

REACTIONS OF CHROMATES AT HIGH TEMPERATURES

PART XXI—MECHANISM OF THE REACTIONS OF CHROMATES AT HIGH TEMPERATURES

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The structural formulæ given to the several compounds obtained in the decomposition of chromates at high temperature by Datar and Jatkar (*Jour. Ind. Inst. Sci.*, 1939, **22A**, 287) clearly show that in chromates and in basic chromates of the general formula $12RO \cdot 8CrO_3$, molecules consist of a large number of CrO_3 groups, so arranged as to make them possible to decompose in stages. The basic chromate $2RO \cdot CrO_3$ contains, however, a single CrO_3 group and decomposes without the formation of intermediate compounds.

In the decomposition of mixtures of chromates with bases the basic chromates are initially produced. The formation of $2RO \cdot CrO_3$ is generally favoured by the presence of oxide. The basic chromate $12RO \cdot 8CrO_3$, is formed readily as a result of the reactions of chromates with carbonates. The chromate-carbonate mixtures decompose at temperatures at which both the carbonate and the chromate are stable, due to the formation of $12RO \cdot 8CrO_3$, and the reaction is complete when the carbonate does not decompose otherwise than due to this reaction. In case the carbonate decomposes separately the formation of $2RO \cdot CrO_3$ is indicated. It is usually noticed that the complete decomposition of the carbonate has to be carried out at high temperature when the basic chromate $12RO \cdot 8CrO_3$ initially produced subsequently decomposes to $12RO \cdot 6CrO_3 \cdot Cr_2O_3$. Whenever $12RO \cdot 8CrO_3$ is decomposed as fast as it is formed the stable basic chromium chromates are obtained. On the other hand if the decomposition of the carbonate occurs faster, an oxide phase arises as soon as the system is saturated with respect to $12RO \cdot 8CrO_3$ and the reaction proceeds with the formation of $2RO \cdot CrO_3$.

As a rule weak basic oxides form higher basic compounds and strong bases, the lower ones. Thus calcium chromate readily forms $CaO \cdot Fe_2O_3 \cdot CrO_3$ and $CaO \cdot Cr_2O_3 \cdot CrO_3$ (part XVII). The reactions of chromates with strong bases however exhibit an

incomplete formation of both $2RO \cdot CrO_3$ and $12RO \cdot 8CrO_3$, the formation being more or less complete at high temperature. Whereas the results on the reactions of calcium chromate and strontium chromate with magnesium oxide show that in these reactions the formation of $8CaO \cdot 4MgO \cdot 8CrO_3$ or $8SrO \cdot 4MgO \cdot 8CrO_3$ is complete and the possibility of the formation of $CaO \cdot MgO \cdot CrO_3$ or $SrO \cdot MgO \cdot CrO_3$ is minimum (parts XIII-XIV). These compounds are stable only in solid state and decompose in solution.

It has already been pointed out that the amount of $12RO \cdot 8CrO_3$ produced in the equilibrium reaction is limited. The quantity produced is small for a strong base and increases on addition of a weaker base. This is apparent from the consideration of the reactions between strontium chromate with calcium oxide and of calcium chromate with strontium oxide (part XVIII). Thus though the former reaction produces the stable basic chromate $8SrO \cdot 4CaO \cdot 8CrO_3$ along with $CaO \cdot SrO \cdot CrO_3$, the formation of $8CaO \cdot 4SrO \cdot 8CrO_3$ is not at all indicated in the latter reaction. The stable basic chromate $8CaO \cdot 4SrO \cdot 8CrO_3$ can however, be prepared by the reaction between calcium chromate with strontium carbonate. Also magnesium oxide combines with calcium chromate and with strontium chromate to produce only the stable mixed chromium chromates.

Similarly the results of the previous workers on the decomposition of the chromates of Ca, Sr and Ba with the corresponding carbonates show that the formation of $12RO \cdot 8CrO_3$ is more or less complete in case of calcium chromate; slight indefiniteness appears in the decomposition of strontium chromate; whereas in the decomposition of the mixture of barium chromate with barium carbonate, the decomposition is accelerated by addition of excess of barium carbonate clearly indicating the formation of $2BaO \cdot CrO_3$. The formation of $2BaO \cdot CrO_3$ due to the presence of barium oxide phase in the system was confirmed by heating a mixture of barium chromate with barium oxide (2:1 mols.) at 900° for 15 hours in air which gave 28.6% decomposition. As $12BaO \cdot 8CrO_3$ is stable in air at 900° , the decomposition is obviously due to that of the compound $2BaO \cdot CrO_3$,

which must have been produced. Thus the tendency to produce $12\text{RO } 8\text{CrO}_3$ is enhanced with the decreasing basicity of the oxides though with very weak bases, the higher basic chromate 2RO CrO_3 is only produced.

Considerable data on the various basic chromium chromates are available. In view of the structures assigned to these compounds by Datar and Jatkar (part XI) the results have been discussed on the basis of the reactions and properties of the chromium chromates.

In the decomposition of mixtures of chromates with oxides, the basic chromates are initially formed. The basic chromate $12\text{RO } 8\text{CrO}_3$ decomposes in stages, while the basic chromate 2RO CrO_3 decomposes directly to the final stage.

25% Stage.—The basic chromate $12\text{RO } 8\text{CrO}_3$ on decomposition gives $12\text{RO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$ at the 25% stage. Datar, Athavale and Jatkar (*Ibid.*, 1939, **22A**, 111) have reported the formation of $12\text{CaO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$, $12\text{SrO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$ and $12\text{BaO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$ (see also parts XV, XVI, XIX-XX). The mixed basic chromium chromates $4\text{Na}_2\text{O } 8\text{CaO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$ (Datar and Jatkar, *Ibid.*, 1939, **22A**, 225), $4\text{MgO } 8\text{CaO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$, $4\text{MgO } 8\text{SrO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$ and $4\text{SrO } 8\text{CaO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$ (parts XIII, XIV, XVIII) have also been prepared. Datar and Jatkar (*Ibid.*, 1939, **22A**, 287) suggested a structural formula for these compounds and from theoretical considerations concluded that the compound is capable of reacting with extra base. The experiments on the decomposition of $4\text{SrO}8\text{CaO}6\text{CrO}_3\text{Cr}_2\text{O}_3 + 4\text{SrO}$, $4\text{SrO } 8\text{CaO}6\text{CrO}_3\text{Cr}_2\text{O}_3 + 4\text{MgO}$ and $8\text{SrO}4\text{MgO}6\text{CrO}_3\text{Cr}_2\text{O}_3 + 4\text{MgO}$ however showed no alteration in the original decomposition pressures, clearly indicating that the different groups of atoms are so arranged as to make the compounds at the 25% stage as stable as the compounds formed at the further decomposition stages.

28.6% Stage.—Though Simon and Schmidt (*Zeit Anorg., chem.*, 1926, **153**, 191) and Ryss and Seljanskaja (*Acta physico chemica*, 1938, **5**, 623) have reported the formation of the chromium chromate corresponding to this stage, Datar and Jatkar (*Ibid.*, 1939, **22A**, 119) have shown that chromium chromate corres-

ponding to this stage, if it exists, is not characterised by distinctive rates of decomposition. The experiments carried out to determine the existence of the corresponding basic chromium chromate also show that the closed system at this stage gives the decomposition pressures identical with those of $12\text{RO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ formed at the 25% decomposition stage (*cf.* also part XIV).

33.3% Stage.—The chromium chromate corresponding to this stage is $4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ the corresponding basic chromium chromate being $9\text{RO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (Datar and Jatkar, 1939, **22A**, 119; 287). The compound $9\text{CaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, $9\text{SrO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, $9\text{BaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (Athavale and Jatkar, *Ibid.*, 1939, **22A**, 179, 273; Datar, Athavale and Jatkar, *Ibid.*, 1939, **22A**, 111, parts XV, XIX, XX) $3\text{Na}_2\text{O} \cdot 6\text{CaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (Datar and Jatkar, *Ibid.*, 1939, **22A**, 225), $3\text{MgO} \cdot 6\text{CaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, and $3\text{MgO} \cdot 6\text{SrO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (parts XIII, XIV) have so far been prepared. An alternate real chromium chromate structure suggested for the compound by Datar and Jatkar (*Ibid.*, 1939, **22A**, 287, table III) has to be abandoned as it cannot explain the formation of a compound with 9 moles. of the base, the maximum moles. it can take up, being 8.

40% Stage.—Datar and Jatkar obtained the oxide $3\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ at 40% decomposition of chromic anhydride (*Ibid.*, 1939, **22A**, 119) and assigned the formula $15\text{RO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ to the corresponding basic chromium chromate (*Ibid.*, **22A**, 287). The compounds $15\text{CaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$, $15\text{SrO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$, $15\text{BaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ (Athavale and Jatkar *loc. cit.*; parts XV, XIX, XX) $5\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ (Datar and Jatkar, 1939, **22A**, 225), $5\text{MgO} \cdot 10\text{CaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ and $5\text{MgO} \cdot 10\text{SrO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ (parts XIII, XIV) have been prepared. An alternate structure suggested by Datar and Jatkar (*Ibid.*, 1939, **22A**, 287, table III) can form $6\text{RO} \cdot 3\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, and has to be abandoned as it cannot show the reactions actually taking place in the decomposition of chromates at high temperature.

50% Stage.—Datar and Jatkar obtained the chromium chromate $2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ in the decomposition of chromium trioxide at 50% stage (*Ibid.*, 1939, **22A**, 119). The compound $2\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ obtained by Nargund and Watson in the reactions of calcium chromate with

chromic oxide is really $\text{CaO Cr}_2\text{O}_3 \text{CrO}_3$ (*cf.* part XVII). The decomposition of mixtures of calcium and strontium chromates with magnesium oxide yielded $4\text{CaO } 2\text{MgO } 2\text{CrO}_3\text{Cr}_2\text{O}_3$ and $4\text{SrO}2\text{MgO } 2\text{CrO}_3\text{Cr}_2\text{O}_3$ (parts XIII, XIV). The formation of $6\text{CaO } 2\text{CrO}_3\text{Cr}_2\text{O}_3$ has been shown in the synthesis and decomposition of calcium chromate (part XIX). The only basic chromium chromate at this stage appears to be $6\text{RO } 2\text{CrO}_3 \text{Cr}_2\text{O}_3$. The alternate chromium chromate structure proposed by Datar and Jatkar (*Ibid.*, 1939, **22A**, 287, table III) has to be discarded as it shows formation of $4\text{RO } 2\text{CrO}_3\text{Cr}_2\text{O}_3$ which is not formed (parts XIX, XX).

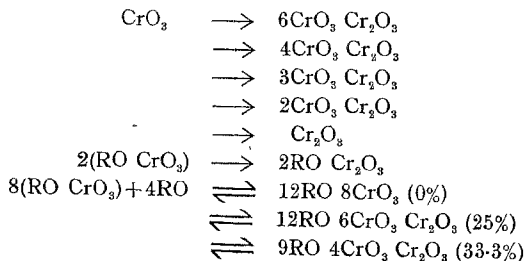
100% Stage.—A large number of basic chromites with varying content of base is known. The formation of $\text{RO } 2\text{Cr}_2\text{O}_3$ (*Ibid.*, 1926, **9A**, 163) $\text{RO } 1.5\text{Cr}_2\text{O}_3$ (part XVII), $\text{RO } \text{Cr}_2\text{O}_3$ and $2\text{RO } \text{Cr}_2\text{O}_3$ (*Ibid.*, 1938, **21A**, 65 and parts XIX, XX) and $4\text{RO } \text{Cr}_2\text{O}_3$ (parts XV, XVI, XVII, XVIII) has been observed in the decomposition of chromates. The basic chromate $3\text{RO } \text{Cr}_2\text{O}_3$ is initially formed in the reactions between chromic oxide and base (parts XIX, XX) in vacuum at high temperature.

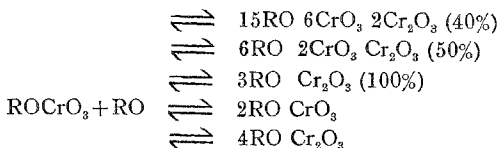
Athavale and Jatkar reported the formation of $4\text{RO } 2\text{CrO}_3 \text{Cr}_2\text{O}_3$, $3\text{RO } \text{CrO}_3 \text{Cr}_2\text{O}_3$ and $8\text{RO } 2\text{CrO}_3 \text{ } 3\text{Cr}_2\text{O}_3$ at 50, 66.6 and 75% decomposition of pure chromates. It has been shown that the compounds formed at these stages are identical with the compounds occurring in the decomposition of basic chromate. The chromate decomposes irreversibly to the chromite $2\text{RO } \text{Cr}_2\text{O}_3$. The basic chromate is formed at the intermediate stage by the reaction between the chromate and the oxide made available from $2\text{RO } \text{Cr}_2\text{O}_3$. The basic chromate $12\text{RO } 8\text{CrO}_3$ thus produced then decomposes in stages forming compounds $12\text{RO } 6\text{CrO}_3\text{Cr}_2\text{O}_3$, $9\text{RO } 4\text{CrO}_3\text{Cr}_2\text{O}_3$, $15\text{RO } 6\text{CrO}_3 \text{ } 2\text{Cr}_2\text{O}_3$ and $6\text{RO } 2\text{CrO}_3 \text{Cr}_2\text{O}_3$ (parts XIX, XX). It will thus appear that the reactions of chromates at high temperature occur with the formation of definite compounds corresponding to the chromium chromates $6\text{CrO}_3\text{Cr}_2\text{O}_3$, $4\text{CrO}_3\text{Cr}_2\text{O}_3$, $3\text{CrO}_3\text{Cr}_2\text{O}_3$ and $2\text{CrO}_3\text{Cr}_2\text{O}_3$ which are produced in the decomposition of chromium trioxide.

Datar and Jatkar (*Ibid.*, 1939, **22A**, 119) have already shown that

the products of decomposition of chromic oxide at 25%, 33.3%, 40% and 50% stages are definite compounds. In the study on the thermal decomposition of CrO_3 by magnetic properties, Bhatnagar, Cameron, *et al* (*Jour. Chem. Soc., 1939, 1933*) however observed that paramagnetic properties appear when the oxide $\text{CrO}_{2.63}$ is formed, the susceptibility at this stage being 36×10^{-6} . This value increases gradually to 40.8×10^{-6} in the first nonstoichiometric range Cr_6O_{12} . The oxide shows ferromagnetic properties in the range Cr_6O_9 . They did not observe any significant change in the magnetic properties during the decomposition and concluded that two nonstoichiometric oxides are formed in the decomposition and that variations in the magnetic properties are due to the susceptibility varying as oxygen is removed from the lattice. The considerations discussed by Datar and Jatkar (*Ibid.*, 1939, **22A**, 287, 309) however, show that the magnetic susceptibility of the system gradually increases from 0 to 27.5×10^{-6} , indicating ferromagnetic properties when the decomposition exceeds 40%. The magnetic properties therefore cannot be successfully employed for determining whether the oxides produced at the various stages in the decomposition of CrO_3 are nonstoichiometric compounds or mixtures of stoichiometric compounds. As the decomposition of basic chromate also occurs in four stages, the four corresponding chromium chromates must be real stoichiometric compounds.

The complete scheme which represents the reactions of chromic anhydride and chromates at high temperatures is given below:—





The chemical properties of the several chromium chromates have so far not been systematically investigated, though the solubility of the oxides in various reagents has formed a part of several investigations. Braun (*Jour. Prakt. Chem.*, 1863, (1) **90**, 856) observed that $4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$, dissolved slightly in cold water and showed a greater solubility in boiling water. Traube (*Annalen*, 1884, **66**, 89) prepared $\text{Cr}_2\text{O}_3 \cdot 3\text{CrO}_3$ by heating CrO_3 to 250° and observed that the oxide was insoluble in water and converted into a soluble modification by keeping in contact with water for a long time. Dobernier (*Z. anorg. Chem.*, 1908, **62**, 440) observed that Cr_6O_{12} dissolved in hot water with the formation of a solution of colloidal character. Simon and Schmidt (*loc. cit.*) observed that Cr_6O_{13} was partly soluble in hot water. The results indicate that water slowly reacts with the oxides, to form a corresponding acid, which is soluble in water to a certain extent. The avidity of the oxides for water is clearly shown by the hygroscopic nature of the decomposition products of CrO_3 at the various stages (Simon and Schmidt: *loc. cit.*). A large number of hydrates of the oxides are also known. The simultaneous evolution of H_2O and O_2 in the decomposition of the hydrates of the oxides of chromium (Simon and Schmidt: *loc. cit.*) also indicates that water molecules are in chemical combination with the oxides. The observation that chromium chromates take up a large amount of base to form stable basic chromium chromates points out to their acidic behaviour.

Recently Roy Chaudhari (*J. Ind. Chem. Soc.*, 1939 **16**, 652) measured the equivalent conductivity, freezing point, P_H value and absorption spectra of aqueous solution of $3\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ and concluded that the oxide is not a simple chromium chromate $\text{Cr}_2(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$ but it is $\text{Cr} [\text{Cr}(\text{H}_2\text{O})_3 \text{CrO}_4]_3$. The structure given by Datar and Jatkar (*Ibid.*, 1939, **22A**, 287) is on the supposition that the oxide is

dimolecular. The oxide reacts with water to form an acid, which is soluble in water and dissociates to a slight extent. The apparent molecular weight determined by Roy Chaudhari is less than half of the true molecular weight due to the breaking up of the double molecule and to the ionic dissociation of the weak acid formed. The P_H of the solution indicates that about 12% of the acid formed is dissociated. The conductivity measurements are also in accordance with this result. On boiling with water a brownish precipitate is given out, probably due to the formation of $2CrO_3 \cdot Cr_2O_3$. Although $3CrO_3 \cdot Cr_2O_3$ breaks up completely by alkali or ammonium hydroxide, it does not indicate the presence of free CrO_4^{--} ions in its aqueous solution.

The following reactions observed for the chromium sulphate $Cr_5O_3 \cdot 3SO_3$ show a great similarity in the properties of the two compounds $Cr_2O_3 \cdot 3SO_3$ and $Cr_2O_3 \cdot 3CrO_3$. A formula $Cr_2O_3 \cdot 3SO_3 \cdot 7.5H_2O$ has been proposed to the chromic sulphate having all the SO_4^{--} ions marked. The sulphate gives no reaction for Cr^{+++} or SO_4^{--} and is hydrolysed when boiled with water in dilute solution to $Cr_2O_3 \cdot 2SO_3 \cdot H_2O$. The molecular weight determinations of the sulphate have shown that it is a double molecule $2Cr_2O_3 \cdot 6SO_3$ (*cf.* Mellor, XI, 438). The above considerations are evidently in support of the structure proposed by Datar and Jatkar to $3CrO_3 \cdot Cr_2O_3$ and to the corresponding basic chromium chromate $15RO \cdot 6CrO_3 \cdot 2Cr_2O_3$.

Datar and Jatkar have shown that it is possible to obtain the average valency of chromium in different oxides from their magneton numbers. The average valency is fractional in most of the cases, which is in confirmation of the structure to these oxides, in which chromium exists in two valency states, *viz.*, 3 and 6. (*Ibid.*, 1939, 22A, 309).

X-ray investigations of Cr_2O_3 show that every atom of chromium is surrounded by 6 oxygen atoms and that the metal atoms are immediately below and above the centre of the equilateral triangle formed by three oxygen atoms (*Davey : Phys. Rev.*, 1923 (2), 21, 716). In CrO_3 every chromium atom is surrounded by six oxygen atoms forming a somewhat deformed octagon. The elementary cell of CrO_3

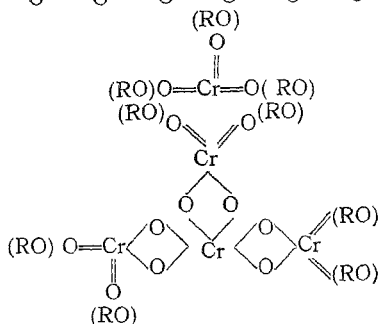
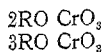
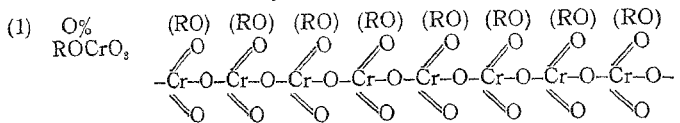
contains many molecules (*Braken. Z. Krist* 1931, 484). The compounds formed at the intermediate stages in the decomposition of CrO_3 have not been studied by X-ray. In the reactions involving solids, the position of the atoms of the reactants is either completely fixed or fixed within relatively small units. Consequently the main characteristic of the solid reactions must be a tendency to keep the original configuration. A very definite relation should exist between the original crystal and the crystals of the new variety formed from it.

The reactions which leave the original configuration only slightly changed, will occur very much readily than those which require serious alterations. Consequently the reactions in which a chemical bond has to be broken in different places and rejoined in another will be sluggish and will take place at temperatures at which movement of atoms is quite considerable (*Bernal, Trans. Faraday Soc.*, 1938, **34**, 834).

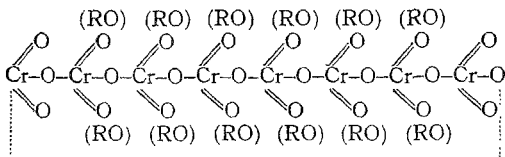
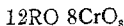
The configuration of both CrO_3 and Cr_2O_3 being known, it can be presumed that all the chromium atoms are arranged in a ring so that every chromium atom is surrounded by six oxygen atoms as in the case of CrO_3 and Cr_2O_3 , the two end chromium atoms coming together to form Cr_2O_3 group.

The chromium chromates obtained in the decomposition of chromium trioxide and of chromates at high temperature can be best represented by the structures assigned by Datar and Jatkar and presented below, which are in conformity with the basic properties, chemical behaviour, X-ray structures, magnetic measurements and the reactions at high temperatures. The structural formula serve to indicate the manner in which chromium chromates decompose in successive stages, corresponding to 25, 33²/₃, 40, 50%. The chromium chromate structures suggested alternatively (*Datar and Jatkar Ibid.*, 1939, **22A**, 287, table III) are to be discarded as they are not in conformity with the chemical properties and the X-ray structure of chromium oxides,

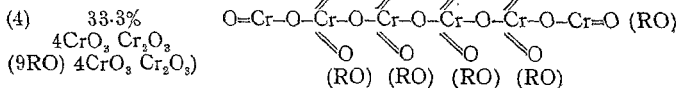
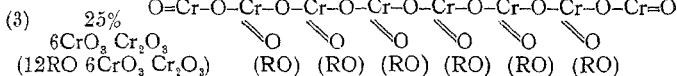
Structure of Chromium Chromates

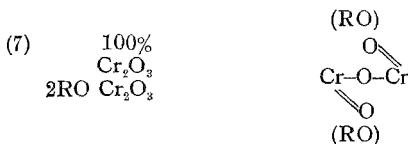
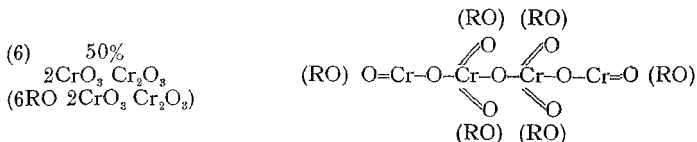
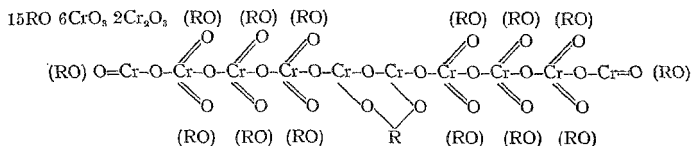
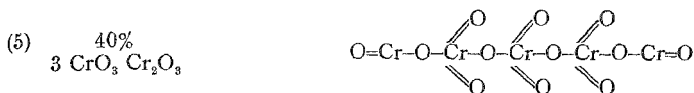


or



or





In the reactions of chromates, the systems can be regarded as two component systems possessing three separate phases. The system has one degree of freedom. A constant pressure of oxygen evolved is obtained at constant temperature. There should be no possibility of solid solutions as the reaction occurs at the boundary lines of the phases.

The general property of autocatalysis in the reactions occurring at the intersurface of two solid phases due to increase of intersurface area (*Langmuir, Jour. Am. Chem. Soc.*, 1916, **38**, 2221) is shown by strontium chromate irreversibly decomposing to strontium chromite (part XX). The other reactions take place too rapidly for the measurement of the reaction rates. The observation in the reactions of chromates that the percentage of the chromate decomposed in rapid decomposition is less than that in slow decomposition

(part XIX) is in agreement with the findings of Benton and Emmet (*Ibid.*, 1924, **46**, 2728) that the intersurface area present at any time depends not only on the extent to which the reaction has proceeded but also on the manner in which it begun and that if reaction starts at few centres considerable reaction takes place before the maximum rate is reached, while if the process begins at many centres, the maximum rate occurs at an early stage of the reaction, further reaction being slow.

The formation of solid solutions is favoured by the existence of several compounds in the decomposition products. The solid solution diminishes the vapour pressures and the extent of decomposition. Besides this the side reactions have not a limited possibility. The equilibrium decomposition pressures of the various compounds cannot therefore be accepted without caution. However, it is surprising to find the remarkable agreement shown by the heats of reaction calculated in accordance with the Nernst's equation for the various mixed basic chromium chromate.

Heats of decomposition of the mixed basic chromium chromates

(1) *Basic Chromates*

$2\text{CaO} \cdot \text{CrO}_3$	$2\text{SrO} \cdot \text{CrO}_3$	$\text{CaOSrO} \cdot \text{CrO}_3$	$\text{CaOCr}_2\text{O}_5 \cdot \text{CrO}_3$
42.1	46.2	42.5	52.7

(2) *Mixed Basic Chromium Chromates*

% decomposition	Na_2OCaO	CaOMgO	CaOCaO	SrOMgO
0	52.1	57.5	55.6	60.7
25	63.0	60.4	58.9	61.9
33.3	60.4	61.5	61.8	63.4
40	62.0	63.5	63.1	67.5
50		64.8	68.1	67.6

Oxidation of chromites.—All the compounds produced at the intermediate stages, viz., 25, 33.3, 40 and 50% decomposition of chromate, also exist in the oxidation of chromite (parts XIX, XX). The observation of Wachtel (*J. Russ. Phys. Chem. Soc.*, 1885, **17**, 109; *Bull. Soc. Chim.*, 1886, (2) **45**, 179) that a part of chromic oxide acquires a property of dissolving in acids on the oxidation follows from the consideration that the intermediate oxidation products are basic chromium chromates soluble in acids. The results on the oxidation of Cr_2O_3 and chrome ore in presence of different oxides are shown in fig. 1 (Raman Nayar, Watson and Sudborough curves 1–11,

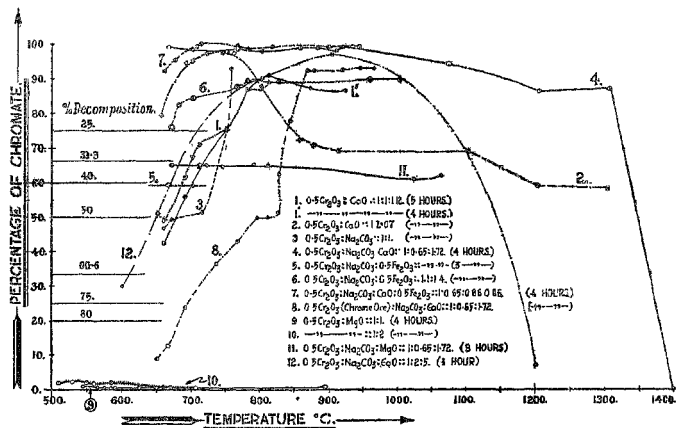
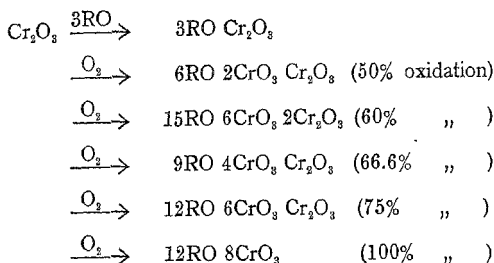


FIG. 1

Bogitch, *Comptes Rend.*, 1924, **178**, 2254, curve 12). It must be made clear that the results of Raman Nayar, Watson and Sudborough and other authors have not been obtained under equilibrium conditions. The oxidation stages are not shown except in few cases, the extent of oxidation being the only guide in ascertaining the course of the reactions. The results can only be analysed by a careful consideration of the mechanism of the reactions in the oxidation of chromite to chromate which can be represented as follows (*cf.* Parts XIX-XX.)



The temperature at which the oxidation of the chromite occurs is comparatively lower than the temperature at which decomposition of chromate starts, as the latter reaction generally occurs at high temperatures. The rate of oxidation increases with temperature.

The oxidation of chromic oxide in presence of bases always takes place with the initial formation of $3\text{ROCr}_2\text{O}_3$ into basic chromium chromates. The complete oxidation product consists mainly of $12\text{RO } 8\text{CrO}_3$ along with $2\text{RO } \text{CrO}_3$ and $\text{RO } \text{Cr}_2\text{O}_3 \text{ CrO}_3$ depending upon the proportion of base and Cr_2O_3 present in the system (parts XIX-XX).

Accordingly if the oxidation of Cr_2O_3 in presence of CaO is carried out at high temperature in air, 100% oxidation is not possible as $2\text{CaO } \text{CrO}_3$ or $\text{CaO } \text{Cr}_2\text{O}_3 \text{ CrO}_3$ produced subsequently decomposes (*cf.* curves 1, 1', 2).

Comparison of curves 2, 3 and 4 shows that Cr_2O_3 oxidises at lower temperatures in presence of CaO than in presence of sodium carbonate and also that the oxidation is very rapid if both calcium oxide and sodium carbonate are added to Cr_2O_3 . Curves 4 and 12 show that addition of lime to a mixture of sodium carbonate with chromic oxide facilitates the oxidation and the yield is almost theoretical at 900° .

The oxidation of chromic oxide in presence of sodium carbonate and lime probably occurs with the formation of the complex chromium chromates at the intermediate stages. The oxidation of chromic oxide with lime and soda with and without ferric oxide (curves 4 and 7) show that ferric oxide practically plays no part in the reaction,

only stable basic chromium chromates of calcium and sodium being formed during the oxidation. However, if chromic oxide is initially combined with ferric oxide, the reaction is slow at low temperature being complete only at high temperatures (curves 4 and 8). Thus with a mixture of chrome ore instead of Cr_2O_3 , with sodium carbonate and calcium oxide, the oxidation is slow. In a similar case Nayar, Watson and Sudborough have observed that although chromic oxide readily converted into chromates by sodium carbonate in presence of MgO , magnesium chromite reacts with sodium carbonate only with difficulty.

A break at 50% chromate formation is observed in the oxidation of a mixture of Cr_2O_3 with Na_2CO_3 (curve 3) due to the formation of $6\text{Na}_2\text{O} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, further reaction being very slow at low temperature. A break at this stage is also observed in the oxidation of a mixture of chrome ore with sodium carbonate and calcium oxide (curve 8). The results of Nargund and Watson (part II) on the oxidation of mixture of Cr_2O_3 and CaO at 1030° and 20 mm. pressure of oxygen indicate the formation of $6\text{CaO} \cdot 2\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$.

A break at 60% oxidation is shown by curves 5 and 11. There is insufficient sodium carbonate in the mixture ($0.5 \text{Cr}_2\text{O}_3 : \text{Na}_2\text{CO}_3 : 0.5 \text{Fe}_2\text{O}_3$ or $\text{MgO} :: 1 : 0.65 : 1.72$). The reaction stops at 60% oxidation and does not show the formation of the stable mixed basic chromium chromates of sodium and magnesium for the formation of which enough base is present in the mixture. This is in accordance with the observation that the oxidation of Cr_2O_3 in presence of CaO is not affected by the presence of magnesium oxide (part XIX) except perhaps by way of acceleration of the several reactions. The reactions shown by curves 5, 6 and 11 differ from the oxidation of Cr_2O_3 in presence of Na_2CO_3 alone (curve 3) probably only in their oxidation rates. The decomposition of the final product at higher temperature is due to the formation of ferric chromate and magnesium chromate by double decomposition.

Curves 9 and 10 show that chromic oxide is not oxidised in presence of MgO between $500\text{--}900^\circ$. N. Milbauer (*Chem. Ztg.*,

1916, 40, 587) however obtained 82.7% conversion of chromic oxide with MgO or MgCO_3 heated to 480° in oxygen at 12 atmospheres. This is readily explained as magnesium chromate starts decomposing under vacuum at about 500° and is completely decomposed at 550° according to the results obtained in our laboratory.

Oxidation of chromic oxide in presence of magnesium oxide was studied in a closed system. The oxidation of $\text{Cr}_2\text{O}_3 + 3\text{MgO}$ started at about 380° . The oxidation was continued, a long time being given for oxidation at different temperatures. Though an increase was shown in the extent of oxidation with the rise in temperature, the total oxidation at 780° was less than 3%. The product could be decomposed only by raising the temperature still higher. The results can be explained on the assumption that the major portion of chromic oxide and magnesium oxide combine to produce $2\text{MgO} \cdot \text{Cr}_2\text{O}_3$ which is not capable of taking up oxygen. The basic chromite $3\text{MgO} \cdot \text{Cr}_2\text{O}_3$ which is formed in traces only oxidises to produce comparatively stable basic chromium chromates. The results of Raman Nayar, Watson and Sudborough (*loc. cit.*) show that $2\text{MgO} \cdot \text{Cr}_2\text{O}_3$ is formed in the reactions of magnesium oxide and chromic oxide at about 600° .

It will thus be seen that the oxidation of chromic oxide is possible only when the basic chromite $3\text{RO} \cdot \text{Cr}_2\text{O}_3$ is produced. If the formation of mixed basic chromites corresponding to this formula is possible, the oxidation also occurs with the formation of complex mixed basic chromium chromates. The observation that magnesium oxide has no effect on the oxidation of chromic oxide in presence of calcium oxide or sodium carbonate indicates the inability of magnesium oxide to form mixed basic chromite. On the other hand, an experiment on the oxidation of $\text{Cr}_2\text{O}_3 + 2\text{SrO} + \text{CaO}$ indicated that the oxidation takes place with the formation of mixed calcium strontium chromium chromates. The product of complete oxidation consisted of a large proportion of $\text{CaO} \cdot \text{SrO} \cdot \text{Cr}_2\text{O}_3$.

The possibility of the formation of several mixed chromium chromates of sodium and calcium in varying proportions is a matter

for further investigation. It will be interesting especially to study the stability range of the compounds $8\text{Na}_2\text{O} \cdot 4\text{CaO} \cdot 8\text{CrO}_3$ (I), $8\text{Na}_2\text{O} \cdot 4\text{CaO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (II), $6\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (III), $10\text{Na}_2\text{O} \cdot 5\text{CaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ (IV) and $4\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$. A mixture of 2 mols. of sodium chromate with 1 mol. of calcium carbonate started decomposition in vacuum at about 300° probably due to the reaction. $\text{Na}_2\text{CrO}_4 + \text{CaCO}_3 \rightarrow \text{CaCrO}_4 + \text{Na}_2\text{O} + \text{CO}_2$. The experiment had to be discontinued as the fused mass crept out of the platinum boat and attacked the reaction tube (quartz). A complete set of experiments could not be carried out owing to the fusibility of sodium chromate and also of sodium carbonate.

It seems likely that the oxidation of chromic oxide in presence of sodium carbonate and calcium carbonate takes place with the formation of the complex compounds corresponding to those described above and that the final product of oxidation is a complex basic chromate of the general formula $12\text{RO} \cdot \text{SCrO}_3$, in which R represent $\text{Na} + \text{Ca}$ in different proportions.

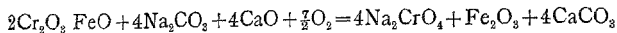
MANUFACTURE OF CHROMATES

The process for the manufacture of chromate from chrome ore are divided generally, into three classes, *viz.*, (1) Dry process, (2) Wet process and (3) Electrolytic process. It is intended to discuss the mechanism of the reaction in the preparation of chromates by those methods which come under the first heading. A brief survey of the literature dealing with the commercial process is made by Mellor (*A comprehensive Treatise on Inorganic and Theoretical Chemistry*, 1931, **11**, 129-32).

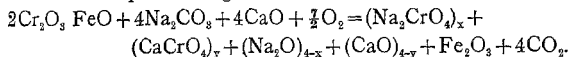
Chrome ore is FeOCr_2O_3 , in which iron is more or less replaced by magnesium and chromium by aluminium, and Cr_2O_3 content in this ore is generally between 45 and 55% of the ore. In the modern methods for the manufacture of alkali chromates, the powdered mineral is mixed with an alkali and lime and roasted by an oxidising flame in a reverberatory furnace at about 1000°C .

Although the manufacture of alkali chromates is a long known process, the mechanism of the complex reactions, which take place

in the chromate furnace is not known. The reaction has been represented by the following equation :—



As this formulation suggested the existence of calcium carbonate in the oxidation products, which is unstable at the high temperature of the reaction, Sofianopoulos (*J. Soc. Chem. Ind.*, 1930, **49**, 279 T) modified the equation as given below :—



He showed that $x+y$ is equal to 4 and also that x and y are functions of temperature of the system and that the value of x tends to 4 at higher temperature. Farbenind (E. P. 1927, 261, 647) used a mixture of the ore, sodium carbonate, ferric oxide and a small quantity of magnesia and represented the reaction as $2\text{FeOCr}_2\text{O}_3 + 4\text{Na}_2\text{CO}_3 + 4\text{Fe}_2\text{O}_3 + \frac{7}{2}\text{O}_2 = 4\text{Na}_2\text{CrO}_4 + 5\text{Fe}_2\text{O}_3 + 4\text{CO}_2$ and suggested that sodium ferrite is formed as an intermediate compound.

As the mixture of chrome iron ore, lime and sodium carbonate is generally used in the manufacture of chromates, the complex reactions that take place in the furnace can only be determined from the behaviour of the components of the mixture at higher temperatures. Raman Nayar, Watson and Sudborough (*loc. cit.*) investigated the reactions between chromium sesquioxide and the oxides of iron, calcium and magnesium and sodium carbonate at various temperatures in air. In the subsequent study on the reactions of chromates at high temperatures, Nargund and Watson, and Athavale and Jatkar, reported that chromates and basic chromates decompose at high temperatures with liberation of oxygen and with the formation of various intermediate stages. Several mixed basic chromium chromates have been prepared. The possibility of the formation of similar compounds in the reverse reaction of the oxidation of chromite to chromate has been shown and now it is possible to suggest a mechanism and to obtain optimum conditions for the manufacture of chromates from chrome iron ore.

In table I the whole data on the manufacture of chromates has been summarised. When the amount of Cr_2O_3 in the ore is not known the calculations are made on the assumption that any ore of good quality contains about 50% of Cr_2O_3 . A theoretical quantity of sodium

TABLE I

Author	Year	$\text{Cr}_2\text{O}_3 : \text{Na}_2\text{CO}_3 : \text{CaO}$ or K_2CO_3	REMARKS
Wachtel ⁵	... 1885	1 : 2 : 4.9	
Bess ¹	... 1922	1 : 1.8 : 6	95% oxidation
Bogitch ⁶	... 1924	1 : 0.7 : 8	90% oxidation
		1 : 2 : 5	97% oxidation in one hour at 900°.
Yushkevich ²	... 1925	1 : 2 : 5.4	The oxidation is slow at 700°, 95% in 30 mins. at 116°, decomposition starts at 1260°.
Popoff ³	... 1926	1 : 2 : 5	(1) for various grades of ore, (2) above 1100° excess of lime required.
Sofianopoulos ⁶	... 1980	1 : 1.95 : 8.7	(1) Temp. 800-900°, (2) yield 98.68%.
Mutual Chemical ⁴ Company	... 1931	1 : 2 : 2.8	The ore is heated initially with lime and with alkali carbonate to combine with only a part of chromium.
	... 1935	1 : 1.75 : 2.8	(1) mixed with a leached residue from a previous roast, (2) heated initially at low temperatures and then above 1000° to decompose alkali silicates and aluminates formed.
Carpenter and Stevenson ⁵	... 1935	1 : 2 : 3.4	The finely ground mixture formed into briquettes employed.

1. L' Ind. Chim. 1922, **9**, 148 ; Chem. Trade Journal, 1922, **70**, 595.
2. Trans. Russ. Inst. Econ. Min. 1925, **13**, 1-29 (cf. Mellor XI, 132).
3. J. Russ. Chem. Ind., 1926, **2**, 465 ; Cont. (Met. Chem. Engg. 1927, **1**, 148).
4. U. S. Patent, 1931, 17,52,863 ; 1935, 19,48,143.
5. *Ibid.*, 1935, 19,64,719.
6. *Loc. cit.*

carbonate for the formation of sodium chromate is always added. The amount of calcium oxide per Cr_2O_3 mol. present in the mixture ranges between 3 and 5 mols. but in most of the cases the ratio of $\text{CaO} : \text{Cr}_2\text{O}_3$ is near about 3. As it is likely that an excess of reactants is added in most of the cases the molecular proportion in which CrO_3 , Na_2CO_3 and CaO should be present in the mixture is possibly 1 : 2 : 3.

It is likely that the oxidation of Cr_2O_3 in presence of Na_2CO_3 and CaO during the first stages, proceeds mainly with the formation of the compound $6\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$. A mixture of 1 mol. of Cr_2O_3 with 3 mols. of CaO is required for the first stage in the reaction. On further oxidation this compound reacts with sodium carbonate giving a basic chromium chromate of calcium and sodium. At the complete oxidation stage the basic chromate $\text{Na}_2\text{OCaOCrO}_3$ begins to form. The final oxidation product is thus a mixture of $8\text{Na}_2\text{O} \cdot 4\text{CaO} \cdot 8\text{CrO}_3$ and $\text{Na}_2\text{OCaOCrO}_3$, which on treatment with water gives sodium chromate and lime. $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{CrO}_3$ is unstable above 900° . Sofinanoupolos observed the formation of dark coloured nucleus enclosed in a hard yellow shell at high temperature obviously due to the decomposition of $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{CrO}_3$ at high temperature.

The chrome ore consists of oxides of iron, magnesium and aluminium, which influence the oxidation by the formation of ferrites and aluminates. Addition of Fe_2O_3 to replace a part of CaO in the mixture has been recommended by some authors (*Wise, J. Soc. Chem. Ind., 1895, 14, 865*; *Farbenind, loc. cit.*) in order to reduce the cost of manufacture. At high temperatures the oxidation will take place as if these oxides are absent, as the basic compounds containing these metals are comparatively easily decomposed.

As sodium compounds are fusible at high temperature, these oxides are in a way useful in preventing fusion and increasing the surface of oxidation and avoiding difficulties in the extraction of the chromate from the fused mass. The oxidation of the chromite thus take place with the intermediate formation of several basic chromium chromates, the final product of oxidation being always a mixture of $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{CrO}_3$ with the stable basic chromate of the general formula $12-x\text{Na}_2\text{O} \cdot x\text{CaO} \cdot 8\text{CrO}_3$.

The partial formation of sodium chromate in the reaction along with the basic chromate stabilises the final oxidation product. The oxidation temperature can therefore be greatly increased without encountering a harmful reduction in the yield of chromate.

SUMMARY

The thermal decomposition of chromium trioxide and of the basic chromates of the general formula $12RO \cdot 8CrO_3$ has shown that they decompose in four stages into chromium chromates having a general formula $nCrO_3 \cdot Cr_2O_3$ and the corresponding basic salts respectively where $n=1$ to 6. The oxides of chromium are not characterised by any definite decomposition pressures but possess distinctive reaction rates. The corresponding basic chromium chromates possess characteristic decomposition pressures. The structures of the compounds have been assigned on the basis of their properties and reactions based upon the ordinary valencies of chromium, *i.e.*, 3 and 6.

The basic chromate $2RO \cdot CrO_3$, which is usually produced in the reactions of chromate and oxide, when the oxide phase is in excess decomposes without the formation of compounds at intermediate decomposition.

Oxidation of chromic oxide in presence of base always occurs with the initial formation of $3RO \cdot Cr_2O_3$ and of basic chromium chromates on oxidation. The oxidation does not take place if basic chromites other than $3RO \cdot Cr_2O_3$ are initially produced.

The reactions in the chromate furnace have been fully discussed. The oxidation occurs with the formation of several basic chromium chromates, the final oxidation product being always a mixture of $xCaO \cdot 12-xNa_2O \cdot 8CrO_3 + Na_2CrO_4 + Na_2O \cdot CaO \cdot CrO_3$. The previous data on the manufacture of chromates has been reviewed.

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