On the Phase Diagram of the Cr-O System at High Pressure of Oxygen and Some Properties of the Compound CrO_{2+x}

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The pressure versus temperature diagram of the chromium oxides (Cr_2O_3 , CrO_2 and Cr_2O_5) was determined by the closed vessel method in the range of higher oxygen pressures up to 600 atms. Chromium pentaoxide Cr_2O_5 is comparatively stable below 200°C , but it dissociates into CrO_2 above this temperature. The stable ranges of CrO_2 and Cr_2O_3 in the diagram are separated by the dissociation pressure curve of CrO_2 which rises exponentially with increasing temperature through the points (450° , 100 atms.) and (520°C , 600 atms.). The presence of Cr_3O_8 , which had been reported to be stable at room temperature, was not confirmed above 200°C in the present experiments. The results of determination of oxygen contents in CrO_2 phase indicate that this phase is non-stoichiometric; their composition varies from $\text{CrO}_{1.90}$ to $\text{CrO}_{2.02}$ depending on the equilibrium conditions. The ratio of O/Cr increases with the fall of temperature and increasing oxygen pressure. The lattice constants of CrO_{2+x} (rutile type structure) decrease with increasing oxygen contents. The latter effect is quite consistent when we assume that the excess Cr ion are present as interstitials at the interlattice points of oxygen. The accurate lattice constants of stoichiometric compound CrO_2 are found to be $a=4.408$, $c=2.910$ a.u., $a/c=1.51$. The saturation magnetization of CrO_{2+x} at room temperature seems to increase with increasing O/Cr ratio. The ferromagnetic Curie point of them, however, seems not to change with O/Cr ratio by more than 10°C . (Received April 20, 1962)

I Introduction

Recently chromium dioxide CrO_2 was found to be ferromagnetic, and much interest is directed toward its mechanism. The compound was first synthesized by Wöhler¹⁾ and the magnetic properties has been investigated by Guillaud et al.²⁾. Oxides having higher O/Cr ratios than $3/2$ are never obtained by means of the calcination of metallic chromium at atmospheric pressure. However, it was found that CrO_2 could be prepared when metallic chromium or chromic anhydride was heated under higher pressure of oxygen. In these connections, the determinations of the accurate dissociation pressure of oxygen of these oxides at various temperatures are required.

Now these pure oxides are actually prepared in various methods³⁾, but the systematic studies of the chemical equilibrium among these oxides have not yet been made. Furthermore, the ratios O/Cr of the CrO_2 phase, and therefore their physical properties, are supposed to be dependent largely on the equilibrium conditions under which the oxides are prepared. In the present works, these points have been dealt with in details.

II Experimental Procedure

When chromic trioxide CrO_3 is heated in a closed vessel, it dissociates into lower oxides through the process as follows; $\text{CrO}_3 \rightarrow \text{Cr}_3\text{O}_8 \rightarrow \text{Cr}_2\text{O}_5 \rightarrow \text{CrO}_2 \rightarrow \text{Cr}_2\text{O}_3$. Therefore, the pressure of

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oxygen developed by the dissociation may be calculated from the confirmation of the species of end products, under the assumption of non-leakage of evolved oxygen from the vessel. The latter condition were secured by the attentive use of packing material. Accurately weighed chromium trioxide of Merk were closed in the vessel such as depicted in Fig. 1. The body of it was made of 18-8-stainless steel and aluminium foils were used for packing material which prevented the escape of oxygen gas. The vessel was designed so as to be used even for 1200 atms of pressure at 600°C. After keeping the vessels at required temperature for 5-200 hours until the equilibrium state were attained, and then the vessel were quenched into ice water. The pressure of evolved oxygen were calculated by detecting the species of end products and the initial amount of packed CrO_3 . Geiger counter spectrometer was used for identification of end products using $\text{Cu K}\alpha$ radiation.

Fig. 1 The gas-tight reaction vessel made of 18-8-Cr stainless steel.

Analysis of oxygen content in CrO_{2+x} were carried out by the measurement of the weight loss during the calcination at 800°C for 30 minutes in air: by the latter treatment CrO_2 dissociates into stoichiometric chromium sesquioxide⁹⁾. The accuracy of the results are believed to be within $\pm 0.3\%$. Lattice constants of CrO_{2+x} specimens were accurately determined for each compositions.

III Results and Discussion

(1) The P-T Diagram of the Cr-O System at High Pressure of Oxygen and Some Thermodynamical Considerations.

The results of X-ray analyses for the oxides obtained at various temperatures and oxygen pressures are summarized in Fig. 2. The presence of three compounds Cr_2O_3 , CrO_2 and CrO_{2+x} are identified at these experimental conditions. The stable range of these oxides are separated by two boundary lines. The neighbouring phases coexist on these lines. The rates below 200°C were so slow that the boundary line between Cr_2O_3 and CrO_2 phase could not be determined so accurately. Inasmuch as the compound Cr_2O_3 did not undergo a dissociation into CrO_2 below 200°C within 200 hours, there may be some ambiguity in the dissociation curve of Cr_2O_3 denoted by broken line.

Fig. 2 Phase equilibrium of chromium oxides in oxygen pressure versus temperature diagram.

The oxides having higher oxygen content than Cr_2O_3 were not obtained as stable forms in the present experiments. The compound Cr_3O_8 are likely to be stable at the lower temperature, but not certain.

Kubota⁶⁾ reported a similar diagram for this system with somewhat differences from the present data, especially concerning with the phase boundary between Cr_2O_3 and CrO_2 . As a conceivable origin of the difference there may be a experimental errors caused by the leakage of evolved oxygen during experiments. In this connection, some thermodynamical considerations are given as follows. The changes in free energy ΔF and heat of reaction ΔH of the reaction

are calculated using the P-T curve of the present study shown in Fig. 2 with the aid of two equation (1) and (2).

$$\Delta F = -RT \ln P_{\text{O}_2} \quad (1)$$

$$\Delta H = RT \ln P_{\text{O}_2} / dT \quad (2)$$

where R is gas constant, T is absolute temperature and P_{O_2} is pressure of oxygen. The plot of the values of $\ln P$ as a function of the reciprocal of temperature gives a straight line as practically shown in Fig. 3. The free energy change and the heat of reaction are respectively given as

$$\Delta F = -1.2 \text{ Kcal/mol} \cdot \text{CrO}_2$$

$$\Delta H = 6.6 \text{ Kcal/mol} \cdot \text{CrO}_2$$

On the other hand the heat of reaction ΔH was directly estimated from the specific heat measurement. Fig. 4 shows the specific heat versus temperature curve of CrO_2 . The chromium dioxide begins to decompose at about 560°C at this heating condition in air. Graphical integration of specific heat curve gives the value of the heat of reaction, i.e., the shaded area of figure. The above mentioned values which was estimated from the P-T diagram may be said to be fairly in good agreement with these values in order, when considering the accuracy of the experiment of this sort.

Fig. 3 The $\ln P$ - $1/T$ relation for the dissociation pressure of oxygen of CrO_2 .

Fig. 4 The result of heat measurement. Vertical axis expresses the time required for arising the temperature of specimens and Pt crucible by 2°C.

(2) The Nonstoichiometry of CrO_{2+x}

The deviation of oxygen contents from stoichiometric composition in CrO_2 phase were determined by the measurement of the weight loss during the reduction of the specimens into Cr_2O_3 , in relation to equilibrium condition. The results are shown in Fig. 5. The deviation x increases with both increasing oxygen pressure and decreasing temperature, extending from -0.10 to 0.02 . Fig. 6 shows the variation of the lattice constants with x . Both of the parameter a and c decrease with increasing amount of oxygen. It may be indicated that such a change of lattice parameter is not due to the oxygen interstitials but to the cation vacancies. Similarly in the samples of the lower contents than stoichiometry, Cr ion are supposed to occupy the interstices of oxygen frame work.

The a/c ratio of the parameter slightly decreases as the oxygen ratio becomes higher. Accurately measured lattice constants of the stoichiometric CrO_2 are found to be

$$a = 4.408 \pm 0.004 \text{ a.u.},$$

$$c = 2.910 \pm 0.004 \text{ a.u.},$$

$$a/c = 1.51$$

(3) Saturation Magnetization of the Compound CrO_{2+x}

The mechanism of ferromagnetism has been discussed by many investigator and explained by considering cation-anion-cation superexchange interaction. The Bohr magneton number per Cr ion was reported to be $2.07^{(8)}$ or $2.01^{(9)}$.

The temperature dependency of electrical resistivity of CrO_{2+x} was measured by Kubota²⁷. And it became clear that the compound is semiconductive and the resistivity at room temperature extends from 0.1 to 1.0 ohm·cm, showing no dependence on the O/Cr ratio.

Although the nonstoichiometry of the compound would probably affect the magnetic and electrical properties, they have not measured precisely owing to the difficulties in sample preparations. In the present experiments the saturation magnetization was measured as a function of oxygen contents at room temperature. The results are shown in Fig. 7. Measurements were made using the magnetic torsion bala-

Fig. 5. The difference in O/Cr ratios of CrO_2 phase at several equilibrium conditions.

Fig. 6 The variation of the lattice constants as a function of atomic ratio in CrO_{2+x} phase.

nance improved by Mekata and Takaki⁹⁾. The saturation magnetization seems to increase with increasing O/Cr ratio. In the specimens containing excess Cr ion over stoichiometry, chromium ion would occupy the tetragonal face center of rutile structure probably as Cr^{3+} ion, reducing therefore the superexchange interaction. The ferromagnetic Curie temperature did not differ so much as could be detected.

IV Results

(1) The pressure versus temperature diagram of the Cr-O system was determined at high oxygen pressure as shown in Fig. 2.

(2) The solid phase of rutile structure is non-stoichiometric, whose O/Cr ratio extends from 1.90 to 2.02.

(3) The lattice constants a and c of the rutile type compound CrO_{2+x} both decrease with increasing x values.

(4) The saturation magnetization at room temperature of the compound CrO_{2-x} seems to increase with increasing x values.

Fig. 7 Change in saturation magnetization at room temperature of CrO_{2+x} for various oxygen contents.

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