised in air and in nitrogen at temperatures up to 800'C using DTA, TGA, XRD, electron transmission microscopy and BET surface area measurements in order to gain an insight into its reactivity towards a chloridising enpironment. This is relevant to a proposed new low-temperature process for the production of anhydrous chromic chloride, $CrCl_3$. The value of $\triangle H$ glow for $NH_3$-precipitated chromic hydrate in an atmosphere of nitrogen was found to be -58 kJ $mol^{-1}$ and occurred in two steps at 587 and 636'C.

## INTRODUCTION

While investigating a new process (1)(2) for the production of anhydrous chromic chloride by the low temperature chloridisation of dried chromic hydrate, prepared by precipitation (3) with an aqueous suspension of light magnesia from a solution of aqueous chromic chloride obtained by reduction of a solution of sodium chromate in hydrochloric acid by methanol (4), it was necessary to study the thermal dehydration and recrystallization characteristics of the chromic hydrate in order to gain an insight into its possible reactivity in a chloridising environment. The work on the behaviour of the chromic hydrate in a cloridising atmosphere (5) at low temperatures will be the subject of further publications. The slow precipitation, dehydration and recrystallization of chromic hydrate from CrIII solution is summarised in Figure 1 (3)(6).

## MATERIALS

'AnalaR' grade chromic hydrate and G.P.R. grade light magnesium oxide were supplied by Hopkin & Williams Ltd.

Three batches of chromic hydrate were prepared and analysed as previously described (3):

**Batch A)** A solution of 0.513 kg of $CrCl_3.6H_2O$ in 1.56 litres of water was slowly neutralised with 0.316 litres of 35 % $NH_3$ solution; the precipitated chromic hydrate was filtered, re–pulped with water to 2.25 litres filtered, then repulped and filtered thrice more. The product, which was relatively pure as all of the likely impurities are water soluble, was dried for 5 hours at 110°C and used as a reference material.

**Batch C)** Chromic hydrate was precipitated at pH 5.75 from 0.860 litres of a solution of 0.804 M chromic chloride in 1.98 M HCl at 62°C with an aqueous suspension of 10 % w / v light magnesia and gently agitated for 20 minutes. The precipitate was filtered at 45°C, washed with 1l of water and dried for 5 hours at 110°C.

**Batch D)** Chromic hydrate was precipitated at 80°C and pH 6.85 with 10 % w / v light magnesia in 5.9 % stoichiometric excess from 0.860 litres of a solution of 0.804 M chromic chloride in 1.98 M HCl and gently agitated for 20 minutes. The precipitated product was then filtered at 42 °C, washed with 1l of water and dried for 5 hours ta 110 °C.

## APPARATUS

### Thermogravimetry and differential thermal analysis:

TG–DTA experiments were carried out with a Stanton 'Massflow' thermobalance with DTA attachment and a direct temperature measuring assembly, using a constant heating rate of 6 °C / min in (i) still air and (ii) flowing $O_2$– free nitrogen (1 l / min at S.T.P.). The reference solid, 60 mg of $\gamma$– $Al_2O_3$, and 60 mg of the sample were placed in adjacent platinum crucibles mounted in an alumina block with a Pt–Pt / Rh thermocouple in contact with the dimpled base of each crucible. Corrections were made for buoyancy effects and temperature calibrations were confirmed using anhydrous sodium chromate as a standard: exothermic DTA peaks were observed at 414°C and 782°C compared with the reported crystalline transition and fusion temperatures of 413°C and 792°C respectively (7).

## EXPERIMENTAL AND DISCUSSION

### Ammonia-precipitated chromic hydrate

In order to simulate the physiochemical properties of magnesia –precipitated chromic hydrate, ammonia–precipitated chromic hydrate was studied in admixture with light magnesia:

Sample (i): 50ml of 0.45M $CrCl_3$ solution was neutralised with 1.4 % $NH_3$ solution, filtered, washed with water and dried for 2 hours at 110°C. TG–DTA curves were obtained in air and in nitrogen (Table 1; Figures 2 and 3).

Sample (ii): 200 mg of Sample (i) was finely ground with 10 mg of light magnesia.

Sample (iii): 400 mg of Sample (i) was finely ground with 100 mg of light magnesia; 0.6 g of water was added in order to hydrate the magnesia. Samples (ii) and (iii) were examined by DTA in an atmosphere of nitrogen (Table 1; Figure 4). In nitrogen, Sample (i) exhibited and attenuated endothermic peak at 185°C, attributed to the loss of structural water and corresponding with a maximum in the slope of the TG curve (composition: $Cr_2$–$O_3$.2.1–2.1$H_2O$). The glow exotherm oc-

Table 1. DTA DATA: Ammonia-Precipitated Chromic Hydrate With Added Light Magnesia.

| Sample | Magnesium content % | Atmosphere | Temperature of DTA peak, °C | |
|---|---|---|---|---|
| | | | Endothermic | Exothermic |
| (i) | 0.0 | nitrogen | 185 | 587 (Glow I)<br>636 (Glow II) |
| | | air | 87 | 299<br>390 (Glow) |
| (ii) | 2.6 | nitrogen | 45<br>205 | 600 (Glow I)<br>649 (Glow II) |
| (iii) | 11 | nitrogen | <110<br>339 | 590 (Glow) |

curred in two stages: an oxidation step at 587°C (composition: $Cr_2O_3.0.5H_2O$) followed by reduction and recrystallization of $\alpha$–$Cr_2O_3$ at 636°C. Removal of the surface hydroxyl groups was not complete until 900°C, in agreement with previous evidence (8) that the surface structure of $\alpha$–$Cr_2O_3$ prepared by the thermal dehydration of chromia is not perfected unless it has been calcined at a temperature above 900°C. The presence of air modified the DTA pattern of Sample (i) considerably: the attenuated endotherm observed at 185°C in nitrogen was partly masked by a broad oxidation endotherm (CrIII–CrVI) at 299°C (composition: $Cr_2O_3.0.9H_2O$). The glow exotherm at 388–390°C was complicated either because of the recrystallization of anhydrous chromic oxide in two distinct forms or, more probably, as the result of consecutive dehydration and recrystallization steps in accordance with the overall stoichiometric equation (9):

$$Cr_2O_3.\tfrac{1}{2}H_2O\ (\text{amorph.}) = Cr_2O_3\ (c) + \tfrac{1}{2}H_2O\ (g)$$

The DTA pattern of Sample (ii) heated in nitrogen was similar to that of Sample (i): an attenuated endotherm with a maximum at 205°C followed by a two–stage glow exotherm with peaks at 600°C and 649°C. The DTA pattern of Sample (iii) in nitrogen, however, consisted of a broad low temperature endotherm, attributed to the loss of surface–adsorbed water from the magnesia at temperatures below 180–190°C (10), with a superimposed attenuated endotherm at about 200°C associated with the loss of co–ordinated and surface–adsorbed water from the chromic hydrate. A further endotherm at 339°C was probably due to the loss of one molecule of water from $Mg(OH)_2$ (11). The glow exotherm peak at 590°C was remarkably attenuated.

**Magnesia-precipitated chromic hydrate:**

Samples of dried magnesia–precipitated chromic hydrate (Batches C and D) were similarly examined by TG and DTA in air and in nitrogen (Table 2 and Figures 5–8). Batch C: The attenuated low temperature endotherms observed at 102°C and 268°C in nitrogen are due to the loss of co–ordinated and surface–coordinated water; the glow exotherm at 795°C was preceded by a broad exothermic peak in the region from 600 to 740°C that is assumed to be caused by the pre–glow oxidation effect. In air a broad, low temperature endotherm corresponding with an inflection in the TG curve (composition: $Cr_2O_3$.

Table 2. DTA DATA: Magnesia-Precipitated Chromic Hydrate

| Batch | Atmosphere | Temperature of DTA peak, °C | |
|---|---|---|---|
| | | Endothermic | Exothermic |
| C | nitrogen | 102<br>268 | 795 (Glow) |
| | air | <103 | 151<br>361 (Glow) |
| D | nitrogen | 85<br>306 | |
| | air | 44 | 239<br>393 (Glow) |

$4.5H_2O$) was followed by the oxidation exotherm at 151°C (composition: $Cr_2O_3.2.3H_2O$) which commenced at a second TG inflection (composition: $Cr_2O_2.3.0H_2O$). A further TG inflection (composition: $Cr_2O_3.0.9H_2O$) at about 220°C preceded the glow exotherm at 361°C and the last few surface hydroxyl groups were expelled at about 550°C. At 550°C an exothermic 'drift' developed, possibly as a result of the formation of magnesium chromite with consequent sintering of the chromic hydrate.

Batch D: Endothermic peaks were observed in nitrogen at 85°C (composition: $Cr_2O_2.3.3H_3O$) and 306°C (composition: $Cr_2O_3.1.1H_2O$); slow exothermic oxidation at 570–705°C was followed by the glow exotherm at 715°C. In air, Batch D exhibited an exothermic oxidation peak at 239°C (initial composition: $Cr_2O_3.4.6H_2O$; composition at peak: $Cr_2O_3.3.3H_2O$) followed by the glow at 393°C (composition: $Cr_2O_3.1.1 H_2O$). TG inflections were observed at compositions $Cr_2O_3.xH_2O$, where $x = 5.3, 2.9, 1.1$ and $0.6$. An exothermic drift similar to that noted with Batch C commenced at 535°C.

**Thermodynamics:**

The heat evolved during the recrystallization of Sample (i) in nitrogen in the above DTA experiment was estimated by comparing the area under the DTA peak when subliming AnalaR ammonium chloride in nitrogen with the area under the twin DTA glow exotherm peaks. The DTA peaks for the ammonium chloride were found to occur at 190°C and 290°C (Figure 9), compared with the reported $\alpha$–$\beta$ transition temperature of 184.7°C ($\triangle$H: 3.93 kJ mol$^{-1}$) (12) and sublimation temperature of 340°C ($\triangle$H: 144.6 kJ mol$^{-2}$) (11)(12)(13). The estimated value of $\triangle$H for the glow phenomenon in nitrogen was –58 kJ mol$^{-1}$; previous workers have obtained widely varying values in the ranges (14) –95 to –188 kJ mol$^{-1}$ and –5 to –7 kJ mol$^{-2}$. The The value of $\triangle$H is apparently dependent on (14) the specific surface area, the conditions of preparation and the subsequent treatment of the chromic hydrate: for example, the glow effect is hindered by the presence of sulphate when precipitationg $Cr^{3+}$ ions with $NH_3$ solution; the glow also appears to vary in intensity with the rate of heating and the amount of chromic hydrate present.

**Batch annealing:**

1g samples of dried chromic hydrate were annealed in a stream of nitrogen (space velocity: 166 mm min$^{-1}$ at S.T.P.) at 200–648°C (Batch A: 15–60 min; Batch D: 30 min) and in still air at 160–725°C (Batch A: 10 min; Batch C: 1h).

The true loss in weight of the chromic hydrate, with a description of the corresponding changes in colour, are detailed in Table 3. Figure 10 shows the reduced loss in weight on annealing relative to the loss on ignition at 700°C and is complementary to the above TG–DTA data: in particular, the rate of dehydration in air with respect to temperature in the region of the glow exotherm, about 400°C, was lower for Batch C then for Batch A, and the difference is attributed to the magnesium present as an impurity in the former sample. The composition of chromic hydrate (Batch A) that had been annealed in nitrogen at 360–480°C for 15–60 min was found to be independent of the time of annealing (Fig. 11). It has been shown previously in preliminary TG–DTA experiments (15) that variations in heating rate from 2–12 °C min$^{-1}$ have no observable effect on the thermal behaviour of chromic hydrate, which suggest that the initial rate of dehydration is very rapid although it is well known that chromic hydrate annealed at 100–400°C does not achieve a constant weight for many weeks (14).

Table 3. Annealed Chromic Hydrate: Phase Relationships

| | Annealing Conditions | | | Loss in weight % | Annealed Product | |
|---|---|---|---|---|---|---|
| Batch | Atmosphere | Time min | Temp. °C | | Colour | Crystalline phase |
| A | nitrogen | 30 | 225 | 30.4 | blue | — |
| | | | 265 | 30.0 | | |
| | | | 300 | 34.9 | greenish-blue | |
| | | | 325 | 37.0 | | |
| | | | 360 | 38.6 | v. dark green | |
| | | | 380 | 39.3 | olive green | |
| | | | 395 | 39.5 | | |
| | | | 410 | 40.6 | | |
| | | | 430 | 41.2 | | |
| | | | 450 | 41.9 | | |
| | | | 464 | 42.4 | | |
| | | | [a]480 | 42.9 | | |
| | air | 10 | 160 | 16.7 | blue | — |
| | | | 190 | 21.8 | | |
| | | | 240 | 27.8 | v. dark brown | |
| | | | 285 | 31.0 | | |
| | | | 300 | 30.8 | | |
| | | | 325 | 36.8 | | |
| | | | 345 | 35.7 | | |
| | | | 350 | 39.0 | | |
| | | | 375 | 40.0 | | |
| | | | [b]400 | 46.7 | green | $Cr_2O_3$ |
| | | | 430 | 48.0 | | |
| | | | 450 | 46.9 | | |
| | (ignited) | 20 | 700 | 47.9 | | |
| D | nitrogen | 30 | 200 | 46.5 | bluish-green | — |
| | | | 307 | 56.6 | green | |
| | | | 375 | 55.0 | olive green | |
| | | | 430 | 54.7 | | |
| | | | 430 | 54.7 | | |
| | | | 464 | 53.4 | | |
| | | | 527 | 56.8 | | |
| | | | [c]590 | 58.6 | | |
| | | | [d]648 | 60.4 | green | $Cr_2O_3$ |
| | (ignited) | 10 | 700 | 62.0 | green | $Cr_2O_3$ + $MgCr_2O_4$ |
| C | air | 60 | 175 | 22.6 | blue | — |
| | | | 280 | 42.4 | brown | |
| | | | 370 | 41.0 | | |
| | | | 425 | 45.8 | olive green | $Cr_2O_3$ |
| | | | 475 | 47.2 | | |
| | | | 579 | 46.1 | | $Cr_2O_3$ + $MgCr_2O_4$ |
| | | | 675 | 46.7 | green | |
| | | | [e]725 | 47.1 | | |

### BET surface area

The BET surface area of dried chromic hydrate that had been annealed at various temperatures in nitrogen (Batch A: 10 min; Batch C: 1h) and in air (Batch A: 10 min; Batch C: 1h) was determined by the adsorption of krypton at 77 K (Figure 12). A rapid increase in specific surface area with respect to annealing temperature occurred immediately before the glow; this increase was hastened in air, probably owing to the favouring of oxidation (16), but the earlier 'triggering' of the glow exotherm apparently prevented the surface area from developing so extensively. The presence of magnesium also appeared to retard the development of specific surface area in the region of the glow exotherm, and in air the post–glow decrease in surface area was both retarded and diminished.

### X-ray powder diffraction

Specimens of dried chromic hydrate annealed in nitrogen and in air were examined by X–ray powder diffraction techniques using Cu –$K\alpha$ radiation. Results and annealing conditions are summarised in Table 3 and a selection of typical XRD patterns are presented in Table 4.

### Techniques:

Batches A and C: XRD patterns were obtained by the Inter–collegiate X–ray Service with a Guinier camera. Samples were ground and mounted between strips of 'Sellotape', and patterns were interpreted with the aid of a diffraction–spacing ruler. All data are presented after screening out the pattern of a Sellotape blank (relative intensities in parentheses): 4.45 (100), 4.05 (100), 3.02 (10).

Batch D: XRD patterns of ground samples from Batch D were obtained with a diffractometer by Analytical Services in the Department of Metallurgy. Samples of chromic hydrate annealed at temperatures below the glow exotherm were found to be essentially amorphous to X–rays. Annealed at the glow temperature, however, the pattern of $\alpha$–$Cr_2O_3$ appeared, becoming progressively sharper with increase in annealing temperature, thus indicating increasing crystallinity (17). Magnesia–precipitated chromic hydrate annealed at 648°C in

Table 4. Typical X-Ray Powder Diffraction Patterns: Annealed Chromic Hydrate

| Sample | | | | | | | | | | | | Reference data | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| a | | b | | c | | d | | e | | f | | $Cr_2O_3$ | | $MgCr_2O_4$ | |
| dA | I | dA | I | dA | I | dA | I | dA | I | dA | I | dA | I | dA | I |
| | | | | | | | | 4.783 | 15 | 4.791 | 85 | | | 4.813 | 65 |
| | | 3.60 | 40 | | | 3.62 | 90 | 3.616 | 75 | | | 3.633 | 75 | | |
| | | | | | | | | 2.936 | 5 | 2.933 | 15 | | | 2.945 | 14 |
| 2.82 | 100 | | | | | | | | | | | | | | |
| 2.78 | 100 | | | 2.80 | 100 | 2.81 | 10 | | | | | | | | |
| | | 2.66 | 50 | | | 2.66 | 90 | 2.657 | 85 | | | 2.666 | 100 | | |
| | | | | | | | | 2.504 | 25 | 2.503 | | 100 | | 2.512 | 100 |
| | | 2.47 | 50 | | | | | | | | | | | | |
| | | 2.46 | 100 | | | 2.47 | 100 | 2.472 | 100 | | | 2.480 | 95 | | |
| | | | | | | | | | | | | | | 2.406 | 14 |
| | | 2.26 | 1 | | | 2.26 | 1 | | | | | 2.264 | 12 | | |
| | | 2.17 | 5 | | | | | | | | | | | | |
| | | 2.16 | 20 | | | 2.174 | 30 | | | | | 2.176 | 40 | | |
| | | | | | | | | 2.078 | 10 | 2.077 | 55 | | | 2.083 | 55 |
| | | | | | | 2.06 | 1 | | | | | | | | |
| | | | | | | 2.04 | 1 | | | | | 2.048 | 10 | | |
| | | | | 1.98 | 10 | 1.99 | 1 | | | | | | | | |
| | | | | | | | | | | | | | | 1.912 | 6 |
| | | 1.803 | 5 | | | 1.815 | 20 | | | | | 1.8156 | 40 | | |
| | | 1.800 | 5 | | | 1.806 | 10 | | | | | | | 1.701 | 4 |
| | | 1.664 | 40 | | | 1.67 | 70 | | | | | 1.672 | 90 | | |
| | | 1.658 | 90 | | | 1.66 | 5 | | | | | | | | |
| | | | | | | | | 1.601 | 5 | 1.601 | 30 | | | 1.603 | 40 |
| | | | | | | 1.57 | 5 | | | | | 1.579 | 14 | | |
| | | | | | | | | | | 1.471 | 50 | | | 1.4731 | 55 |
| | | 1.458 | 1 | | | 1.465 | 20 | | | | | 1.465 | 25 | | |
| | | 1.452 | 1 | | | 1.455 | 10 | | | | | | | | |
| | | 1.424 | 1 | | | 1.430 | 20 | | | | | 1.4314 | 40 | | |
| | | 1.418 | 5 | | | 1.424 | 10 | | | | | | | | |
| | | | | | | | | | | | | | | 1.4089 | 14 |
| | | | | | | | | | | | | | | 1.3176 | 2 |
| | | | | | | 1.295 | 5 | | | | | 1.2961 | 20 | | |
| | | | | | | | | | | | | | | 1.2563 | 10 |
| | | | | | | 1.238 | 1 | | | | | 1.2398 | 18 | | |
| | | | | | | | | | | | | 1.2101 | 8 | | |
| | | | | | | | | | | | | | | 1.2028 | 10 |

Note: a,b,c,d,e: see Table 3. f: chromic hydrate (Batch D: ignited in air at approx 700°C; screened for $MgCr_2O_4$.

nitrogen was found to contain an unidentified second crystalline phase; the non–stoichiometric compound $Cr_2O_{3\cdot 2}$ has previously been identified (16) in chromic hydrate annealed in oxygen at 350°C for 2h and heated to 500°C.

The XRD patterns of the original dried chromic hydrate did not reveal the presence of any crystalline impurity, but after being ignited at 700–725°C the X–ray pattern of $MgCr_2O_4$ (18) was detected in Batches C and D. The reaction between chromic oxide and magnesia (12) (13) is known to be accelerated in the presence of gaseous oxygen at 735–1300°C (19) and 400–800°C (20):

$$Cr_2O_3 + MgO = MgCr_2O_4 \qquad (\triangle G,\ 1000\ K:\ -196\ kJ\ mol^{-1})$$

### Electron transmission micrographs:

Electron transmission micrographs of magnesia–precipitated chromic hydrate (Batches C and D) annealed at various temperatures in air and nitrogen respectively (see Table 3) were obtained by the Department of Chemical Engineering with a Japan Electron Optics Co. Ltd. JEM–7 electron microscope. Samples were suspended in methanol using ultrasonic agitation and deposited on a carbon grid for examination. The small size of the particles of chromic hydrate (20–50 nm) made them unsuitable for surface replication and so scanning electron microscopy was not feasible.

Chromic hydrate annealed in air at 110°C and 175°C was found to be opaque to electrons. At annealing temperatures in the range 280 –370°C, however, the edges of the still amorphous particles became translucent, indicating microporosity (21); by 425°C crystals were visible and the proportion of crystalline material increased thereafter with increasing temperature of annealing. Chromic hydrate annealed in nitrogen behaved in an apparently analagous manner but crystalline $\alpha$–$Cr_2O_3$ did not appear until the annealing temperature had reached 648°C.

## CONCLUSIONS (22)

The degree of hydration of annealed chromic hydrate decreases with increase in annealing temperature until anhydrous $\alpha$–$Cr_2O_3$ recrystallises via the glow phenemenon; thermogravimetry and differential thermal analysis have confirmed that the glow effect occurs at a higher temperature in nitrogen than in air. The composition, determined with a batch annealing technique, of ammonia–precipitated chromic hydrate annealed at various temperatures in the range 265–480°C in an atmosphere of nitrogen is temperature–dependent, but not time–dependent in the range 365–480°C for a period of 60 minutes from the commencement of annealing.

The twin glow exothermic DTA peaks, with estimated value of $\triangle$H glow of $-58$ kJ $\text{mol}^{-1}$, that were observed at 587 and 637°C in nitrogen become conjoined, retarded and attenuated in the presence of 2.6 % w / w light magnesia; magnesia–precipitated chromic hydrate generally exhibits a single, attenuated glow exotherm in nitrogen with a maximum in the temperature range 715–795°C. It has been confirmed by batch annealing tests that the low exotherm is preceded by a rapid rate of increase in BET surface area with respect to annealing temperature, accompanied by a corresponding increase in microporosity that is apparent when viewed with an electronic transmission microscope. These effects both commence at 410–430°C with ammonia –precipitated chromic hydrate but at about 500°C with magnesia–precipitated chromic hydrate.

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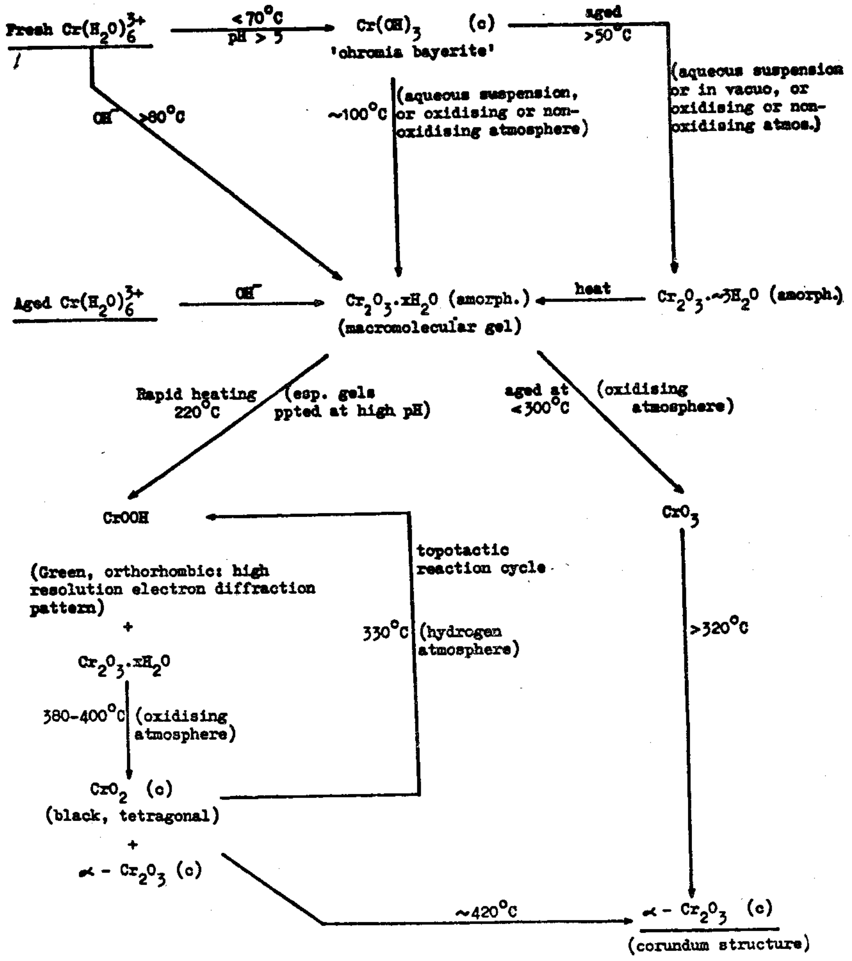

Fig. 1. The slow precipitation, dehydration and recrystalisation of chromic hydrate from Cr III solution.

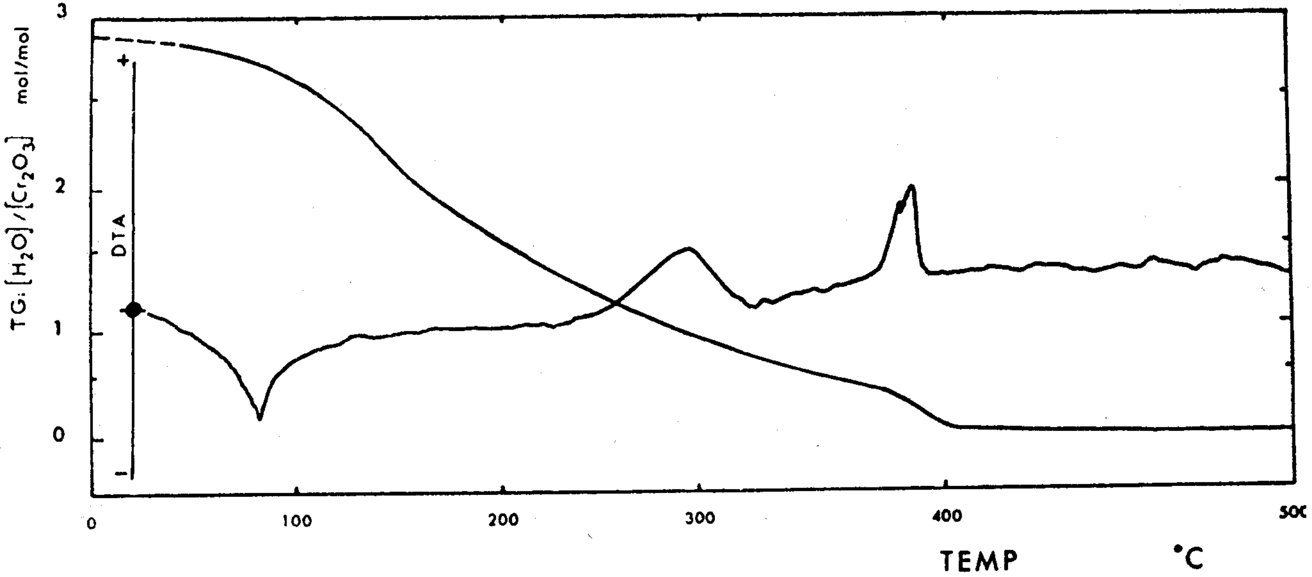

Fig. 2. Sample (i): TG-DTA in air.

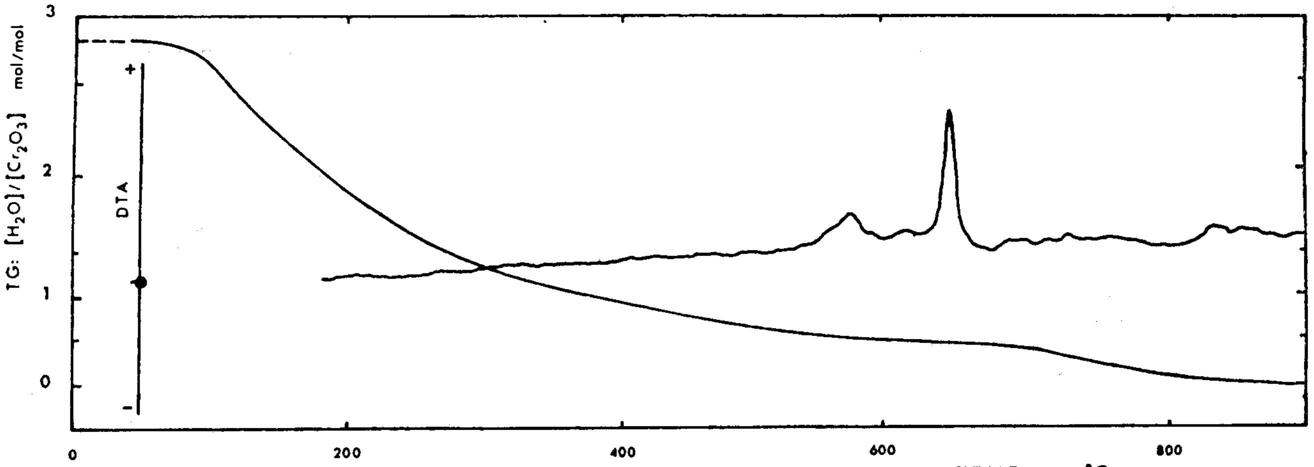

Fig. 3. Sample (i): TG-DTA in nitrogen.

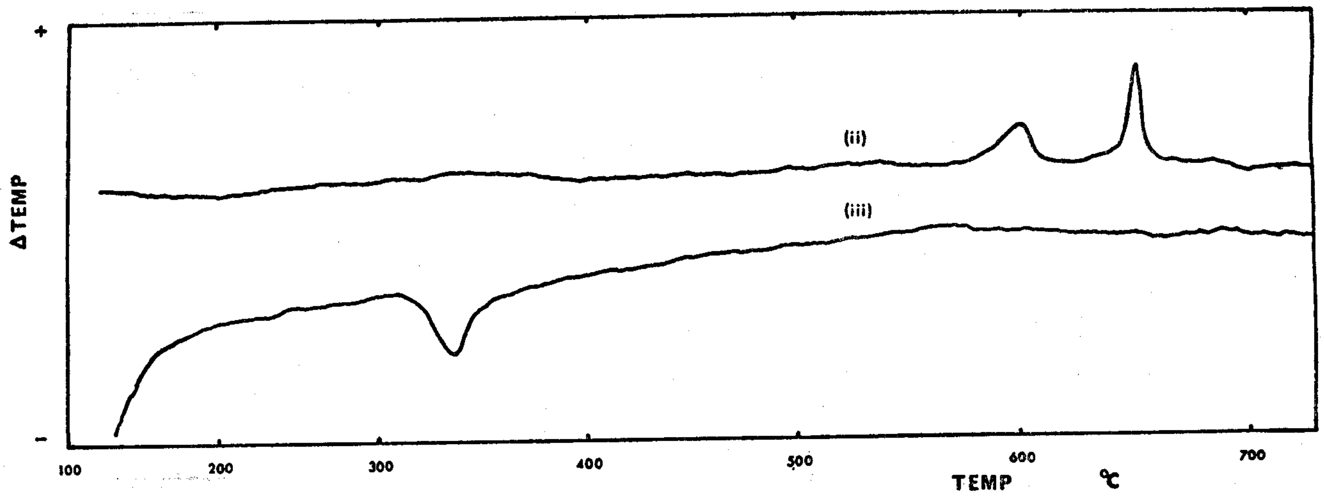

Fig. 4. Samples (ii) and (iii): DTA in nitrogen.

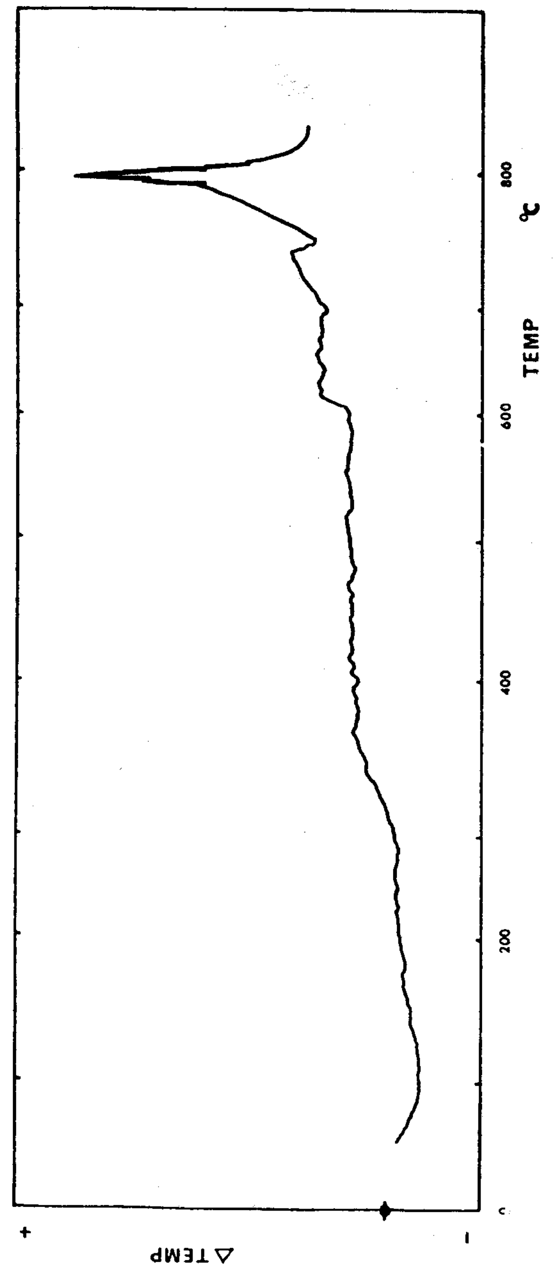

Fig. 5. Chromic hydrate (Batch C): DTA in nitrogen.

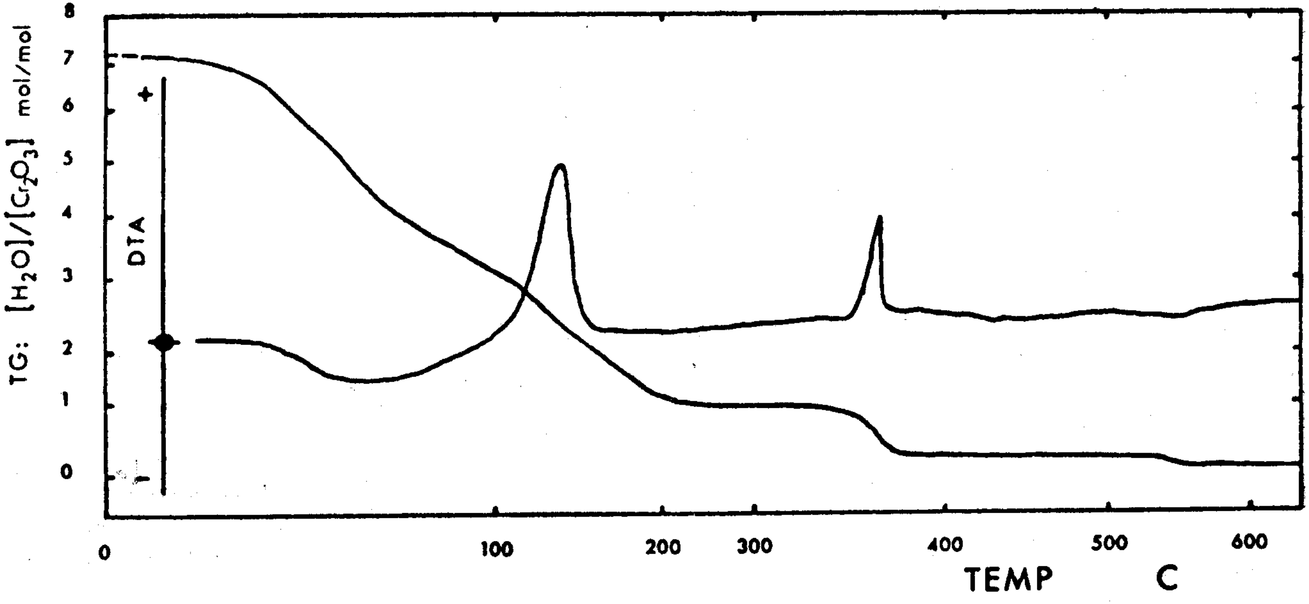

Fig. 6. Chromic hydrate (Batch C): TG-DTA in air.

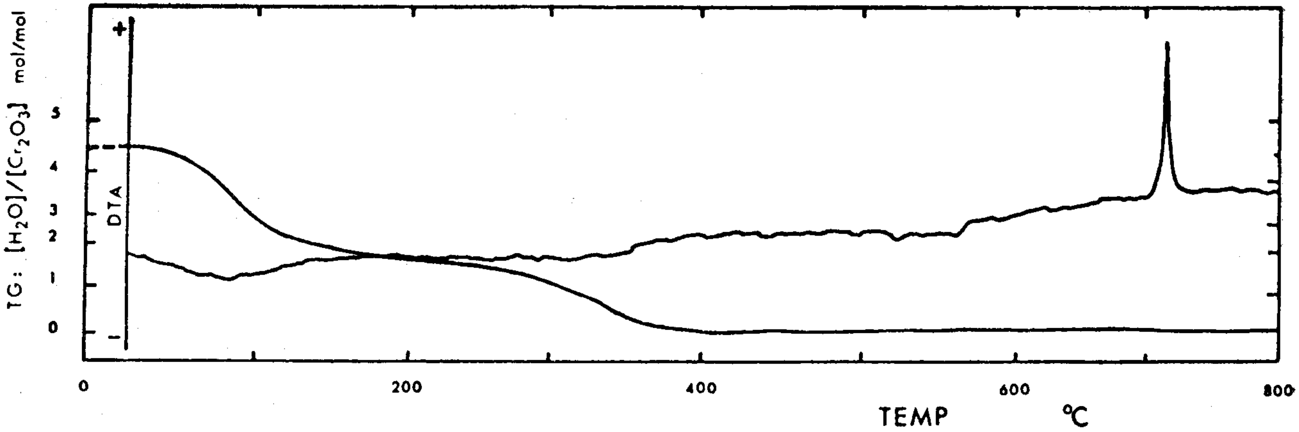

Fig. 7. Chromic hydrate (Batch D): TG-DTA in nitrogen.

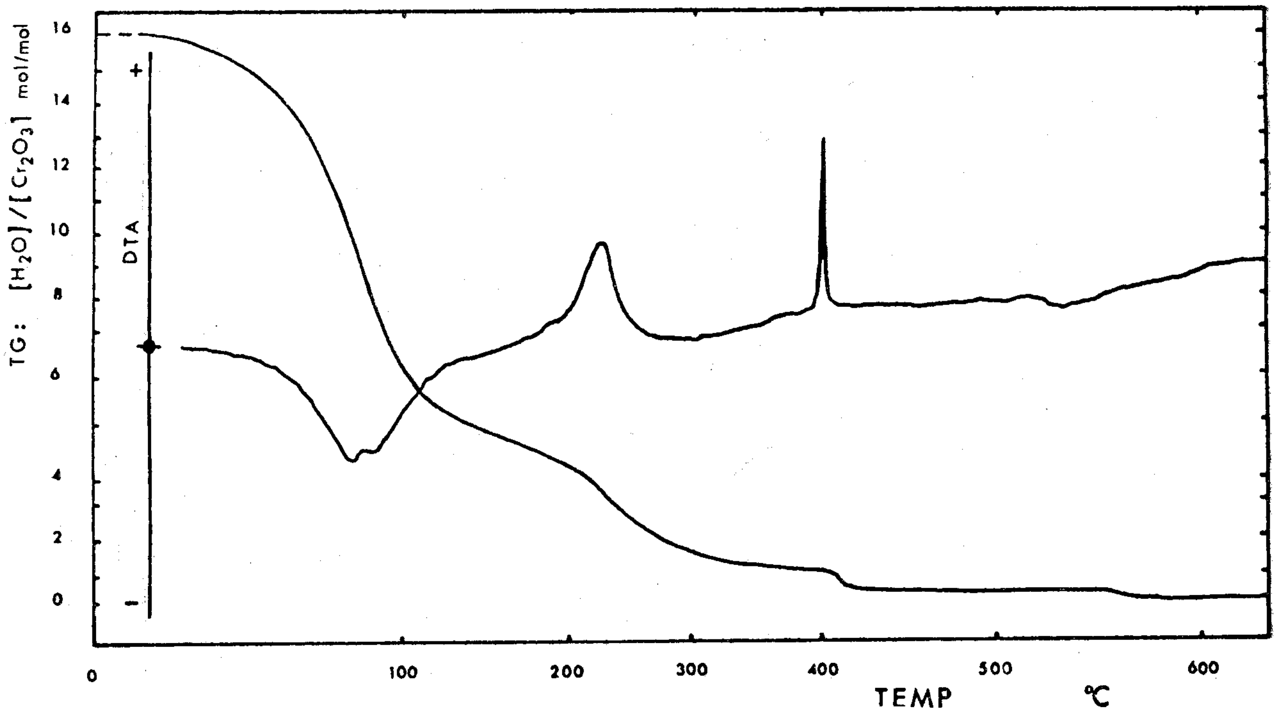

Fig. 8. Chromic hydrate (Batch D): TG-DTA in air.

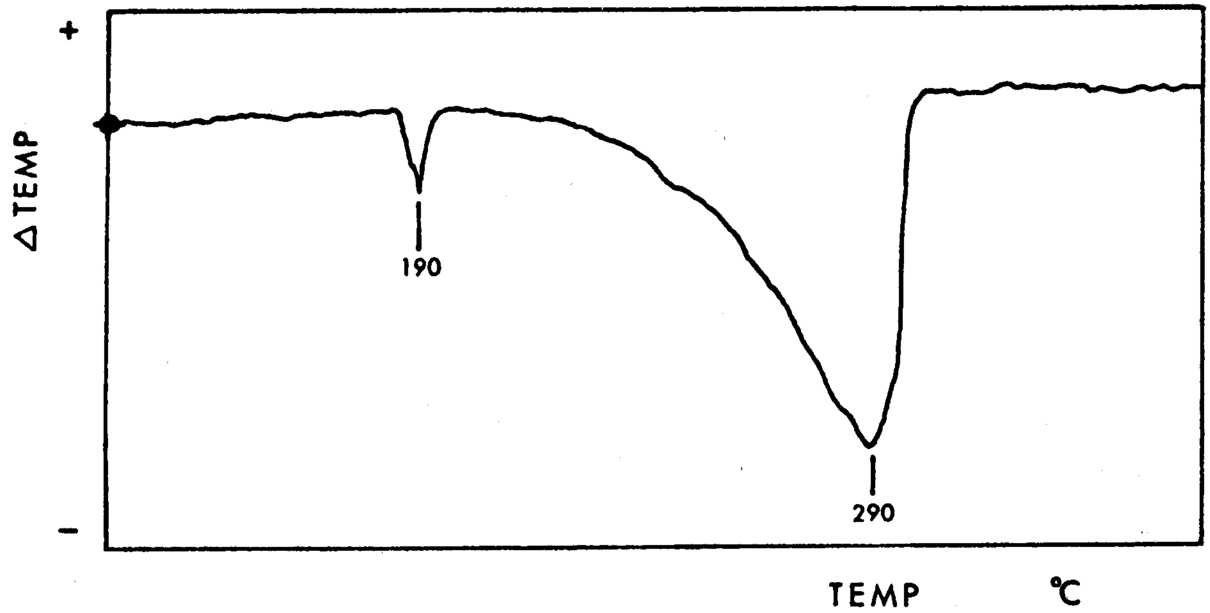

Fig. 9. Ammonium chloride: DTA in nitrogen.

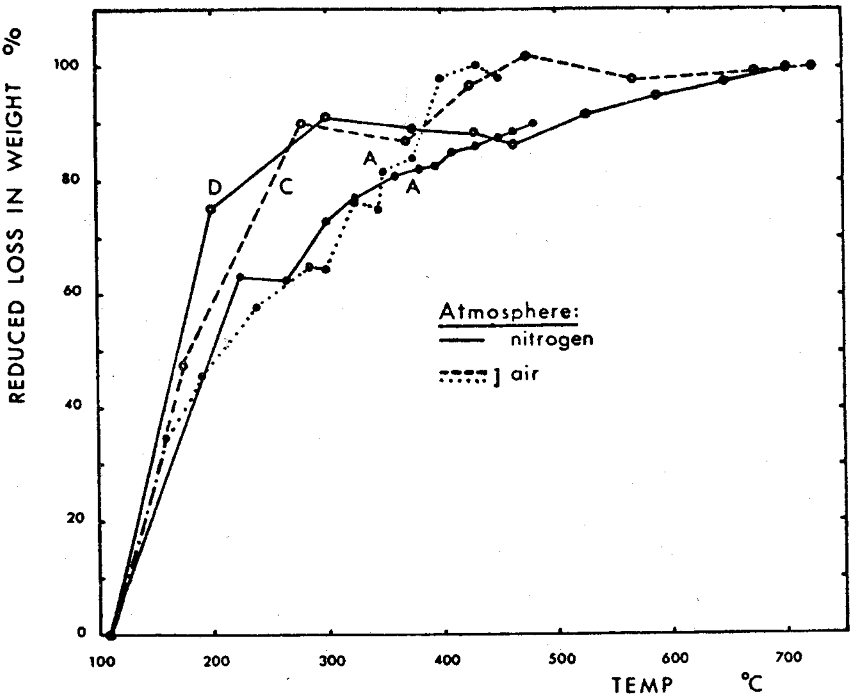

Fig. 10. Annealed chromic hydrate (Batches A, C and D): reduced loss in weight vs. temperature of annealing.

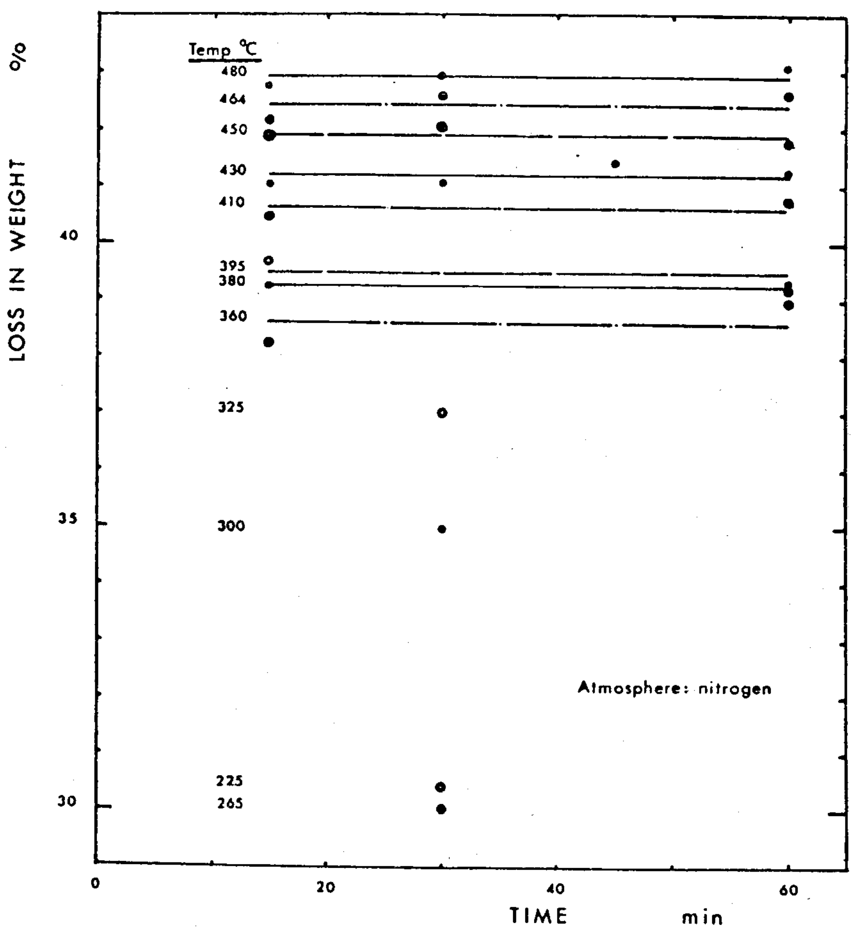

Fig. 11. Annealed chromic hydrate (Batch A): Loss in weight vs. time of annealing.

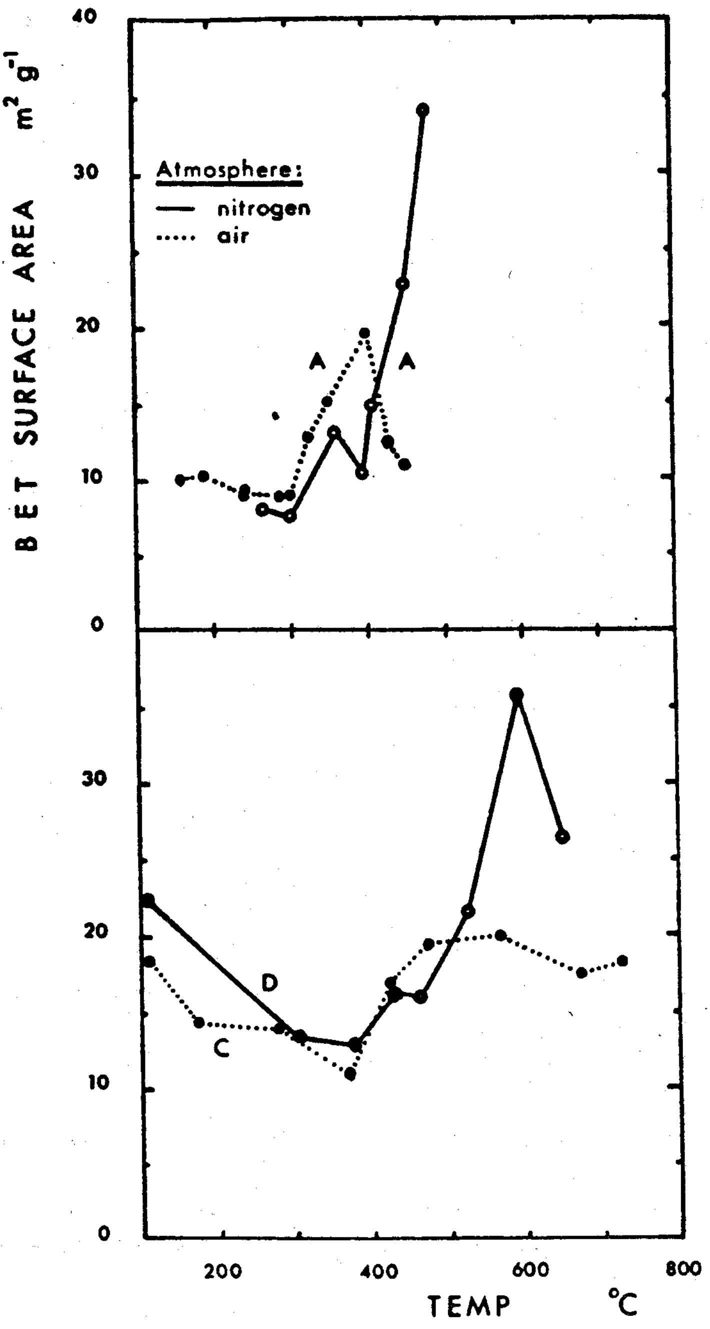

Fig. 12. Annealed chromic hydrate (Batches A, C and D): BET surface area vs. temperature of annealing.

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