

REACTIONS OF CHROMATES AT HIGH TEMPERATURES

PART XIII—DECOMPOSITION OF MIXTURES OF CALCIUM CHROMATE WITH MAGNESIUM OXIDE

By D S Datar

INTRODUCTION

In a systematic work on the decomposition of mixtures of chromates of calcium, strontium and barium with the corresponding carbonates, Athavale and Jatkari and Datar, Athavale and Jatkari (This Journal 1938, **21A**, 119, 176, 273, 1939, **22A**, 111) reported the existence of several basic chromium chromates at intermediate decomposition. Datar and Jatkari (*Ibid.*, 1939, **22A**, 287) pointed out that the optimum mixtures for the formation of basic chromium chromates contain the chromate and the oxide in the ratio of 2 : 1 mols and that the initial formation of the basic chromium chromate $12\text{RO} \cdot 8\text{CrO}_3$ is followed by the formation of the basic chromium chromates $12\text{RO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, $9\text{RO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ and $15\text{RO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ at 25%, 33.3% and 40% stages of the complete decomposition.

A mixture of calcium chromate with sodium carbonate in the ratio of 2 : 1 mols when heated decomposes with evolution of carbon dioxide and forms a basic chromate $4\text{Na}_2\text{O} \cdot 8\text{CaO} \cdot 8\text{CrO}_3$, which decomposes in stages corresponding to 25%, 33.3% and 40% decomposition of the chromate to form the compounds $4\text{Na}_2\text{O} \cdot 8\text{CaO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, $3\text{Na}_2\text{O} \cdot 6\text{CaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$, $5\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ (Datar and Jatkari *Ibid.*, 1939, **22A**, 255). The object of this investigation is to find out whether stages similar to those obtained in the decomposition of mixtures of calcium chromate with calcium carbonate and with sodium carbonate, also occur in the decomposition of mixtures of calcium chromate with magnesium oxide. A knowledge of the stability of the different compounds obtained is useful in the manufacture of chromates, as the oxidation of the chrome ore takes place in presence of magnesium oxide, which is generally present to the extent of 15% in the chrome ore.

EXPERIMENTAL

The experimental procedure followed was the same as used and described by Athavale and Jatkari (*Ibid*, 1937, **20A**, 111) A diagrammatic sketch of the new apparatus is given in fig 1 All the

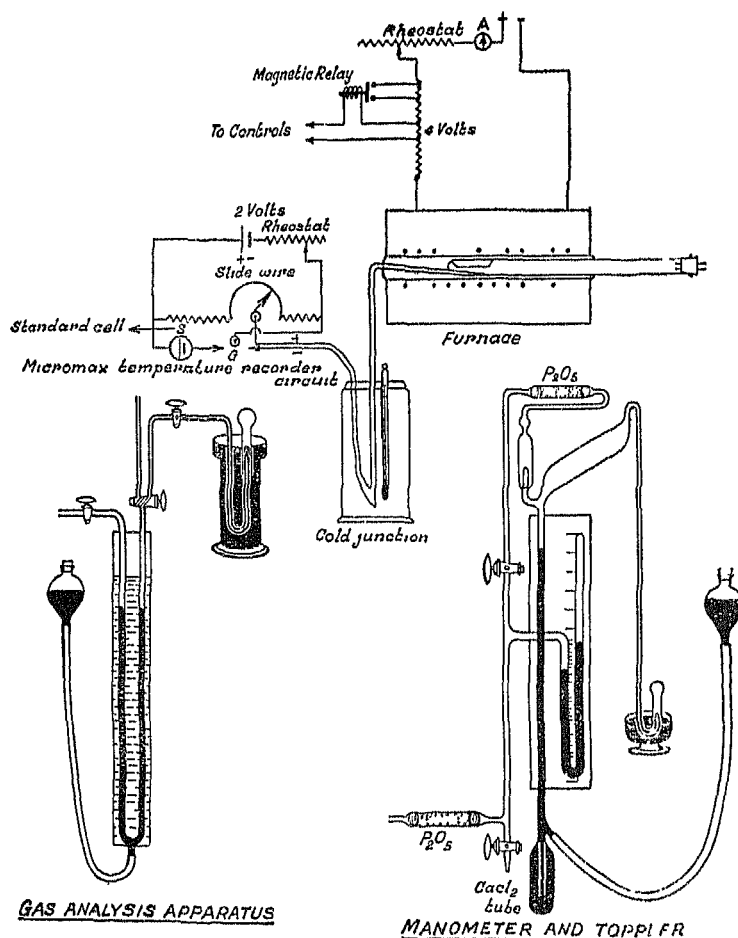


FIG 1

experiments (upto 1100°C) were carried out in a furnace wound with nichrome wire. The substances under study were pure (better than 99.5%) and the mixtures were prepared by thoroughly grinding in an agate mortar. The charge was put in a platinum boat placed in a quartz tube in the furnace in such a way that the boat came in the centre of the furnace. The quartz tube was joined through a rubber

cork covered with sealing wax, to the rest of the apparatus consisting of a manometer to note the pressures, a Topley pump to evacuate the apparatus whenever necessary and two phosphorus pentoxide tubes to dry the gases evolved. The apparatus was completely evacuated and vacuum was maintained overnight for detecting leaks. The furnace was then heated gradually, the sealing wax cover over the rubber cork joint being kept cool under wet cloth. The temperature was recorded and automatically controlled within 1° by a Micromax automatic recorder and controller (*cf* fig 1). The readings were occasionally checked against a standard platinum resistance thermometer. As the vapour pressures were low, the measurements of pressure (upto 25 mm) were made on a cathatometer reading to hundredth of a mm. The higher pressures were read on a meter scale fixed alongside the manometer. The decomposition was determined by the measurement of gases evolved. The gas was measured in a burette enclosed in a water jacket (fig 1) at atmospheric pressure. The gas was analysed for carbon dioxide, oxygen and any admixed air, by treating with potassium hydroxide and phosphorus in succession.

The formation of compounds at intermediate decomposition was always determined by the measurements of the characteristic dissociation pressures. The formation of solid solution was indicated by a gradual drop in pressure at constant temperature when successive quantities of gas evolved were removed. It was very essential to keep the closed system for a few hours at constant temperature to allow the reaction between solids to proceed to equilibrium especially at low temperatures and pressures.

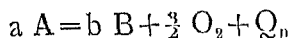
The heats of reactions of several chromium chromates have been calculated by the application of Neinst's approximation formula

$$\log K_p = \frac{-Q}{4.571T} + \sum n \cdot 1.75 \log T + \sum n C$$

where K_p is equilibrium constant expressed as partial pressures of the gaseous reactants in atmospheres divided by the partial pressures of the gaseous resultants in atmospheres, $\sum n$ is change in the number

of gaseous molecules, T is absolute temperature, $\sum n C$ is the algebraic summation of the conventional chemical constants of the gases and Q is the heat of the reaction

The reaction of chromium chromates at high temperature may be represented by a following general equation



where 'a' molecules of chromium chromate A decompose producing 'b' molecules of chromium chromate B and $1\frac{1}{2}$ molecules of oxygen

Then

$$\log K_p = \log p$$

$$\sum n C = 1$$

$$C = 2.8 \text{ per mol of oxygen}$$

The Nernst's equation becomes

$$-\log p = \frac{Q_p}{4.571T} - 1.75 \log T - 2.8$$

If Q is heat of decomposition per mol of oxygen and p is expressed in mms of mercury, the above formula reduces to

$$Q = 4.571 T (\log p - 1.75 \log T - 5.681)$$

The value given in the last column of the tables for Q has been expressed in Calories per mol of oxygen evolved. Q is heat absorbed during the decomposition and must be taken with a negative sign.

The results on the decomposition of the mixtures of calcium chromate with magnesium oxide have been described below.

Decomposition of a mixture of 2 mols of calcium chromate with 1 mol of magnesium oxide—A mixture of 2 mols of calcium chromate with 1 mol of magnesium oxide was heated in vacuum. The oxide used contained 0.25% carbonate, which was decomposed completely by evacuation below 300° . On further heating, a slight pressure of oxygen was developed due probably to side reaction. The pressure did not regain on evacuation. The mixture was stable up to 825° . A long time was required (5–6 hours) for the mixture to attain equilibrium at this temperature, when steady and reproducible vapour

pressures were obtained. The decomposition pressures of the mixture at different temperatures were then measured, which are given in table I. The results are plotted in fig 2a, in which the decomposition pressure is shown as a function of temperature, and

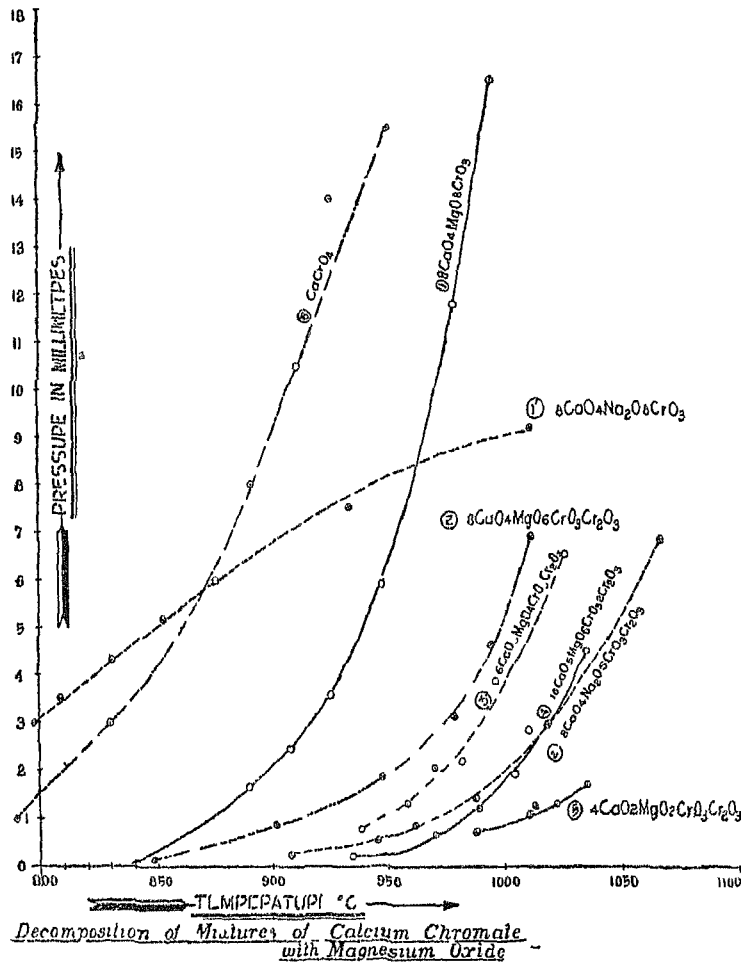


FIG 2a

in fig 2b the logarithm of pressure is plotted against the reciprocal of absolute temperature. The results show that the basic chromate which is formed ($8\text{CaO} \cdot 4\text{MgO} \cdot 8\text{CrO}_3$) is exceedingly stable and has got no vapour pressure at the temperature at which the mixed basic

chromate of calcium and sodium viz, $8\text{CaO} \cdot 4\text{Na}_2\text{O} \cdot 8\text{CrO}_3$, decomposes. The heat of decomposition of the basic chromate to the 25% stage is 57.5 Cals per mol of oxygen evolved. The decomposition takes place according to the equation

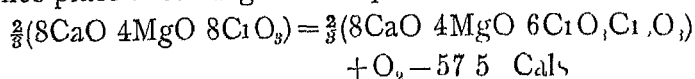


TABLE I

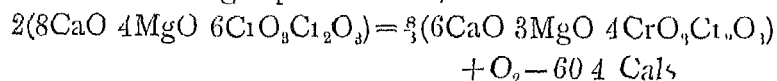
Temp °C	Pressure mm	Q Cals
889	1.64	57.9
907	2.44	57.5
925	3.60	57.5
947	5.92	57.5
978	11.84	57.3
994	16.52	57.3

TABLE II

Temp °C	Pressure mm	Q Cals
848	0.16	60.5
913	0.88	60.3
948	1.88	60.3
978	3.16	60.6
994	4.68	60.5
1011	6.96	60.3

The vapour pressures of the basic chromate were reproducible and the gas was completely absorbed back on cooling.

25% stage—The basic chromate was decomposed by evacuating at 947° until a drop in pressure from 5.92 mm to 1.20 mm was observed, when the decomposition was 25.6%. The product was cooled and the decomposition pressures of the compound $8\text{CaO} \cdot 4\text{MgO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ were measured, which are shown graphically in fig. 2a and 2b and given in table II. The heat of decomposition of the compound is 60.4 Cals, the reaction being represented by



33.3% stage—On further decomposition at 948° by removing the gas evolved, the pressures regained after each withdrawal until 33.3% stage was reached, when a drop in pressure from 1.88 mm to 0.88 mm was observed. The system was cooled down to room temperature and the decomposition pressures of the compound

formed at this stage were measured, which are given in table III and shown graphically in fig 2a and 2b

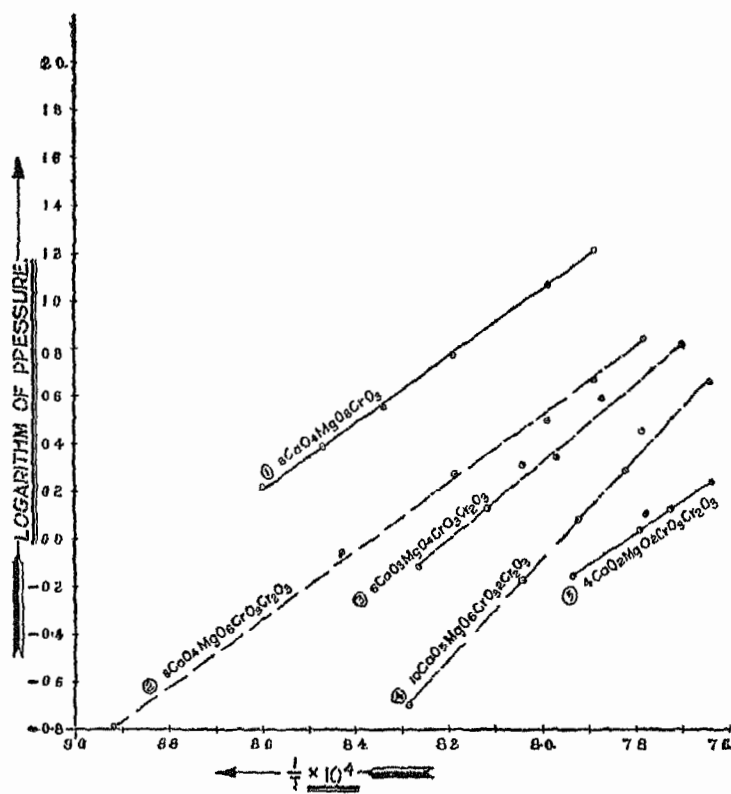


FIG. 2b

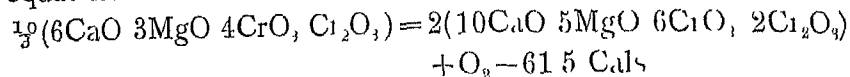
TABLE III

Temp °C	Pressure mm	Q Cals
938	0.78	61.9
958	1.32	61.7
970	2.08	61.2
981	2.22	61.7
996	3.92	61.0
1025	6.60	61.2

TABLE IV

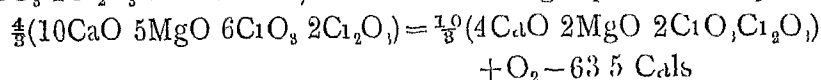
Temp °C	Pressure mm	Q Cals
934	0.20	(65.0)
970	0.68	64.0
988	1.22	63.5
1004	1.96	63.2
1010	2.88	62.5
1034	4.56	62.6

The heat of decomposition of the compound $6\text{CaO} \cdot 3\text{MgO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ formed is 61.5 Cals. The decomposition takes place according to the equation



40% stage—The decomposition was further carried on at 988° until a drop in pressure from 2.14 mm to 1.22 mm was observed when the decomposition was 40%. The vapour pressure measurements are given in table IV and shown graphically in fig. 2

The heat of decomposition of the compound $10\text{CaO} \cdot 5\text{MgO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ is 63.5 Cals, the reaction being represented by



50% stage—On further decomposition at 1010° a drop in pressure was observed from 2.88 to 1.0 mm when the decomposition was 50.4%. The decomposition pressures are given in table V and shown graphically in fig. 2. The formula suggested for the compound is $4\text{CaO} \cdot 2\text{MgO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ and heat absorbed during the decomposition is 64.8 Cals per mol of oxygen.

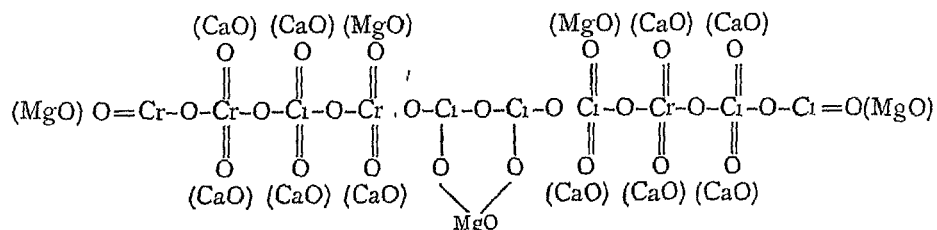
TABLE V

Temp °C	Pressure mm	Q Cals
987	0.72	64.2
1010	1.10	65.0
1012	1.28	64.7
1021	1.32	65.1
1035	1.76	65.1

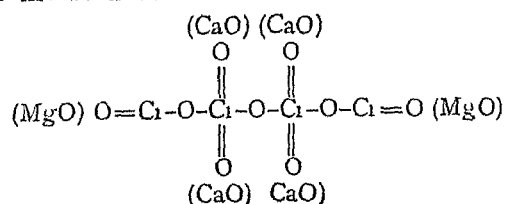
Further decomposition of the compound was carried out by evacuation at 1020° . The pressure did not regain on evacuation. On complete evacuation at 1020° the compound decomposed to 56.5% of the complete decomposition of the chromate.

In all the compounds previously described the ratio of

RO Cr is 1.5 : 1 and the maximum number of mols of the base that the compound corresponding to 66.6% decomposition can take is 4, (RO Cr = 1.33 : 1) (Datar and Jatkar *Ibid*, 287). It is probable, therefore, that the compound $2\text{MgO} \cdot 4\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ is decomposed into mixtures of different compounds at 66.6% stage, in which calcium oxide and magnesium oxide are present in varying proportions. The decomposition pressures of all the compounds formed during the decomposition of the mixture of calcium chromate with magnesium oxide are reproducible at all the temperatures until the next stage is formed on further decomposition. But the vapour pressures of the compound $2\text{MgO} \cdot 4\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ at the 50% decomposition stage, do not regain their original value on decomposition by pumping out the gas evolved, but drop down continuously. This observation in a way supports the assumption that the decomposition product of $2\text{MgO} \cdot 4\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ is not a single substance but a mixture of various compounds, having different compositions. The formulae for the basic chromate and for the compounds corresponding to the stages of decomposition at 25%, 33.3% and 40% can be obtained by replacing Na_2O by MgO in the formula given by Datar and Jatkar (*Ibid*, 225) for the mixed chromium chromates of calcium and sodium. The structural formula for $5\text{MgO} \cdot 10\text{CaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ is accordingly



On decomposition this compound breaks at the dotted line giving the compound $2\text{MgO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (50% decomposition stage) which may have the structure



The mixed basic chromium chromates of calcium and magnesium are all stable, the higher decomposition stages being more stable than the compounds formed at the lower stages. All the basic chromium chromates of calcium and magnesium except that at 25% decomposition are comparatively more stable than the corresponding compounds of calcium and sodium.

Decomposition of a mixture of 3 mols of calcium chromate with 1 mol of magnesium oxide—Athavale and Jatkari observed that in the decomposition of the mixtures of the chromates with the oxides where the oxide is not sufficient for the complete formation of the basic chromium chromates, decomposition occurs with incomplete formation of the compounds and with the decomposition of the remaining chromate independently. The mixtures of 3 mols of calcium chromate with 1 mol of magnesium oxide, however, do not indicate the formation of calcium magnesium chromium chromates described above, but decompose with the vapour pressures corresponding to those of calcium chromate until a stage at about 50% decomposition is reached. The result of this experiment is described below.

A mixture of 3 mols of calcium chromate with 1 mol of magnesium oxide was heated in vacuum at 825° for about 5 hours, when the pressure was 13.9 mm. The gases ($\text{CO}_2 + \text{O}_2$) were pumped out and the system was cooled to the room temperature. The decomposition pressures at various temperatures are given in table VI. On cooling, the gas was completely absorbed back. The decomposition pressures were completely reproducible and corresponded to the vapour pressure values at different temperatures in the decomposition of calcium chromate (Athavale and Jatkari).

The mixture was then decomposed and the vapour pressures at the stages of decomposition at 25%, 33.3% and 40%, were measured. The pressures at all the stages corresponded to those of calcium chromate. When the decomposition reached 50%, a drop in the pressure values was observed, indicating the formation of a new compound at that stage. The decomposition pressures of the compound have been given in table VII.

TABLE VI

Temp °C	Pressure mm
827	1.92
857	4.20
877	7.06
897	12.36
922	21.56

TABLE VII

Temp. °C	Pressure mm
930	1.76
984	2.68
995	3.00
1007	3.80

Decomposition of a mixture of 1 mol of calcium chromate with 1 mol of magnesium oxide—The structural formulæ assigned by Datar and Jatkar to the compounds at different stages show the possibility of the formation of 13 or $14RO \cdot 6CrO_3 \cdot Cr_2O_3$ at the 25%, $10RO \cdot 4Cr_2O_3 \cdot Cr_2O_3$ at the 33.3%, and $8RO \cdot 3CrO_3 \cdot Cr_2O_3$ or $16RO \cdot 6CrO_3 \cdot 2Cr_2O_3$ at the 40% stage. The results of Athavale and Jatkar show, however, that the higher proportion of the base has absolutely no effect on decomposition of the mixtures of the chromate of calcium and strontium with the corresponding carbonate, though the mixtures of barium chromate with barium carbonate containing higher proportion of the carbonate give at constant temperature an increase in the decomposition with increasing amounts of the carbonate. It is now observed that the excess of magnesium oxide in the mixture of calcium chromate with magnesium oxide hinders the formation of the basic chromate and consequently of the further decomposition products and the mixture behaves in its decomposition similarly to calcium chromate. The mixture of 1 mol of calcium chromate with 1 mol of magnesium oxide was particularly chosen for this investigation as it contained the requisite amount of the base for the formation of the basic chromate corresponding to the formula $2RO \cdot CrO_3$. The formation of this compound was however, not indicated in the decomposition of the mixture.

About 1 gm of a mixture of calcium chromate and magnesium oxide (1:1 mols) was heated in vacuum. The decomposition started at about 250°. The mixture initially showed pressure of oxygen

probably due to the decomposition of magnesium chromate formed in the double decomposition of magnesium oxide and calcium chromate. About 5% of the decomposition was due to this side reaction. The vapour pressures of the mixture when the system attained equilibrium have been given in table VIII.

The vapour pressures are comparable to those of calcium chromate. On decomposition, the measurements of the vapour pressures at the intermediate stages did not show any change until a drop in pressure values was observed when the decomposition reached 50%. The decomposition pressures of the compound formed at this stage are given in table IX.

TABLE VIII

Temp °C	Pressure mm	Temp °C	Pressure mm
781	1.24	918	17.60
814	2.20	941	29.46
858	4.64	967	51.00
888	9.48	997	86.50

TABLE IX

Temp °C	Pressure mm
945	1.72
984	2.36
1003	3.60
1025	4.56

The comparison of the vapour pressures at different temperatures show the identity of this compound with the compound obtained in the decomposition of a similar mixture of 3 mols of calcium chromate with 1 mol. of magnesium oxide. It must be mentioned that

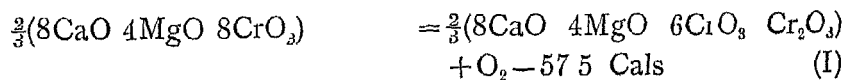
though the original vapour pressures of the mixture are comparable to the decomposition pressures of calcium chromate, the vapour pressures at 50% stage are considerably lower than those for the corresponding stage obtained by Athavale and Jatkar in the decomposition from calcium chromate. This is partly due to the different methods of preparation of calcium chromate. Athavale and Jatkar prepared calcium chromate by neutralisation of chromic acid with lime, while in this investigation the chromate was prepared by precipitating out from calcium chloride solution by potassium chromate. It will also be noticed that the probability that the basic chromate $8\text{CaO} \cdot 4\text{MgO} \cdot 8\text{CrO}_3$ is formed is maximum when calcium chromate and magnesium oxide are present in the mixture in the ratio of 2 : 1 mols.

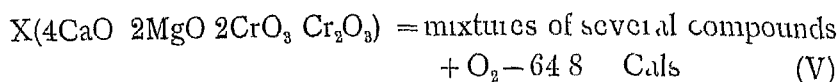
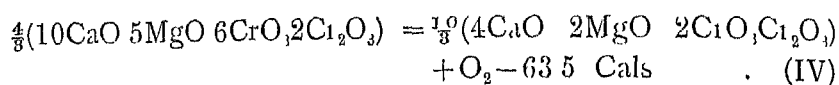
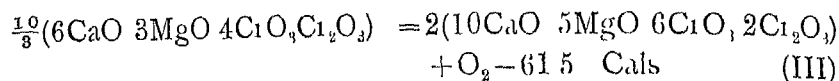
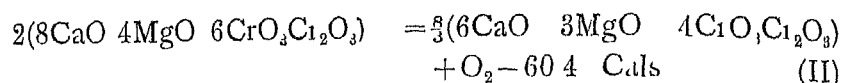
The remarkable property of the chromium chromates of taking up a large amount of the base to form mixed basic chromium chromate of definite composition is further emphasised by the experimental results in this investigation. The property of magnesium oxide in forming highly stable mixed basic chromium chromates is remarkable particularly as magnesium chromate is very unstable and decomposes completely at 550° which is a low temperature compared to the temperature at which basic chromium chromates are found to be stable.

SUMMARY

A mixture of one mol of calcium chromate with 0.5 mol of magnesium oxide decomposes with initial formation of $8\text{CaO} \cdot 4\text{MgO} \cdot 8\text{CrO}_3$ in successive stages at 25%, 33.3%, 40% and 50% decomposition with the formation of the compounds $4\text{MgO} \cdot 8\text{CaO} \cdot 6\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (25%), $3\text{MgO} \cdot 6\text{CaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (33.3%), $5\text{MgO} \cdot 10\text{CaO} \cdot 6\text{CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ (40%) and $2\text{MgO} \cdot 4\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (50)%. The mixtures with lower or higher proportions of the oxide decompose giving pressures identical with those of calcium chromate until the system attains 50% stage.

The heats of decomposition calculated from the characteristic decomposition pressures of the compounds by Nernst's formula are given by the thermochemical equations





The comparison of the stabilities of the different compounds show that the basic chromate is highly stable. All the compounds except that at the 25% stage are more stable than the corresponding compounds in the decomposition of mixtures of calcium chromate with sodium carbonate.

My thanks are due to Dr. S. K. K. Jalkar for his keen interest and helpful guidance during the investigation.

*Department of Pure and Applied Chemistry,
General Chemistry Section,
Indian Institute of Science, Bangalore*

4-7-1941]