Summary

Eleven melts and cooling curves have been prepared in the system Na_2S–FeS which have allowed preparation of a satisfactory liquidus in the temperature–composition phase diagram but insufficient points were taken to determine fully the solidus and a complete outline of the phase diagram. Such points as have been obtained indicate a region between 53 and 73% iron sulfide in which two liquid phases can form, one being a double compound, probably $FeS \cdot Na_2S$, saturated with iron sulfide, and the other being iron sulfide saturated with double compound, or something similar to it. One true eutectic is found at 46% of iron sulfide and 585°. The melting point of sodium sulfide has been determined as 970°, although its purity was such that the melting point of pure sodium sulfide can be expected to be slightly higher. No mixture containing less than 37% of iron sulfide was investigated.

CLARKDALE, ARIZONA

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

EQUILIBRIUM IN THE SYSTEM $Co-H_2O-CoO-H_2$. FREE ENERGY CHANGES FOR THE REACTION $CoO + H_2 = Co + H_2O$ AND THE REACTION $Co + {}^1/_2O_2 = CoO$

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Introduction

In the course of some experiments with cobalt catalysts, we desired to know the ratio of steam to hydrogen above which cobalt is oxidized to cobaltous oxide. The only determinations in the literature seemed to be those of Chaudron[1] and of Wöhler and Balz.[2] The former obtained a value of 20 at 1000°. The latter workers obtained a value of 14 at 450° and 19 at 750°. The apparatus and method of procedure used in both of these researches, however, were those used by Deville[3] in the study of iron oxide equilibria. Such a procedure is not well adapted to the determination of the equilibrium constant in the case of cobalt, since the partial pressure of hydrogen in equilibrium with 25 mm. of water vapor will be a millimeter or less. Any occluded gases in the solid material would cause one to obtain too low a value for the steam–hydrogen ratio. It was, therefore, probable that one or both of the above experiments might be in error, especially since preliminary observations indicated that the equilibrium ratio of steam to hydrogen was 50 or greater at 450°.

[1] Chaudron, *Ann. chim.*, **16**, 243 (1921).

[2] Wöhler and Balz, *Z. Elektrochem.*, **27**, 406 (1921).

[3] Sainte-Claire Deville, *Compt. rend.*, **70**, 834 (1870).

Accordingly, the present work was undertaken with a view to determining accurately, at several different temperatures, the equilibrium ratio of water vapor to hydrogen for the reaction $CoO + H_2 = Co + H_2O$. This paper outlines the essential details of procedure, and presents typical equilibrium data for 335, 450, 515 and 570°.

Apparatus and Materials

For the equilibrium determinations a flow system has been employed, similar in most respects to that used by Pease and Cook[4] in their investigation of the system $NiO–H_2–Ni–H_2O$. The apparatus as finally adopted is shown in Fig. 1. It consists essentially of a steam generator A, an electrolytic hydrogen generator B, a pyrex glass tube C containing the charge, an electric furnace D, a water-jacketed weighing tube E for catching and weighing the condensed steam and a special 100-cc. eudiometer F for measuring the hydrogen. The steam boiler used is similar to the one described by Kuentzel,[5] except that the steam exit has been so modified as to reduce the probability of tiny droplets of liquid water being carried over with the steam. The hydrogen cell was fitted with platinum electrodes and contained potassium hydroxide as an electrolyte. The hydrogen was purified by passage over soda lime and hot platinized asbestos. The tube containing the charge was heated in a furnace 48-cm. long, consisting of an alundum tube wound with nichrome ribbon embedded in magnesia and finally surrounded by an iron jacket. The bulb containing the charge was placed in the alundum tube and packed tightly with mossy copper. Temperature was measured by means of an alumel-chromel thermocouple in conjunction with a Leeds and Northrup portable potentiometer. It was found to remain constant within ±1° during a run.

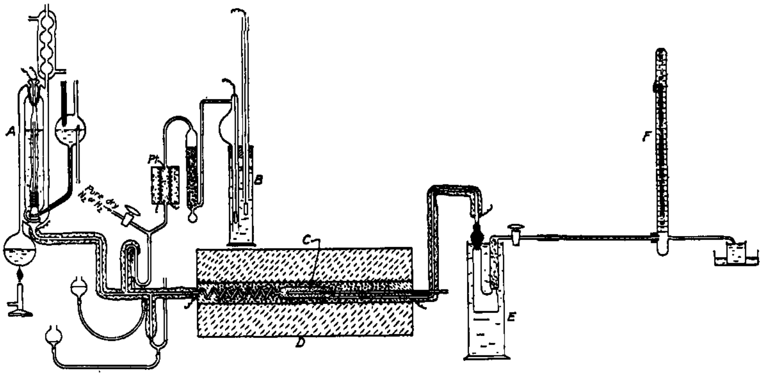

Fig. 1.—Apparatus.

The temperature gradient along the length of the catalyst was found to be less than 2°. It was obtained by moving a thermocouple along the thermocouple well extending coaxially along the entire catalyst tube. In several of the experiments an auxiliary thermocouple was placed in contact with the outside wall of the catalyst container. It showed the transverse temperature gradient to be less than 2° for half the width of the catalyst tube.

The flow of gases through the apparatus was regulated by mercury cut-offs rather than by dry stopcocks, since the latter when used are inclined to leak. The mercury

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[4] Pease and Cook, This Journal, **48**, 1199 (1926).

[5] Kuentzel, unpublished material.

in the cut-offs was always covered with a centimeter or more of water and hence did not come directly in contact with any heated portion of the tubes. The top of the steam generator was water-sealed during all runs in order to preclude any possibility of air diffusing into the apparatus. The lead wires to the hydrogen generator were welded to tungsten which in turn was sealed through the pyrex glass of the generator.

Two different cobalt oxide preparations were used in the present experiments. Catalyst No. 1 was prepared by fusing a sample of nickel-free metallic cobalt with an oxyhydrogen flame in a crucible of cobalt coated with cobaltous oxide. Excess oxygen was blown into the melt during the fusion. The resulting oxide analyzed very nearly pure cobaltous oxide. It was used in the form of 10- to 14-mesh material.

Catalyst No. 2 was prepared by first gently and finally strongly igniting a sample of C. P. recrystallized cobaltous nitrate. The first gentle heating was in an open porcelain dish. The final higher heating to approximately 500° was of several hours duration and took place in a glass tube with a stream of air passing continually. The apparent density[6] of catalyst No. 1 was 2.65, and of No. 2, 0.76. The composition of this latter material was very nearly Co_3O_4. It accordingly had to be reduced for some hours with a steam–hydrogen mixture in which the ratio of steam to hydrogen was slightly too high to permit the reduction of the CoO formed. By such procedure a pure CoO was obtained.

Experimental Procedure

The reaction tube filled with 20 to 25 cc. of one of the cobalt oxides was packed into the furnace, connected to the steam and hydrogen generators and brought to the desired temperature in a slow stream of oxygen-free nitrogen. After being suitably reduced by hydrogen, the catalyst was subjected to various definite steam–hydrogen mixtures and the effluent gases were analyzed for water and hydrogen. The inlet and exit steam–hydrogen ratios were determined by three measurements: (1) the weight of exit steam condensed in the water jacketed U-tube in a given time; (2) the volume of exit hydrogen (corrected to S. T. P.) collected during the same period of time; and (3) the current passed through the hydrogen cell during the run. The effluent hydrogen, in addition to being corrected to S. T. P. on a dry basis in the usual way, had also to be corrected first for the volume of the gas displaced into the measuring buret by the condensation of steam in the U-tube, and second for the volume forced out of the U-tube by slight heating resulting from the rapid flow of steam. The first of these two corrections was, of course, easily and accurately made. The second was also definitely determined by using as the inlet tube to the eudiometer F a pipet stem graduated in 0.1 cc. divisions and easily readable to 0.01 cc. Immediately on shutting off the steam flow at the end of a run, the water from the eudiometer quickly sucked back into the pipet entrance tube as the heated portions of the U-tube rapidly cooled. This heating correction was usually of the order of 0.3 cc. It was very constant and easily obtained under a given set of conditions.

Experiments in general were repeated many times at each particular temperature, using first, Catalyst No. 1 and then Catalyst No. 2. Equilibrium was approached at each temperature from both the steam and the hydrogen sides.

Experimental Results

In order to obtain approximate values for the equilibrium constant and to learn how rapidly equilibrium could be attained, numerous preliminary experiments were carried out over a temperature range of 335

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[6] By "apparent density" of a sample is here meant its weight in grams divided by its approximate apparent volume as measured in a graduated cylinder.

to 515°. During these runs 6 or 7 different types of apparatus were tried. By a process of elimination the poor features of different analytical devices were remedied and eventually the final apparatus described in Fig. 1 was obtained.

In the three hundred or more preliminary runs it became apparent that the material was often not very active, particularly at 335°. Even at 450° considerable trouble was experienced in getting sufficiently large changes in the exit as compared to entering gas ratios. However, these preliminary results in spite of analytical difficulties give a fair approximation to the equilibrium constants.

Table I

Preliminary Runs at 335°

Run no.	Inlet mixture Steam, cc./min.	Inlet mixture H_2, cc./min.	Exit totals Water, g.	Exit totals H_2, cc. (S. T. P.)	H_2O/H_2 In	H_2O/H_2 Out
			50 Grams of Catalyst No. 1			
36	49.3	1	0.469	6.79	49.3	85.9
126	94.2	1	1.006	14.99	94.2	83.5
127	95.7	1	1.032	15.00	95.7	85.6
128	93.5	1	1.023	14.97	93.5	85.0
252	99.3	1	1.212	17.24	99.3	87.4
			14.5 Grams of Catalyst No. 2			
193	67.7	1	0.448	7.03	67.7	79.3
196	94.5	1	.473	6.76	94.5	87.0

From the results, part of which are shown in Table I, it is believed that the equilibrium constant at 335° is 85 ± 5. Due to the slowness with which a gas mixture attained equilibrium over the oxide mixtures at this low temperature, no final measurements at 335° were attempted. The 450 and 515° preliminary results are not listed since the final results are much more significant and more closely indicative of the true equilibrium constants. The preliminary results at these temperatures indicated that the value of the constant at 450° would be 65 ± 5, and at 515° would be 53 ± 5.

The final runs were all made using the apparatus as described in Fig. 1. Each experiment was continued until 90 to 100 cc. of effluent hydrogen was collected in the eudiometer. The 450° values are shown in Table II. Herein are included only those final runs in which the exit ratio differs by 5% from the entering and in which the final value is within the range of 63 to 71. None of the omitted values contradicts any of the values in Table II. The single contradiction in the runs at 450° (Run 393) is included in Table II, and is believed to have been caused by some unaccountable experimental error. Furthermore, the first two readings after either a 100% steam treatment or a reduction with pure hydrogen (designated in Tables II and III by *a* and *b*, respectively) have not been included in the final choosing of the equilibrium constant, in that the former are usually low by about 5 to 10% and the latter high by about the same amount. It is believed from the results obtained that a value of 67 ± 1, represents closely the equilibrium constant of the reaction.

TABLE II

FINAL RUNS AT 450°

Run no.	Inlet mixture		Exit totals		H_2O/H_2		Approx. % of metallic cobalt
	Steam, cc./min.	H_2, cc./min.	Water, g.	H_2, cc.	In	Out	
			70.8 Grams of Catalyst No. 1				
359	122.7	2	4.564	83.22	61.4	68.3	7
361	105.0	2	4.872	83.03	52.5	73.0[a]	7
364	86.8	2	4.722	83.81	43.4	70.1	7
382	142.8	2	4.560	83.42	71.4	67.9	61
			23.8 Grams of Catalyst No. 2				
393	187.6	4	2.914	84.53	46.9	42.9	23
397	211.8	3	4.489	83.28	70.6	67.0	9
398	183.6	3	4.236	83.68	61.2	63.7	9
410	155.4	2	4.101	85.42	77.7	59.7[b]	80
440	177.5	2	4.285	83.65	88.8	63.7[b]	76
441	148.5	2	4.505	83.42	74.3	67.2	76
442	145.8	2	4.549	83.37	72.9	67.8	76
443	123.5	2	4.393	83.38	61.8	65.6	76
444	121.5	2	4.272	83.74	60.8	63.5	76

[a] Pure steam was passed over catalyst for thirty minutes or more immediately prior to this run. [b] 200 cc./min. of pure hydrogen was passed over catalyst for five minutes or more immediately prior to this run.

TABLE III

FINAL RUNS AT 515°

Run no.	Inlet mixture		Exit totals		H_2O/H_2		Approx. % of metallic cobalt
	Steam, cc./min.	H_2, cc./min.	Water, g.	H_2, cc.	In	Out	
			70.8 Grams of Catalyst No. 1				
346	125.7	2	4.000	85.17	62.9	58.5	7
347	76.2	2	3.807	83.63	38.1	56.6	7
348	90.1	2	3.804	83.22	45.0	56.9	7
350	139.5	2	3.800	82.84	69.8	57.1	7
366	110.1	2	4.773	83.55	55.1	71.0[a]	7
367	77.0	2	3.976	85.62	38.5	57.7	7
368	85.0	2	3.953	85.85	42.5	57.3	7
369	150.6	2	3.910	85.62	75.3	56.8	7
370	138.8	2	3.922	85.28	69.4	57.2	7
371	146.8	2	3.888	85.82	73.4	56.3[b]	84
372	141.0	2	3.882	85.83	70.5	56.3	84
373	140.2	2	3.881	85.79	70.1	56.3	84
374	97.8	2	3.815	85.88	48.9	55.3	84
375	128.0	2	3.971	95.14	64.0	58.0[a]	61
376	137.7	2	4.158	84.86	68.9	60.9	61
377	118.2	2	3.927	84.68	59.1	57.6	61
378	102.5	2	3.828	84.43	51.2	56.4	61

TABLE III (*Concluded*)

Run no.	Inlet mixture		Exit totals		H_2O/H_2		Approx. % of metallic cobalt
	Steam, cc./min.	H_2, cc./min.	Water, g.	H_2, cc.	In	Out	
			23.8 Grams of Catalyst No. 2				
403	155.7	3	3.720	84.01	51.9	55.0	9
404	221.0	3	3.969	83.36	73.3	59.2	9
405	186.5	3	3.928	83.56	62.2	58.4	9
406	163.0	3	3.835	83.60	54.3	57.0	9
407	156.3	3	3.696	83.45	52.1	55.1	9
429	153.5	3	3.758	83.66	51.2	55.9[b]	61
430	193.8	3	3.811	83.57	64.6	56.8	61
431	206.0	3	3.867	83.33	68.6	57.6	61

[a] Pure steam was passed over catalyst for thirty minutes or more immediately prior to this run. [b] 200 cc./min. of pure hydrogen was passed over catalyst for five minutes or more immediately prior to this run.

The values obtained for 515° are given in Table III. All values obtained have been included (excepting 4 values to be listed and explained in connection with Table V) in which the entering and exit ratios differ by 5% or more and the final value lies between 55 and 60. From the data thus obtained, the equilibrium constant for 515° appears to be 57 ± 0.3. At this temperature, too, the results of the first run following treatment with 100% steam or with pure hydrogen are higher or lower, respectively, than the normal equilibrium values and accordingly are not considered in choosing the equilibrium constant.

In Table IV are given the results obtained at a temperature of 570°. Except for one group of 8 runs, reserved for Table V, all of the final 570° experimental values are included. The equilibrium constant at 570° is 50.5 ± 0.2.

TABLE IV

TEMPERATURE, 570°

Run no.	Inlet mixture		Exit totals		H_2O/H_2		Approx. % of metallic cobalt
	Steam, cc./min.	H_2, cc./min.	Water, g.	H_2, cc.	In	Out	
			70.8 Grams of Catalyst No. 1				
354	80.0	2	3.428	84.15	40.6	50.7	7
355	124.4	2	3.428	84.55	63.7	50.4	7
356	122.6	2	3.412	84.12	62.8	50.5	7
			23.8 Grams of Catalyst No. 2				
408	130.8	3	3.380	83.59	43.6	50.3	9
409	181.6	3	3.396	83.71	60.5	50.4	9
432	122.1	3	3.374	82.77	40.7	50.7	61
433	122.3	3	3.373	82.95	40.8	50.6	61
434	117.1	3	3.215	82.73	39.0	48.4	61
435	167.3	3	3.372	83.14	53.7	49.9	61
436	181.7	3	3.384	83.18	60.5	50.6	61
437	171.3	3	3.381	82.96	57.1	50.7	61

One group of experiments was carried out to ascertain whether or not the same equilibrium constant prevailed even when the solid phase consisted of a small amount of oxide and a large amount of metal. A definite shift in the equilibrium constant would indicate the formation of solid solutions over a limited range. The results of the twelve runs thus made are shown in Table V.

TABLE V

RESULTS OF EXPERIMENTS

Run no.	Inlet mixture Steam, cc./min.	 H_2, cc./min.	Exit totals Water, g.	 H_2, cc.	H_2O/H_2 In	 Out	Approx. % of metallic cobalt
			Temperature, 515°				
412	97.9	2	3.516	85.15	49.0	51.4	80
413	107.2	2	3.639	85.17	53.6	53.2	80
414	134.8	2	3.687	84.83	67.4	54.0	80
415	123.3	2	3.674	83.86	61.7	54.5	80
			Temperature, 570°				
416	88.9	2	3.220	84.40	44.5	47.5	80
417	121.0	3	3.227	84.44	40.3	47.5	80
418	150.2	3	3.139	84.17	50.1	46.4	80
419	164.3	3	3.179	83.73	54.8	47.2	80
420	185.4	3	3.121	84.58	61.8	45.9	88
421	185.0	3	3.262	84.48	61.3	48.0	88
422	185.6	3	3.352	84.79	61.9	49.3	88
423	187.4	4	3.313	84.47	46.9	48.8	88

Run 412 was made immediately after reducing a sample until it contained only 20% of cobaltous oxide. Just before Run 420, additional reduction dropped the oxide content to approximately 12% of the sample. It was at first thought that the results indicated a definite shift in equilibrium constant. Unfortunately time limitations prevented the obtaining of further data upon this point. If due allowance is made for the already noted tendency of ratios immediately following long reduction to be low, the results in Table V are believed to be explainable without assuming the formation of solid solutions. Particularly, Runs 420, 421 and 422 suggest the probability that the low ratios are the result of the long reduction, for the exit ratio is in these runs definitely increasing toward the 50.5 value, believed to be the true equilibrium constant. Furthermore, as will be seen from the x-ray photographic data given below, no evidence of solid solutions for these samples is furnished by the powder photographs taken.

It should be noted that Runs 429 to 444 shown in Tables II to IV were all taken after those in Table V, the only change being that between Runs 428 and 429 the catalyst was steamed for seventeen hours at 500°. Hence it is certain that the analytical apparatus was operating in the same way before and after the twelve runs of Table V.

From the data presented in Tables I to V, it can be concluded that the equilibrium ratios of steam to hydrogen in contact with the oxide–metal mixture present are as follows:

Temperature, °C.	335	450	515	570
Ratio	85 ± 5	67 ± 1	57 ± 0.3	50.5 ± 0.2

The 335° value is only approximate and was determined in preliminary runs.

It was next necessary to establish definitely that the cobalt oxide in the above experiments was CoO and not Co_3O_4, Co_2O_3 or a solid solution of two of the oxides.

We were fortunate in having facilities available for checking the composition of all the materials used in these determinations by x-ray photographs.[7]

In Table VI are listed the samples of which powder photographs were taken as a means of ascertaining definitely the solid phases existing in the equilibria measurements. These photographs were made with MoKα radiation. Since all the substances present in these samples have been previously examined by means of their x-ray powder diffraction patterns, it was not considered necessary to list in detail the results obtained.

TABLE VI

POWDER PHOTOGRAPH RESULTS

	History of sample	Phases revealed by powder photographs
a	Pure CoO (Sample of Catalyst No. 1)	CoO
b	Co_3O_4 (Sample of Catalyst No. 2)	Co_3O_4
c	Catalyst No. 1, 9% reduced at 283°	CoO and hexagonal Co
d	Catalyst No. 1, 75% reduced at 288°	CoO and hexagonal Co
e	Mixture of Sample c and CoO	CoO (no line displacement) and hexagonal Co
f	Mixture of Sample d and CoO	Same as in e
g	Final material remaining after Run 444 in the equilibrium measurements	Cubic Co and CoO
h	Sample obtained by steaming a completely reduced Co_3O_4 sample for eight hours at 500° with rapid flow of steam. During this time the sample was 70% reoxidized, as detd. by hydrogen formed	Cubic Co and CoO
i	Sample prepared by passing a mixture containing steam and hydrogen in the ratio of 70 to 1 over a sample of Co_3O_4 at 500° for ten hours	Strong CoO Faint Co_3O_4
j	Co_3O_4 reduced at 310°	Hexagonal Co
k	Co_3O_4 reduced at 340°	Hexagonal Co
l	Co_3O_4 reduced at 383°	Cubic cobalt
m	Co_3O_4 reduced at 360°	Cubic and hexagonal cobalt

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[7] For these powder photographs and their interpretation we are indebted to Dr. S. B. Hendricks of this Laboratory. We wish to express our appreciation for his cooperation.

Substances identified by the powder lines on the photograph are indicated in the table.

With the exception of Samples a and b, all the materials listed in the above table were examined without allowing them to come in contact with the atmosphere.

These photographic results we believe enable us to conclude (1) that cobaltous oxide and cobalt were the only solid phases present during the equilibrium measurements; (2) that no evidence for the existence of a solid solution between cobaltous oxide and cobalt under the conditions of these experiments can be found in the powder photographs obtained.

In view of the above facts, it seems justifiable to conclude that the equilibrium results summarized above apply to the equilibrium Co–CoO–H_2O–H_2.

The results summarized under j, k, l and m were taken by Dr. Hendricks in order to fix the transition temperature of cobalt. It has previously been known that cobalt obtained by reduction of the oxide at 600°, has a "face-centered" cubic structure while that usually present in cast cobalt has a "close-packed" hexagonal structure. The transition temperature was not even approximately known nor could it be determined by the usual method of thermal analysis, since the rate of transformation of one form to another is very sluggish at 300–400°. From the information listed in Table VI, it can be concluded that the transition temperature is between 340 and 360°.

It should be noted in the results in Tables I, II, III, IV and V that values for the effluent ratio of steam to hydrogen are higher than normal immediately after oxidation and lower immediately after reduction. Such runs are designated by *a* and *b*, respectively, as described in Table II. This is analogous to the effect mentioned by Richardson, Vibrans and Bell[8] for iron oxide reduction, and by Pease and Cook[4] in the case of the equilibrium determination of hydrogen–steam ratio over Ni–NiO mixtures. A similar phenomenon is reported for metallic iron catalyst by Almquist and Black.[9] In this latter case the circulation over an iron catalyst of a 3:1 hydrogen–nitrogen mixture containing from 0.008 to 0.32% of water vapor was found to form small but definite amounts of oxide upon the surface of the iron. This oxide has been interpreted by Almquist[10] as being due to the oxidation of surface atoms having free energies of the order of 10,000 calories greater than that of normal surface iron atoms. Eastman and Evans[11] have noted the tendency of the equilibrium hydrogen–steam ratio over Fe-FeO to increase as the

[8] Richardson, Vibrans and Bell, *Science*, **56**, 27 (1922).

[9] Almquist and Black, THIS JOURNAL, **48**, 2814 (1926).

[10] Almquist, *ibid.*, **48**, 2820 (1926).

[11] Eastman and Evans, *ibid.*, **46**, 888 (1924).

oxygen content of the solid phases decreased, and have mentioned it as being indicative of a solid solution existing between iron and ferrous oxide. This phenomenon, however, quite probably is distinct from the one noted by Almquist and Black in that it was obtained under conditions making solid solution much more likely than in the case of their experiments. In the present work the values marked with a *a* or *b* in Tables II, III and IV are of such magnitude and obtained under such conditions as probably to be due to a surface effect rather than to the formation of a solid solution. Furthermore, as already pointed out, powder photographs reveal no shifting of lines of cobaltous oxide containing small amounts of cobalt or cobalt containing small amounts of cobaltous oxide, making the existence of solid solutions between these solid phases improbable.

One difference between the above-mentioned effect on nickelous oxide as reported by Pease and Cook and on cobaltous oxide as recorded in the present work should be noted. The former authors give data showing a rather high hydrogen consumption by nickelous oxide on passage of a steam-hydrogen mixture. Thus, one 84-g. sample of NiO when treated with 150 cc. per minute of a 150-1 steam-hydrogen mixture permitted no hydrogen to pass during the first twenty hours. Had the exit gases contained the normal equilibrium hydrogen some 554 cc. of hydrogen would have been collected during this time. Accordingly, hydrogen equivalent to about 2.1% of the oxygen of nickelous oxide was consumed before any appeared in the effluent gas. In contrast to this, the cobaltous oxide samples of the present work never absorbed more than a few cc. of hydrogen when similarly treated. The very first reading usually differed from the true equilibrium value by only 5 or 10%. Complete equilibrium usually resulted within an hour of the first passage of steam-hydrogen over the oxide. This excessive consumption of hydrogen by nickelous oxide as compared to cobaltous oxide may indicate an unusually large surface effect by the nickelous oxide preparation as compared to the cobaltous oxide. On the other hand, it may in part at least be due to the consumption of some hydrogen by small amounts of Ni_2O_3 present in the NiO. This possibility would necessitate that the oxide be of the empirical composition $NiO_{1.021}$ approximately. The highest percentage of oxygen reported by Pease and Cook was 21.8% in contrast to the 21.43% theoretically needed for NiO. This corresponds to a composition of $NiO_{1.018}$. Furthermore, Benton and Emmett[12] reported certain samples of NiO which were prepared by ignition of the nitrate in air at 360 to 400° for many hours to have a composition as rich in oxygen as $NiO_{1.032}$. Accordingly, it does not seem unreasonable that part of the effect reported by Pease and Cook was in reality due to the reduction of small amounts of one of the higher oxides of nickel. Hence, in nickelous oxide the true "surface" effect

[12] Benton and Emmett, This Journal, **46**, 2728 (1924).

causing hydrogen from a steam–hydrogen mixture in contact with pure metal to be consumed in excess of equilibrium requirements may not be different from that found for cobaltous oxide.

Free Energy Calculations.—From the equilibrium data obtained in the present investigation, the standard free energy and heat content changes for the reaction

$$CoO + H_2 = Co + H_2O \qquad (1)$$

can easily be calculated. Inserting the values 67, 57.0 and 50.5 for K at 723, 788 and 843°, respectively, into the equation[13]

$$\Delta F^\circ = -RT \ln K$$

one readily obtains ΔF°_{723}, ΔF°_{788} and ΔF°_{843}, as -6045, -6335 and -6574 calories, respectively. In the absence of specific heat data for cobaltous oxide, we have used a value of 10, obtained by Kopp's law as outlined in Noyes and Sherrill[14] and for cobalt a value of 6. These specific heat values, together with those for water vapor and hydrogen given by Lewis and Randall, yield a ΔC_p value of $-1.69 - 0.0028T + 0.00000222T^2$. Inserting ΔF° values for the three temperatures given above in the equation

$$\Delta F^\circ = \Delta H_0 - \Delta\Gamma_0 T \ln T - {}^1/_2\Delta\Gamma_1 T^2 - {}^1/_6\Delta\Gamma_2 T^3 \ldots\ldots + IT$$

and solving the three sets of resulting equations for I, values of -18.91, -18.83 and -18.87 are obtained. Using an average I value, an average ΔH_0 value of -1040 calories is obtained. Whence $\Delta H_{298} = -1646$ calories, and $\Delta F^\circ_{298} = -3678$ calories for Reaction 1 above.

In Fig. 2 the smooth curve represents a plot of $1/T$ against the logarithm of the equilibrium constant as calculated for temperatures between 335 and 1050° from the ΔF° equation given above, using for ΔH_0 -1040 calories, for I a value of -18.87 and for ΔC_p the expression $-1.69 - 0.0028T + 0.00000222T^2$. It is realized that the high temperature extrapolation of our own values hereby obtained is uncertain because of the assumptions as to the specific heats of cobalt and cobalt oxide. More dependable extrapolations to the higher temperatures must await specific heat data on cobaltous oxide. From the figure, assuming the above extrapolation to be approximately correct, we conclude that our own data are consistent with the value of 20 ± 10, obtained by Chaudron, for the constants at 1050°. The results of Wöhler and Balz, however, are much lower than our own. It is tempting to suggest that the value 34 reported by them to be the constant for the oxidation of CoO to Co_3O_4 by steam may actually have been obtained when CoO and Co were present and may accordingly refer to the equilibrium measured in the present research.

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[13] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**.

[14] Noyes and Sherrill, "Chemical Principles," The Macmillan Co., New York, **1928**, p. 93.

By combining the free energy for Reaction 1 with that[13] for the reaction

$$H_2O = H_2 + {}^1/_2O_2 \qquad (2)$$

one obtains the ΔF°_{1373} for the reaction

$$CoO = Co + {}^1/_2O_2 \qquad (3)$$

as +32,050 calories. By the equation $\Delta F^{\circ} = -RT \ln K$, the dissociation pressure of the oxide at 1373° is given as 0.5×10^{-7} mm. This value is consistent with the experiments of Foote and Smith[15] in which the dissociation pressure of cobaltous oxide was too small to be measurable at 1373°.

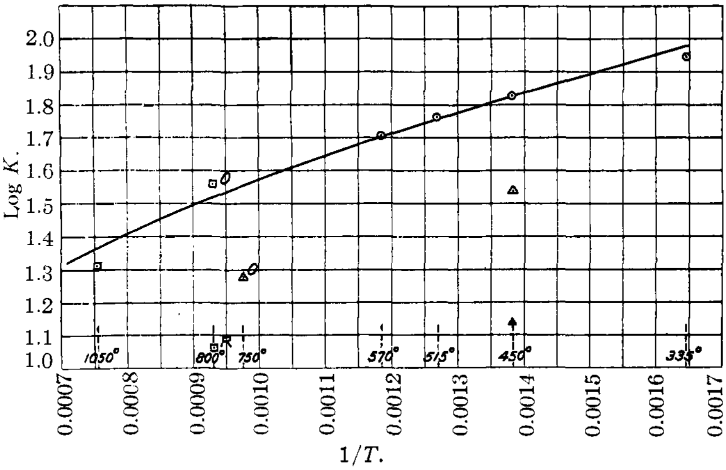

Fig. 2.—⊙, Emmett and Shultz; ⊡, Chaudron; △, Wöhler and Balz.

Experimental ΔH values of Mixter[16] for Reaction 3 above are 57,587 calories for crystalline CoO and 50,180 calories for "amorphous" cobalt oxide. The so-called "amorphous" values were obtained by the indirect oxidation of cobalt by means of sodium peroxide rather than the direct oxidation with gaseous oxygen used in determining the 57,587 value. It is quite probable, accordingly, that this difference in procedure rather than the difference in fineness of subdivision of the final product causes the discrepancy between the two values for the heat of oxidation of cobalt to cobaltous oxide.

It is interesting to calculate indirectly from our own data the ΔH value for Reaction 3. By combining the ΔH_{298} value obtained above for Reaction 1 and the well known ΔH_{298} value for Reaction 2, one obtains $-1646 + 57,800 = 56,154$ calories as ΔH_{298} for Reaction 3. This compares favorably with Mixter's value of 57,587 calories.

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[15] Foote and Smith, This Journal, **30**, 1349 (1908).

[16] Mixter, *Am. J. Sci.*, **30**, 193 (1910).

As confirmation of the fact that no Co_3O_4 was obtained by passage of steam over CoO, a combination of the ΔF° value for the reaction

$$Co_3O_4 = 3CoO + {}^1/_2O_2 \qquad (4)$$

as calculated from the dissociation pressure of (4) given by Foote and Smith[15] and Reaction 2, above, yields ΔF°_{603}, ΔF°_{788} and ΔF°_{1073} values for the reaction

$$Co_3O_4 + H_2 = 3CoO + H_2O \qquad (5)$$

of −34,197, −36,539 and −44,717 calories, respectively. Corresponding ratios of steam to hydrogen necessary to produce oxidation of the CoO to Co_3O_4 are 2.4×10^{12}, 1.3×10^{10} and 1.3×10^{9}. Hence, no formation of Co_3O_4 under the conditions of the above experiments would be expected.

This conclusion is in agreement with our own experimental values but is in direct contradiction to the results of Wöhler and Balz,[2] who reported a value of 34 for the above ratio at a temperature of 450°.

In the above calculations nothing has been said about the possible free energy change involved in the transformation from hexagonal to cubic cobalt. All experiments except those at 335° were carried out in the temperature region in which the cubic modification of cobalt is the stable one. In the absence of the necessary data no correction has been made for any free energy change involved in the transformation from hexagonal to cubic cobalt.

Summary

1. The ratios of steam to hydrogen in equilibrium with a mixture of cobalt and cobaltous oxide have been determined by a flow method. The values obtained for this ratio are 67 ± 1, 57.0 ± 0.3 and 50.5 ± 0.2 at 450, 515 and 570°, respectively. An approximate value of 85 ± 5 has been obtained at 335°.

2. ΔF°_{298} for the reaction $CoO + H_2 = H_2O + Co$ has been calculated as −3678 calories.

3. The calculated value of ΔH_{298}, −1646 calories, for the above reaction is to be compared with a value, −300 cal., obtained by the combination of Mixter's experimental heat of formation of cobaltous oxide and the well-known heat of formation of water.

4. The failure of steam passage over CoO at 500° to form Co_3O_4 has been verified by x-ray photographs. A calculated value has been obtained for the theoretical steam–hydrogen ratio necessary to effect such an oxidation. This was obtained by a combination of the dissociation pressure measurements of Co_3O_4 made by Foote and Smith, and the value for the ΔF° change involved in the formation of water from hydrogen and oxygen. It is believed that the calculated value is approximately correct and accordingly confirms the impossibility of any appreciable amount of Co_3O_4 having been formed by passage of steam–hydrogen

mixture over cobaltous oxide in the temperature range of 330 to 570° in the above experiments.

5. ΔF°_{1373} for the formation of cobaltous oxide from cobalt and oxygen has been calculated by combining the free energy change involved in forming water vapor from hydrogen and oxygen with that found experimentally in the present research for the reduction of cobaltous oxide to cobalt by hydrogen. A value of 32,050 calories so obtained yields a value of 0.5×10^{-7} mm. for the partial pressure of oxygen in equilibrium with CoO–Co mixture at 1100°, that is, in agreement with Foote and Smith's failure to detect measurable dissociation of cobaltous oxide at that temperature.

6. The temperature of transformation of hexagonal to cubic cobalt has been fixed as lying between 340 and 360°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

AN APPARATUS FOR TESTING DÜHRING'S LAW FOR CORRESPONDING BOILING POINTS

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Introduction

In 1877 Dühring[1] found that a linear relation existed between the boiling temperatures of two liquids boiling under the same pressures. So far this law has been tested indirectly by plotting corresponding boiling points from vapor-pressure data obtained for the two liquids separately. If the two liquids could be boiled in different parts of a closed system, then as the pressure is varied in the system, the corresponding boiling temperatures could be observed directly. This was tried out and it has given satisfactory results. The apparatus is of simple construction and is easy to manipulate.

Discussion

The apparatus is illustrated in Fig. 1. Bulbs are blown at the bottom of two upright reflux Liebig condensers. At the top the condensers are connected to each other and to a vacuum pump, which may be an ordinary aspirator. In the latter case a water trap should be provided in the evacuating train. In order to condense the vapors of the boiling liquids at low temperatures ice water should be led through the condensers.

The liquids to be boiled are poured into the bulbs to about the level indicated in the figure. Porous plate or bisque fragments are added to minimize bumping. The boiling temperatures are obtained by two

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[1] Dühring, *Wied. Ann.*, **11**, 163 (1880).