

Contribution from the Department of Chemistry,  
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## Study of the Nonstoichiometric Compositions of Cobaltous Oxide

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The  $y$  values of the nonstoichiometric chemical formula  $\text{CoO}_{1+y}$  have been measured by a specially made quartz microbalance in a temperature range from 500 to 1200° under oxygen pressures from 152 to  $10^{-3}$  mm. The  $y$  values varied between 0.0159 and 0.0015 and the enthalpies of formation of nonstoichiometric compositions were usually larger than -16 kcal/mol under the above conditions. The plots of  $\log y$  vs.  $\log P_{\text{O}_2}$  (or  $\log y = (1/n) \log P_{\text{O}_2}$ ) show linearity, and  $1/n$  values calculated from the slopes of the plots are  $1/4.8$ - $1/2.8$  in the temperature range of 1000-1200° under  $10^{-3}$ - $10^{-1}$  mm  $\text{O}_2$  pressures. Most of the physical properties of the cobaltous oxide, such as electrical conductivity, oxidation, diffusion, and defects, can be explained through  $y$  values and the mechanism forming the nonstoichiometric compositions of the oxide.

### Introduction

The cobalt oxide system includes  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_2\text{O}_3$ , and  $\text{CoO}_2$ . One of them, cobaltous oxide, normally has a slight oxygen excess (or metal deficit) making it a p-type semiconductor<sup>1-3</sup> with a nonstoichiometric chemical formula,  $\text{CoO}_{1+y}$ , and thus a type IV nonstoichiometric substance.<sup>4</sup>

Ando and Umemoto<sup>5</sup> found that decomposition of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$  occurs rapidly at 940° in air, but at 700 to 850° no decomposition takes place.  $\text{CoO}$  obtained by the decomposition of  $\text{Co}_3\text{O}_4$  at 1100° does not oxidize appreciably when heated in air at 500-800°. This shows that the oxidation and decomposition of the cobalt oxide system due to temperature conditions are an irreversible process in air. Studies have also revealed that the intervals of thermodynamic stability<sup>6</sup> of the oxides  $\text{Co}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CoO}$  are respectively below 300, between 300 and 900, and above 900°. Regarding oxidation of cobalt, Paidassi and coworkers<sup>7</sup> have reported that from 400 to 885° the oxide film consists of two layers,  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$ ; from 905 to 1350°, only  $\text{CoO}$  is present. X-Ray diffraction studies on  $\text{CoO}$  have also been carried out by Saito and his coworkers.<sup>8</sup>

From these earlier studies, it can be concluded that only cobaltous oxide can be obtained through the oxidation of cobalt above 1100° under air pressure. This fact was verified by X-ray diffraction study of the samples in this experiment. The cobaltous oxide, however, contains an excess of oxygen which is the main factor determining the physical properties of this material.

For determination of the physical properties of the oxide it is important to have an exact measure of the excess oxygen. All of the earlier studies were carried out by means of the titration method and X-ray or electron diffraction of the quenched samples. In these experiments the results were determined at room temperature and atmospheric pressure rather than under the temperature and pressure conditions of the experiment. The differences between these two conditions will bring about some error in the determination of the

nonstoichiometry of the cobaltous oxide. Fisher and Tannhauser<sup>9</sup> have dealt with the nonstoichiometry of cobaltous oxide through electrical conductivity and gravimetric analysis in order to avoid this error.

In this study the weight changes of the sample have been measured directly under the given conditions by a specially made quartz microbalance and the nonstoichiometric quantities or  $y$  values of the oxide calculated from these weight changes due to excess oxygen. Fisher<sup>9</sup> measured the  $y$  values by a thermobalance which had sensitivity only one-tenth that of our microbalance and therefore the present data should be more accurate. The  $y$  values show the nonstoichiometric chemical formula for given conditions.

Thermodynamic data have been obtained from the oxygen pressure dependence and the temperature dependence of the  $y$  values. In addition, most of the physical properties of the cobaltous oxide, such as electrical conductivity, oxidation, diffusion, and defects can be explained through  $y$  values and the mechanism forming the nonstoichiometric compositions of the oxide.

### Experimental Section

Specpure cobalt rod (diameter 5 mm) supplied by Atomergic Chemetals Co. was used in the preparation of the sample. The cobalt rod was cut into sheets 0.3 mm thick by a milling cutter. These cobalt sheets were etched in dilute  $\text{HNO}_3$  solution and then oxidized in an electric furnace at 1100° for 600 hr. The cobaltous oxide prepared in this way was identified by X-ray diffraction and also by the EDTA determination of Co in cobaltous oxide at standard conditions.

This cobaltous oxide does not contain other phases such as  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_2\text{O}_3$ , and Co but contains small excess oxygen.

The apparatus used in this study is shown in Figure 1. The quartz microbalances used are optimum for this research considering their sensitivity and weakness of axis fiber. For example, the calibration curve of the least sensitive balance used in this study can be expressed by  $\Delta W_1 = 0.00050h \pm 5 \times 10^{-7}$ , where  $\Delta W_1$  is the weight in grams and  $h$  is the balance height change in millimeters read to 0.01 mm using a reading microscope. The height change is proportional to weight change as verified using five standard weights (*i.e.*, 100-500  $\mu\text{g}$ ) checked on a Cahn electrobalance. The nonstoichiometric compositions of  $\text{CoO}$  were measured at various temperatures in the range 500-1200° at intervals of 100° under partial oxygen pressures,  $10^{-3}$ -152 mm. The height of the microbalance was read through a vernier-equipped reading microscope when no more motion was evident, an indication of thermodynamic equilibrium.

The height changes due to buoyancy and thermomolecular flow had to be directly corrected for by the following method. The balance height changes for a pseudosample made of quartz rod and platinum wire, of size and weight equal to those of the real sample but not susceptible to weight changes under the experimental conditions, could be measured under all the required conditions, and then the balance height changes for the sample could also be measured under the same conditions. The effective balance height change for the sample was then the difference between the balance height change

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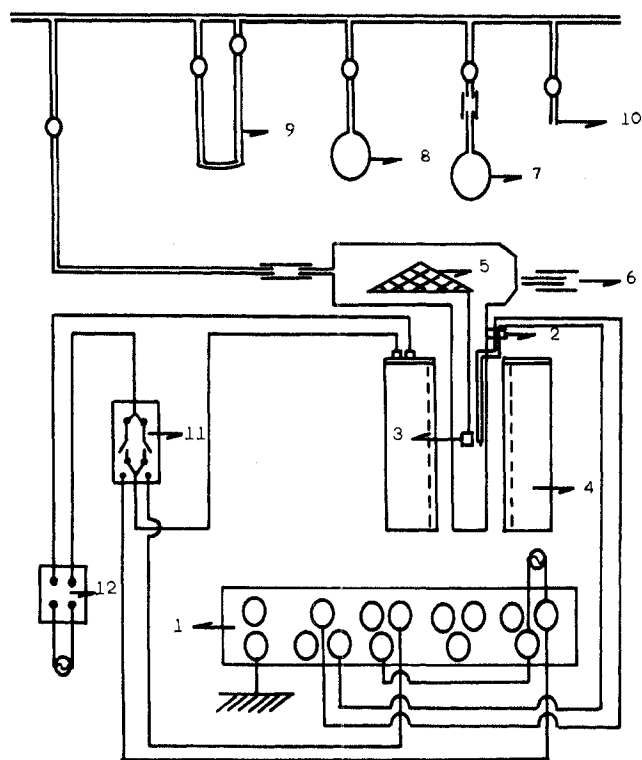


Figure 1. Schematic drawing of measurement assembly: (1) temperature controller, (2) thermocouple, (3) sample (cobaltous oxide), (4) furnace, (5) microbalance, (6) reading microscope, (7) oxygen generator, (8) oxygen tank, (9) manometer, (10) McLeod gauge and ionization gauge, (11) relay, and (12) powerstat.

due to the sample and that due to the pseudosample. The weight change of the sample,  $\Delta W_1$ , is obtained from the effective balance height change from the calibration equation.

The phase transition<sup>7</sup> from CoO to Co occurs at 1400° under  $10^{-3}$  mm of  $O_2$  and therefore it was decided that 1400° under  $10^{-3}$  mm of  $O_2$  is a stoichiometric condition for the formation of the cobaltous oxide. In this research, stoichiometric CoO was identified by the EDTA determination of Co in cobaltous oxide which is quenched after annealing in the stoichiometric condition for 2 hr. The weight losses of a sample between standard condition and given conditions,  $\Delta W_1$ , have thus reduced to the weight gains from stoichiometric CoO,  $\Delta W_2$ . For example,  $\Delta W_1$  was equal to  $2.50 \times 10^{-4}$  g at the stoichiometric conditions (or  $\Delta W_2 = 0$ ) and conversely  $\Delta W_1 = 0$  at standard conditions corresponds to  $\Delta W_2 = 2.50 \times 10^{-4}$  g. Likewise, the transformation of  $\Delta W_1$  to  $\Delta W_2$  is possible at every condition. The  $y$  values of the nonstoichiometric formula,  $CoO_{1+y}$ , can be calculated using  $\Delta W_2$ .

## Results

As shown in Table I, the first series of experiments was designed to establish the temperature dependence of  $y$  values from 500 to 1200° at intervals of 100° under a fixed air pressure of 1 atm. The  $y$  values were calculated from the relationship

$$y = \left( \frac{\Delta W_2}{W} \right) \frac{M_{CoO}}{A_O}$$

where  $W$  is the weight of the sample at the stoichiometric conditions,  $\Delta W_2$  is the weight change from the stoichiometric sample weight,  $A_O$  is the atomic weight of oxygen,  $M_{CoO}$  is the molecular weight of cobaltous oxide, and  $y$  is the number of gram-atoms of oxygen in excess per mole of CoO. The  $y$  values evaluated from the above equation show a regularity for a number of samples irrespective of analogous sample size or weight. The  $y$  values for various combinations of temperature and pressure are listed in Table II. The  $y$  values in the temperature range of 0–400° under various oxygen

Table I. Effective Balance Height Changes, Weight Changes, and  $y$  Values of  $CoO_{1+y}$  at Various Temperatures under 1 Atm Air Pressure

Temp, °C	Eff balance height changes, mm	Wt changes, g		$y$ values
		$\Delta W_1$	$\Delta W_2$	
500	0.07	0.000035	0.000215	0.0159
600	0.08	0.000040	0.000210	0.0155
700	0.09	0.000045	0.000205	0.0152
800	0.10	0.000050	0.000200	0.0148
900	0.12	0.000060	0.000190	0.0141
1000	0.14	0.000070	0.000180	0.0133
1100	0.15	0.000075	0.000175	0.0130
1200	0.16	0.000080	0.000170	0.0122

Table II. Number of Gram-Atoms of Oxygen Per Mole of CoO or  $y$  Values as a Function of Oxygen Pressures and Temperatures

Temp, °C	Oxygen pressures, mm					
	$10^{-3}$	$10^{-2}$	$10^{-1}$	$10^0$	$10^1$	$10^2$
500	0.0096	0.0121	0.0141	0.0143	0.0149	0.0158
600	0.0089	0.0111	0.0130	0.0130	0.0142	0.0152
700	0.0074	0.0095	0.0122	0.0123	0.0132	0.0148
800	0.0069	0.0081	0.0117	0.0119	0.0125	0.0141
900	0.0059	0.0074	0.0107	0.0109	0.0114	0.0133
1000	0.0039	0.0063	0.0104	0.0106	0.0110	0.0130
1100	0.0024	0.0052	0.0096	0.0099	0.0106	0.0124
1200	0.0015	0.0043	0.0089	0.0090	0.0092	0.0118

pressures are not included because the thermodynamic equilibrium could not be obtained in that temperature range in several hours.

Plots of  $\log y$  vs.  $1000/T$  and plots of  $\log y$  vs.  $\log P_{O_2}$  are shown in Figures 2 and 3, respectively. The enthalpies of formation of nonstoichiometric compositions calculated from the slope of the plots of  $\log y$  vs.  $1000/T$  are shown in Table III and the  $1/n$  values obtained from the slope of the plots of  $\log y$  vs.  $\log P_{O_2}$  are shown in Table IV.

## Discussion

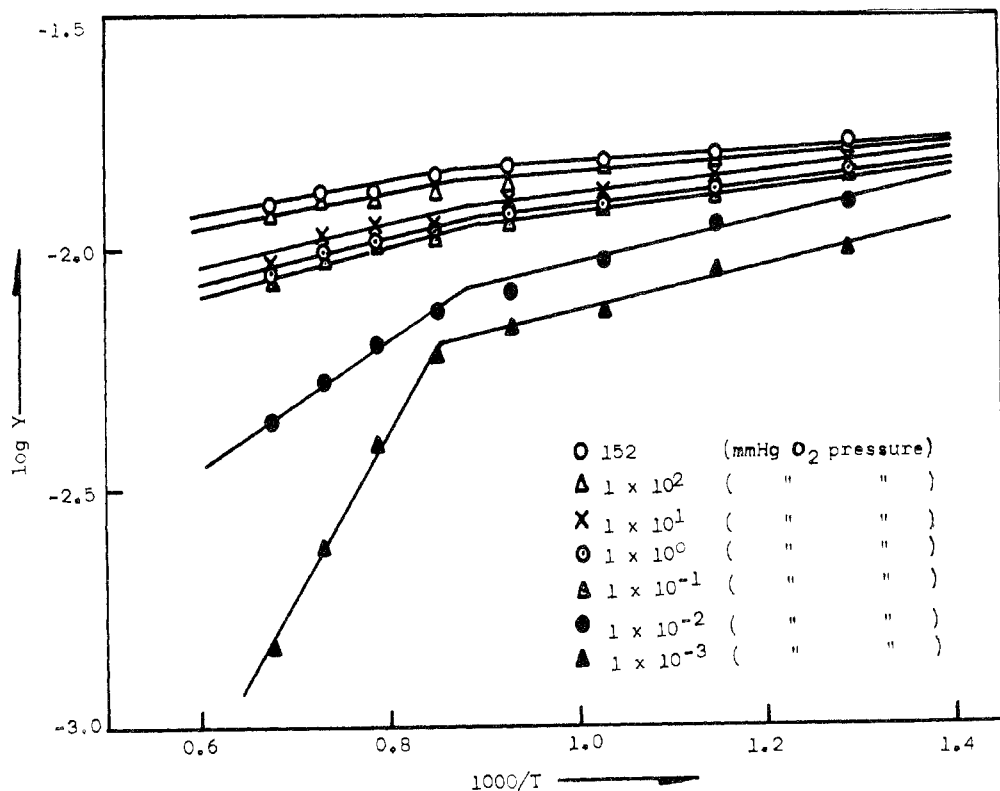
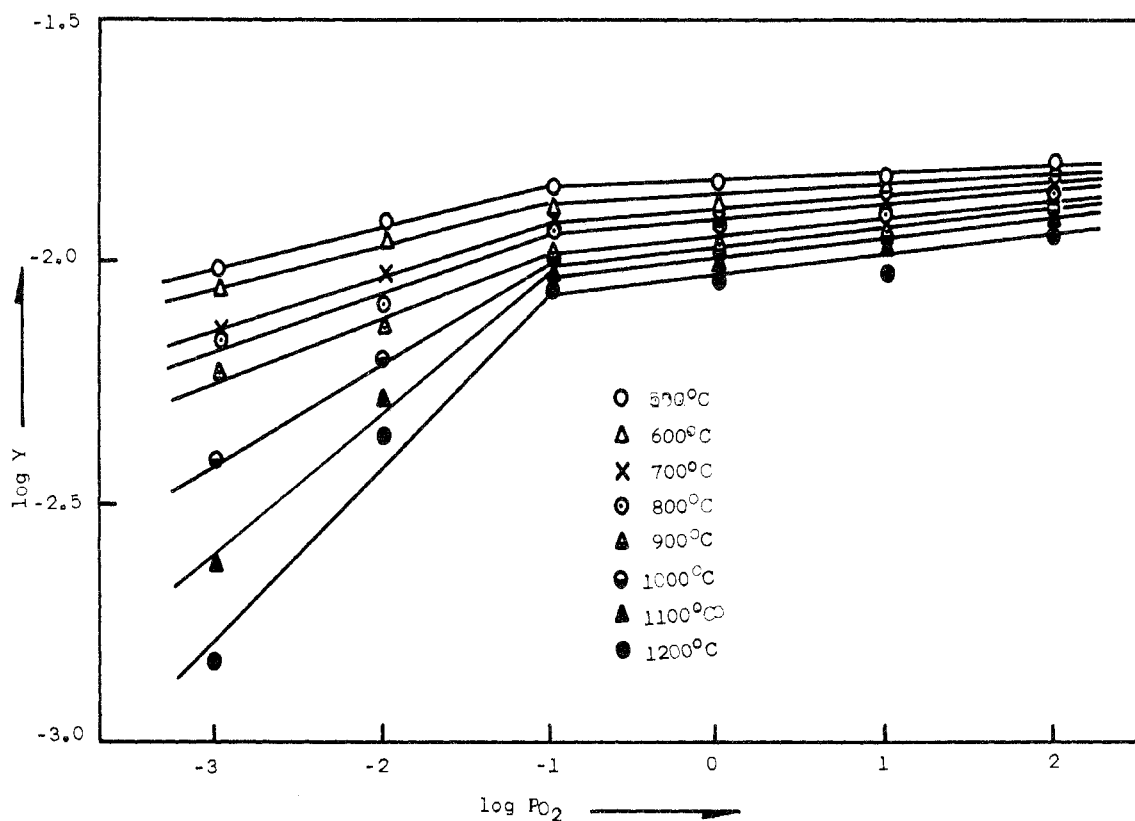
Table I shows the relation between the  $y$  values of the nonstoichiometric chemical formula,  $CoO_{1+y}$ , and the various temperatures under air pressure of 1 atm. For example, the nonstoichiometric formula is  $CoO_{1.0130}$  at 1100° where  $y = 0.0130$ . Thus the  $y$  values show us the nonstoichiometric chemical formula under various conditions. Table II shows the  $y$  values for various temperatures and oxygen pressures.

Tannhauser<sup>9</sup> found that CoO can contain up to 1.2% excess oxygen if prepared at 1300° and 1 atm. This means that the formula  $CoO_{1+y}$  would be  $CoO_{1.012}$ . The  $y$  value at 1200° and 1 atm is 0.0122 in this study and the value would be about 0.012 at 1300° by extrapolation. Thus Tannhauser's work agrees with our data.

The  $y$  values are all less than 0.0159 in this experiment, a fact in agreement with Ando's<sup>5</sup> results which show that CoO obtained at 1100° does not oxidize into  $Co_3O_4$  or  $Co_2O_3$ .

The plots of  $\log y$  vs.  $1000/T$  are linear as shown in Figure 2. At higher temperatures, the  $y$  value decreases until stoichiometric CoO is finally formed. Although linear, a transition point is apparent for which the reason is not clear. The  $y$  values are, however, more temperature dependent at higher temperatures than the transition point. It may probably be explained that the excess oxygen dissolved in the oxide is more activated by the high lattice vibration at higher temperatures than the point and then the physical desorption of

(9) B. Fisher and D. S. Tannhauser, *J. Chem. Phys.*, **44**, 1663 (1966).

Figure 2.  $\log y$  vs.  $1000/T$ .Figure 3.  $\log y$  vs.  $\log P_{O_2}$ .

the oxygen occurs to decrease the  $y$  values for increasing temperature.

Now, Saxer<sup>10</sup> proposed that a thin, discontinuous layer  
(10) R. K. Saxer, *Cobalt*, 36, 157 (1967).

of  $Co_3O_4$  formed on the outer surface of  $CoO$  at temperatures below  $1000^\circ$ . It seems to us that the explanation for the transition point would lie in the fact that  $Co_3O_4$  formed in this manner would be reduced to  $CoO$ .

**Table III.** Enthalpies of Formation of the Nonstoichiometric Compositions (kcal/mol) at Various Conditions

Oxygen pressures, mm	$\Delta H_f$ (temp range >TP), kcal/mol	TP, <sup>a</sup> °C	$\Delta H_f$ (temp range <TP), kcal/mol
152	-1.37	870	-0.57
100	-1.60	870	-0.69
10	-1.83	835	-1.03
1	-1.95	833	-1.03
0.1	-2.29	835	-1.03
0.01	-5.95	850	-2.06
0.001	-15.8	890	-2.06

<sup>a</sup> TP = transition point.

**Table IV.**  $1/n$  Values at Various Conditions

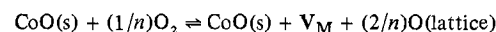
Temp, °C	Oxygen pressure ranges, mm	
	$10^{-3}$ - $10^{-1}$	$10^{-1}$ - $10^2$
500	1/12	
600	1/12	
700	1/9	
800	1/8.3	1/75-1/43
900	1/7.4	
1000	1/4.8	
1100	1/3.4	
1200	1/2.8	

In measuring the nonstoichiometry of CoO, a difficult problem is the proper correction for the nondissociative evaporation of CoO. The evaporations, however, are very limited at higher temperatures than 900° under lower oxygen pressures than  $10^{-2}$  mm. This was corrected for by extrapolation of the data, and as the data used were the mean values of several measurements under each condition, the results are reliable. The corrections were justified by the weight losses of the sample and then by the measurements of nonstoichiometric compositions under ambient gas pressures.

Enthalpies of formation of nonstoichiometric compositions calculated from the slopes of the plot of  $\log y$  vs.  $1000/T$  are listed in Table III. All of the enthalpies of formation are negative values and thus the formations of nonstoichiometric compositions are all exothermic processes under these experimental conditions. The absolute values of the enthalpies of formation,  $|\Delta H_f|$ , are in general larger at lower pressures than the high pressures. This shows us that the lower the oxygen pressures and the higher the temperatures, the smaller are the  $y$  values obtained.

From consideration of the ionic radii<sup>9</sup> (the ionic radius of  $\text{Co}^{2+}$  is 0.75 Å and that of  $\text{O}^{2-}$  is 1.4 Å), it has been concluded that cation vacancies are more probable in CoO. But these defects are more complex. It is suggested that the dominant complex defect consists of an interstitial Co cation and two Co vacancies.<sup>11</sup> The diffusion coefficient<sup>12</sup> for Co in CoO rises with oxygen pressure, and more cation vacancies are formed at higher pressures. Likewise the cobaltous oxide forms a type IV nonstoichiometric composition due to the defects. Finally, the nonstoichiometry of the oxide or  $y$  value increases at higher oxygen pressures. As shown in Figure 3, this theory agrees with our results.

Oxygen pressure dependence of the nonstoichiometric compositions can be expressed as



where  $[V_M]$  is the molar fraction of un-ionized vacancies in the lattice. By the law of chemical equilibrium, with  $K_X$  the

equilibrium constant and  $P_{\text{O}_2}$  the partial pressure of oxygen

$$K_X = [V_M]/P_{\text{O}_2}^{1/n} \quad (1)$$

$$[V_M] = K_X P_{\text{O}_2}^{1/n} \quad (2)$$

Now the  $y$  values are proportional to  $[V_M]$ ; thus

$$y \propto [V_M] \quad (3)$$

From eq 2 and 3, we obtain

$$y \propto K_X P_{\text{O}_2}^{1/n} \quad (4)$$

The  $1/n$  values are calculated from the slopes of the plots of  $\log y$  vs.  $\log P_{\text{O}_2}$ . As shown in Figure 3, the transition point appears at  $10^{-1}$  mm oxygen pressure and the  $y$  values depend greatly on oxygen pressure below this pressure. The  $1/n$  values calculated from the slopes are listed in Table IV.

Nicholas and Wagner<sup>13</sup> indicated that atom defect concentration in CoO is a function of the  $1/4$ th power of the oxygen partial pressure at 900-1200°. Table IV shows that the  $1/n$  values are 1/4.8-1/2.8 at 1000-1200° under oxygen pressures lower than  $10^{-1}$  mm; this means that the mechanism of formation of nonstoichiometric compositions is the same as that of formation of defects under the above conditions.

Oxidation of cobalt is in general a chemical reaction between cobalt and oxygen through the self-diffusion of Co in CoO<sup>14</sup> while the formation of nonstoichiometric cobaltous oxide is a process of increasing or decreasing the excess oxygen dissolved in the oxide system. The above fact is justified by the small values of  $1/n$  as shown in Table IV.

The conductivity of cobaltous oxide may be predicted in accordance with the  $y$  values because the conductivity is proportional to the  $y$  values for the p-type semiconductor. The higher the oxygen pressure, the more cobalt vacancies are formed in the cobaltous oxide, and the vacancies are ionized to form the positive holes as follows:  $P = [V_M'] + 2[V_M'']$ , where  $[V_M']$  is the molar fraction of singly ionized vacancies,  $[V_M'']$  is the molar fraction of doubly ionized vacancies, and  $P$  is the molar fraction of the free hole. It has theoretically been shown that the conductivity of the p-type semiconductors is proportional to  $y$  values as follows. The larger the  $y$  values, the more  $V_M$  is formed and thus the larger  $[V_M']$  and  $[V_M'']$ . Finally, the conductivity is proportional to the  $y$  value because the concentration of positive holes rises with the  $y$  value.

However, we do not agree with Tannhauser's theory<sup>9</sup> that the point of stoichiometry is obtained by extrapolating the straight portion of the  $G$  vs.  $x$  plot to zero conductance. The intrinsic semiconductivity of the cobaltous oxide will be shown even at the point of stoichiometry (or  $y = 0$ ).

The oxidation mechanism<sup>15</sup> of cobalt was determined to be the diffusion of Co ions through the oxide. Diffusion through the oxide layer is, however, the rate-determining step for the oxidation.<sup>16</sup> Thus the phase transition from CoO to  $\text{Co}_3\text{O}_4$  or  $\text{Co}_2\text{O}_3$  and the reduction of CoO to Co due to the changes of temperatures and oxygen pressures are difficult under these experimental conditions. The  $y$  values thus can be interpreted not in terms of phase transitions but in terms of the fundamental properties of the cobaltous oxide system itself. The  $y$  values can thus be used

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for interpretation of the physical properties as basic data of the cobaltous oxide system.

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## Equilibria Involving Polysulfide Ions in Aqueous Sulfide Solutions up to 240°

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The solubility of elemental sulfur in near-neutral aqueous sulfide solutions was determined from 20 to 200°. The resulting polysulfide solutions contain an approximately equimolar mixture of tetra- and pentasulfide ions with hydropolysulfide ions likely to be present only in very small concentrations. The equilibrium constants governing the formation and rearrangement reactions of the four polysulfide ions  $S_nS^{2-}$ , with  $n = 1-4$ , expressed in terms of  $m_{SH^-}$  and  $m_{OH^-}$ , show only little variation with temperature. Above 150° the dissociation of polysulfide ions into radicals,  $S_2^{\cdot-}$  or  $S_3^{\cdot-}$ , and disproportionation into sulfide and thiosulfate become significant. The stability diagram, constructed by use of the equilibrium constants derived, shows that in near-neutral sulfide solutions polysulfide ions are stable with respect to this disproportionation up to 240°; at pH's above 8, however, polysulfide ions become metastable, even at room temperature. Sulfite and sulfate ions apparently are not formed in significant amounts during the disproportionation of polysulfide over the range of conditions studied.

### Introduction

The solubility of sulfur in aqueous hydroxide<sup>1</sup> and sulfide<sup>2,3</sup> solutions has been investigated for temperatures up to 80°. The resulting solutions were reported<sup>4</sup> to contain higher polysulfide ions  $S_nS^{2-}$  with  $\bar{n}$ , the average number of sulfur atoms per polysulfide ion, ranging from 3.7 to 4.4 at room temperature. In all these studies hydropolysulfide ions were assumed to be absent. An investigation into the temperature dependence<sup>5</sup> of polysulfide equilibria up to 80° indicated only minor variations in the equilibrium constants governing the rearrangement reactions between the various polysulfide ions. At elevated temperatures polysulfide ions were found<sup>6,7</sup> to disproportionate into thiosulfate and monosulfide ( $H_2S + SH^-$ ), with the rate and degree of disproportionation proportional<sup>8</sup> to the hydroxide concentration. Based on a previous study<sup>9</sup> supplying information on the equilibrium distribution of polysulfide ions at room temperature, the present work extends quantitative investigations into the effect of temperature on the stability of polysulfide solutions to 240°.

### Experimental Section

Experimental procedures were similar to those described in previous studies.<sup>9,10</sup> Starting solutions were prepared by mixing measured amounts of stock solutions of NaHS (0.5 *m*),  $Na_2S_4$  (0.033 *m*),  $Na_2S_2O_3 \cdot 5H_2O$  (0.1 *m*),  $Na_2SO_3$  (0.1 *m*),  $Na_2SO_4$  (0.1 *m*), HCl (0.5 *m*), and NaCl (2.0 *m*) and water to give 50 ml. The NaHS solutions were prepared by bubbling  $H_2S$  from a tank into 0.5 *m*

NaOH solution. Excess  $H_2S$  was removed by purging the saturated solution with purified nitrogen.

All operations were carried out under nitrogen mainly by use of Schlenk-tube techniques. The concentrations of the stock solutions were checked by standard analytical methods. The ionic strength dependence of the equilibrium constants was determined by varying the amount of NaCl added from 0 to 2 *m*, with most measurements carried out at a constant ionic strength of 0.4 *m*, uncorrected for ionic association.

**Spectra.** Spectroscopic measurements were carried out by use of a gold-lined, high-temperature cell with a solution path length  $l$  of 0.80 cm between silica windows as previously described.<sup>11</sup> Polysulfide concentrations were determined by use of molar absorptivities<sup>9</sup> at wave numbers of 2.50  $\mu m^{-1}$  (waves per micrometer) for the tetrasulfide ion of  $\epsilon_3$  1140 and the pentasulfide ion of  $\epsilon_3$  2000 and for the supersulfide ion<sup>12</sup> at 1.68  $\mu m^{-1}$  of  $\epsilon_6$  2400. All molar absorptivities were assumed to remain constant with temperature. For the sulfur solubility measurements a small amount of excess elemental sulfur (ca. 50 mg) was placed into the cell cavity. In these and the disproportionation measurements, the solution in the cell was replaced by a weak sulfide solution after the cell had cooled down to 80° after a high-temperature run, in order to avoid the deposition of elemental sulfur onto the cell windows. Variations in the distribution of  $H_2S$  between liquid and vapor space within the cell with temperature were taken into account by use of the relationship  $y_2/y_1 = 0.22K_H(1/f - 1/d)/T$ , where  $y_2$  and  $y_1$  are the fractions of  $H_2S$  in the gaseous and liquid phases,  $K_H$  is the Henry law constant<sup>13</sup> for  $H_2S$  at a given temperature,  $f$  is the filling factor of the cell, 0.7 for the cell 70% filled with solution at room temperature, and  $d$  is the density of the solution at the corresponding temperature.

Temperatures in the cell were measured with a chromel-alumel thermocouple to within 1°. The spectrophotometer used was the Zeiss PM QII with the monochromator M4 QIII.

### Results

On heating a sulfide solution at a pH of around 7 at 25°, containing a small amount of zerovalent sulfur, partly present in the form of elemental sulfur and polysulfide, from room temperature to 240°, the color of the solution changes from a deepening yellow through green to blue; at temperatures above 200° this color again starts to fade with the solu-

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