

and the preliminary revised value of the free energy of formation of chloride ion ($-31,345$), we find

$$\text{Fe}(s) = \text{Fe}^{++} + 2\text{E}^-; \text{E}_{298}^{\circ} = 0.4387 \text{ v.}; \Delta F_{298}^{\circ} = -20,245 \text{ cal.} \quad (7)$$

In making these measurements Hampton used powdered reduced iron. The treatment with thallos chloride undoubtedly had the same effect as our treatment with hydrochloric acid of first removing the finer particles of iron; the residual iron might, therefore, be expected to give identical results in the two cases. The small difference between the values in Equations 3 and 7 is explained by the fact that complete equilibrium hardly was attained in Hampton's experiments. The measurements of Hampton in which the equilibrium was approached from the action of ferrous chloride upon thallium do not agree with these measurements, but the reaction is very slow and undoubtedly equilibrium was not attained.

Summary

1. Iron prepared in pure form by electrolysis is shown to have the same potential as pure iron produced by reduction of iron oxide, in ferrous chloride solution.

2. The standard single potential of iron at 25° is found to be 0.4402 volt, and the free energy of formation of ferrous ion to be $-20,310$ calories.

3. The new potential is shown to agree with the equilibrium experiments of Hampton.

4. A table of values of the activity coefficient of ferrous chloride at the freezing point has been calculated.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

THE HEATS OF "ADSORPTION" OF OXYGEN ON NICKEL AND COPPER CATALYSTS

BY W. WALKER RUSSELL AND OSBORNE C. BACON¹

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It is well known that oxygen has no action on nickel or copper² in the massive state at ordinary temperatures. When these metals are sufficiently finely divided to be catalytically active, however, they do take up oxygen readily and may even become pyrophoric.³ Oxygen may also serve as a poison⁴ for the catalytic activity of nickel and copper. A study of the action of oxygen on such surfaces might, therefore, be expected to

¹ From a thesis submitted in May, 1931, by Osborne C. Bacon to the Graduate School in partial fulfillment of the requirements for the degree of Master of Science.

² Dunn, *Proc. Roy. Soc. (London)*, A111, 210 (1926).

³ Tammann and Nikitin, *Z. anorg. allgem. Chem.*, 135, 201 (1924).

⁴ Benton and Emmett, *THIS JOURNAL*, 48, 637 (1926); Pease and Taylor, *ibid.*, 44, 1637 (1922).

give information regarding their nature and function as catalysts. Especially surfaces produced by the removal of oxygen atoms, *e. g.*, low temperature reduction of oxides, might be expected again to take up oxygen with characteristic effects since the activity of such surfaces must be, in part at least, dependent upon some persistence of the metal oxide lattice. Because of such considerations, it was deemed of interest to investigate the behavior of oxygen toward active nickel and copper surfaces and to this end measurements have been made of the magnitudes of the heats of oxygen adsorption⁵ at 0°. In certain cases measurements of the catalytic activity of the same surfaces at 0° have also been carried out.

Apparatus and Experimental Method

Apparatus.—The apparatus consisted essentially of a water jacketed, compensated gas buret, a closed manometer, a Toepler pump and a catalyst bulb. These units were all sealed together to make an all-glass apparatus with suitable stopcocks and connections provided. All of the measuring apparatus was carefully calibrated.

Thermal measurements were made by means of a Bunsen ice calorimeter essentially of the type described by Marshall and Keyes.⁶ Several calibrations of the capillary, which agreed closely, were made using weighed threads of mercury. As a check upon the accuracy of the calorimeter it was calibrated under conditions of actual use by introducing known amounts of heat in the form of Bureau of Standards pure aluminum and zinc. An accuracy of 0.5% or better was indicated when the calorimeter was used under favorable conditions.

Purification of Gases.—The hydrogen used in this work was a compressed, electrolytic material which was purified by passage over heated copper turnings, solid potash, calcium chloride and phosphorus pentoxide in the order named. The helium initially about 96% pure, was further purified by drying over phosphorus pentoxide and very slow passage through activated charcoal⁷ at liquid air temperature. The oxygen was prepared by the electrolysis of sodium hydroxide solution and then passed over heated copper oxide, a red hot platinum spiral, ascarite, calcium chloride and finally phosphorus pentoxide. Very pure oxygen was obtained in this way. Compressed ethylene was passed first over calcium chloride and then through a trap immersed in solid carbon dioxide and ether.

Preparation of Catalysts.—Chemically pure $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$, *e. g.*, 47.5% ThO_2 , were used in the preparation of the catalysts. Prior to reduction the nitrates were ignited at a low temperature until completely changed to oxide. Continued stirring during the ignition resulted in very finely divided oxides. Thoria was incorporated by dissolving the nitrate in the melted nickel or copper nitrate. Supported catalysts were prepared by stirring carefully purified pumice (20–40 mesh) into a nitrate solution of suitable concentration, in such an amount that the liquid was completely absorbed. The mass was then subjected to low temperature ignition. Reduction was carried out by heating in hydrogen until less than 1 mg. of water could

⁵ The word adsorption has been used throughout this paper to indicate what occurs when oxygen is brought into contact with a catalyst surface at 0° and no idea of the way in which the oxygen is held is necessarily implied.

⁶ Marshall and Keyes, *THIS JOURNAL*, 49, 160 (1927).

⁷ This charcoal was very kindly furnished us through the courtesy of Mr. L. M. Currie of the National Carbon Company, Cleveland.

be detected in a weighed phosphorus pentoxide tube in an hour. The temperature of reduction was regulated by means of a thermostat to within $\pm 5^\circ$. Catalysts were reduced in bulbs about 18 mm. in diameter and 70 mm. long, and then sealed in place while still in an atmosphere of hydrogen. Once in place the catalysts were evacuated very completely at the temperature of reduction to remove adsorbed hydrogen.

Heat of Adsorption Measurements.—When it was certain that the calorimeter leak and the room temperature were constant, measurements were begun. Oxygen was admitted from the manometer, which was so calibrated that it measured both pressure and volume. This manometer was read by means of a cathetometer. A pressure of a few tenths of a mm. of helium was always present to ensure rapid attainment of thermal equilibrium. This was essential inasmuch as all but the last increment of oxygen was completely adsorbed. Therefore, dead space measurements were required only for the evaluation of final increments. Helium was used to determine the dead space values and was found not to be adsorbed, although nitrogen was adsorbed.

Reaction Velocity Experiments.—These measurements were made by a static method. The desired amount of a 1:1 ethylene-hydrogen mixture was admitted from the gas buret into the catalyst-manometer system and the reaction was followed by means of the pressure change. Manometer readings were taken every minute until the rate of pressure change became slow. This rate became very slow when reaction was 70 to 80% complete, and then the residual reaction mixture was quickly pumped off, as completely as possible at 0° , and collected. Final traces of the reaction mixture were removed by a slow heating usually to reduction temperature, at all times keeping the catalyst evacuated. Knowing the amount and composition of the reaction mixture initially introduced and the total amount finally pumped off, the extent of the reaction at the time of pumping was readily calculated from the volume change. Therefore, the pressure which would have existed in the system at the time of pumping, had no adsorption occurred, could be calculated. The difference between this calculated pressure and the actually observed pressure gave a measure of the total amount of gas adsorbed. By making the assumption that the magnitude of the total adsorption did not change appreciably between the time of 50% reaction and the time when the system was pumped, it was now possible to read off from a curve relating observed pressures and time, and with an allowance for the effect of adsorption, the time for half reaction. This half time has been used as a criterion of catalyst activity.

Experimental Results

A. Preliminary Work.—Early measurements of the adsorption of oxygen on nickel indicated that this gas is very strongly adsorbed at 0° and that large thermal effects are involved. It was found impossible to desorb any oxygen by evacuation up to temperatures of 300 to 400° . A most interesting observation was made, however, when it was found that even though no oxygen could be pumped from the surface at these temperatures, yet the configuration of the adsorbed oxygen had undergone a marked change during the heating. This was indicated by the fact that the surface was now able again to adsorb large amounts of oxygen with only slightly reduced thermal effects. This behavior is all the more remarkable in view of the fact that the surface prior to heating was completely saturated at 0° with oxygen at atmospheric pressure.

The first measurements were made on pumice carrying 10% (0.5 g.) of

nickel which was reduced at 350° . For a promoter thoria, to the extent of 10% of the nickel present, was used. Only integral heats at pressures close to atmospheric were measured. On original surfaces values of the order of 98,000 and 95,000 cal. were obtained on the promoted and unpromoted catalysts, respectively. After three or four heatings of the oxygen saturated surfaces at 350° , both types of catalyst gave values of about 85,000 cal. On the original surfaces the promoted catalysts adsorbed nearly twice as much oxygen as the unpromoted, *e. g.*, 4.5 and 4.1 cc. against 2.4 cc. The first heating cut the adsorptive capacities of the promoted surfaces almost exactly in half while the unpromoted suffered slightly less. Heating a saturated promoted surface at 250° did not cause it to again adsorb oxygen at 0° .

Because of the relatively small amounts of oxygen adsorbed per unit volume when a support is present, it was next decided to investigate unsupported catalysts whose larger adsorptive capacities would make possible measurements upon partially saturated surfaces. Several unsupported promoted nickel catalysts were reduced at 300° and the heats of adsorption of increments of oxygen varying in size from 0.5 to 7 cc. measured. Catalyst 4 contained 6.4% thoria and weighed 7.086 g. It adsorbed 17.34 cc. of oxygen, before developing any pressure, with an average thermal effect of 92,000 cal. Heating to 300° for three hours caused the amount so adsorbed to decrease to 8.54 cc. with a concomitant thermal effect of 82,000 cal. Catalyst 5 contained a more nearly optimal amount of thoria, namely, 2%, and weighed 7.762 g. In nineteen successive increments it adsorbed 51.75 cc. of oxygen, before developing a pressure, with an average thermal effect of 101,000 cal. The individual heats of adsorption for the first half of the gas taken up were of similar magnitude giving an average value of 96,000 cal. The second half of the gas, however, was adsorbed with increasing thermal effects, a value as high as 108,000 cal. being obtained 7 cc. from the end. Heating this first surface to 300° for three hours caused the adsorption to drop to 11.83 cc. and the average heat of adsorption to 88,000 cal. With catalyst 7, which was similar to 5 but somewhat less active, the oxygen adsorption on the second surface was carried out at -38° and saturation reached at 16 cc. Upon warming up to 0° an additional 1 cc. was adsorbed with a thermal effect of 88,000 cal. It is interesting to note that oxygen is still adsorbed strongly at -38° and that the adsorptive capacity increases up to 0° .

In general, the values of the heats of adsorption obtained in this preliminary work probably correspond more nearly to integral than to differential values, and this is borne out by later experiments which will be presented in greater detail.

B. Work on Nickel.—In view of the results obtained in the preliminary work with nickel it was decided to investigate the phenomena some-

what more thoroughly. The apparatus was altered to conform with that already described and the accuracy⁸ of the subsequent measurements is, therefore, somewhat greater.

Nickel catalysts 8 and 12 were prepared by reduction at 300°. The former was nickel alone while the latter contained 2% of thoria. The behavior of these two preparations toward oxygen should be clear from Tables I and II. It is apparent that, with the exception of the original surface of the promoted catalyst, the thermal values remained essentially constant until a given surface became saturated. Such a constant thermal effect would be explained if at 0° oxygen were adsorbed strongly over a considerable range of types of surface. If so the first increment of the oxygen would be almost entirely adsorbed by the uppermost layers of the catalyst with which it first came into contact, and successive increments would penetrate deeper down through the mass, giving average or nearly integral heats. Assuming that such values should be identical, a check is offered upon the relative accuracy of the measurements by an inter-comparison of the observed values. Upon saturation of the lowest layers of the catalyst, the observed rapid rise in pressure and sharply diminished thermal effect would be anticipated. Prior to the appearance of a pressure, the adsorption was almost instantaneous. This pressure decreased slowly with time and the rate was not appreciably increased by augmenting the oxygen pressure. The equilibrium pressure of the adsorbed oxygen was far too low to measure in the manometer. That this pressure is substantially zero, however, was demonstrated by pumping the unadsorbed gas from the catalyst bulb and then allowing the closed system to stand as long as forty-eight hours, when not the slightest trace of gas could be detected in a large Toepler pump.

The promoter effect of thoria in No. 12 is apparent both in the larger adsorptive capacity and in the greater thermal values of this catalyst as compared with 8. Although the average heat of adsorption is less than a thousand calories higher on 12, yet that there is a real qualitative difference in surface is indicated by the considerable rise in the individual heats observed in the later increments on the promoted catalyst. The reason for this is not apparent although 5, which was also promoted, showed a similar phenomenon.⁹ The effects produced by heating surfaces previously

⁸ Under the most favorable conditions, as illustrated by the heats of adsorption with rapidly and completely adsorbed oxygen on nickel, a relative accuracy of the order of 1% seems probable. In the case of copper where the adsorption is complete but somewhat slower, a relative accuracy of about 2 to 3% is indicated. Final values on copper are least accurate. The absolute accuracy of the measurements while somewhat less should not be materially so.

⁹ No evidence of incompletely desorbed hydrogen has been obtained in any of this work. The first few values of the heat of adsorption on an original surface have not been abnormal; furthermore, no water could be detected by pumping at temperatures up

saturated with oxygen at 0° at several temperatures for different times should be quite apparent from Tables I and II. After the first heating, in which the promoted catalyst suffered the more, there seems to be little evidence of any marked difference between the two catalysts in their response to subsequent heatings. Taken as a whole, however, the observations indicate that the extent of the transformation of oxygen adsorbed at 0° on an active nickel surface depends primarily upon the temperature of heating. The rate of transformation is negligibly slow at 250°, not quite complete in three hours at 300°, essentially complete in this time at 350°

TABLE I
OXYGEN ADSORPTIONS ON NICKEL
Catalyst 8. Weight, 9.037 g.

Original surface	Pressure increase, mm.	Volume adsorbed, cc. N. T. P.	Heat evolved, cal.	Heat of adsorption, cal./mole
1	0.00	4.641	20.126	97,149
2	.00	4.631	20.086	97,160
3	53.30	3.016	10.957	81,378
		<u>12.288</u>	<u>51.169</u>	
Second surface: produced by heating at 300° for three hours				
1	0.00	2.471	10.350	93,824
2	.00	2.567	10.748	93,788
3	60.01	0.815	2.346	64,479
		<u>5.853</u>	<u>23.444</u>	
Third surface: produced by heating at 300° for three hours				
1	0.00	2.514	10.224	91,078
2	71.56	0.459	1.250	61,002
		<u>2.973</u>	<u>11.474</u>	
Fourth surface: produced by heating at 250° for three hours				
1	1.98	0.500
Fifth surface: produced by heating at 350° for half an hour				
1	0.00	0.548	2.271	92,829
2	.00	2.070	8.447	91,407
3	59.10	0.404	0.950	52,647
		<u>3.022</u>	<u>11.668</u>	
Sixth surface: produced by heating at 350° for three hours				
1	0.00	2.100	8.497	90,634
2	3.68	2.060	7.475	81,281
		<u>4.160</u>	<u>15.972</u>	

to that of reduction and higher through a weighed phosphorus pentoxide tube after an oxygen adsorption.

TABLE II
 OXYGEN ADSORPTIONS ON PROMOTED NICKEL
 Catalyst 12. Promoter, 2% thoria. Weight, 6.982 g.

	Pressure increase, mm.	Volume adsorbed, cc. N. T. P.	Heat evolved, cal.	Heat of adsorption, cal./mole
Original surface				
1	0.00	2.023	8.556	94,737
2	.00	2.082	8.765	94,296
3	.00	2.123	8.975	94,691
4	.00	2.053	8.665	94,544
5	.00	5.068	21.902	96,798
6	.00	4.940	21.263	96,415
7	.00	5.140	21.840	95,183
8	.00	5.207	22.862	98,348
9	.00	4.852	22.130	102,167
10	.00	5.589	28.220	113,106
11	70.16	1.591	4.217	59,357
		<hr/>	<hr/>	
		40.668	177.395	
Second surface: produced by heating at 300° for three hours				
1	0.00	3.151	12.904	91,733
2	.00	2.984	12.180	91,429
3	.00	3.013	12.290	91,377
4	.00	3.055	12.465	91,394
5	1.48	2.906	10.115	77,972
		<hr/>	<hr/>	
		15.109	59.954	
Third surface: produced by heating at 350° for three hours				
1	0.00	3.080	12.627	91,832
2	.00	3.132	12.892	92,191
3	.00	3.176	13.041	91,975
4	.00	3.065	12.548	91,714
5	.00 ^a	3.106	11.974	86,344
		<hr/>	<hr/>	
		15.559	63.082	
Fourth surface: produced by heating at 350° for three hours				
1	0.00	3.037	12.412	91,542
2	.00	3.080	12.577	91,475
3	.00	3.145	12.918	92,007
4	.00	3.096	12.579	91,010
5	23.94	2.324	8.049	77,582
		<hr/>	<hr/>	
		14.682	58.535	
Fifth surface: produced by heating at 350° for eight hours				
1	0.00	3.149	12.866	91,533
2	.00	3.172	12.920	91,239
3	.00	3.121	12.760	91,580
4	.00	3.183	12.913	90,859
5	35.12	1.972	6.272	71,254
		<hr/>	<hr/>	
		14.597	57.731	

TABLE II (Concluded)

	Pressure increase, mm.	Volume adsorbed, cc. N. T. P.	Heat evolved, cal.	Heat of adsorption, cal./mole
Sixth surface: produced by heating at 300° for three hours				
1	0.00	3.296	13.292	90,325
2	.00	3.123	12.576	90,190
3	2.62	3.090	11.323	82,076
		9.509	37.191	
Seventh surface: produced by heating at 300° for twelve hours				
1	0.00	3.106	12.543	90,464
2	.00	3.127	12.585	90,137
3	36.56	1.914	6.142	71,881
		8.147	31.270	
Eighth surface: produced by heating at 350° for three hours				
1	0.00	3.122	12.531	89,908
2	.00	3.131	12.427	88,893
3	2.50	3.019	10.503	77,935
		9.272	35.461	
Ninth surface: produced by heating at 400° for three hours				
1	0.00	3.162	12.876	91,215
2	.00	3.146	12.595	89,678
3	.00	3.165	12.705	89,918
4	.00 ^a	3.164	12.351	87,448
		12.637	50.527	

^a Pressure diminished slowly but reached zero within an hour.

and still faster at 400°. Raising the temperature of heating from 300 to 400° causes the transformation to become more comprehensive, as is evidenced by the increased adsorptive capacities and slight though definitely increased heats of adsorption. The magnitudes of these effects and especially the latter must be decreased by the known sintering effects produced when a catalyst is first brought to a temperature substantially above that of its production.

C. Hydrogen Adsorption on Promoted Nickel Holding Previously Adsorbed Oxygen.—Table III contains the results of four hydrogen adsorptions on No. 12 while it held varying amounts of oxygen previously adsorbed at 0°. The results of each oxygen adsorption are given, followed by that of the subsequent hydrogen adsorption. The final pressures for hydrogen were those observed twenty minutes after the gas was admitted. Only slow adsorption was taking place at the end of this time and the thermal values correspond to this interval of adsorption.

The first measurements were made upon the surface produced by heating to 400° for three hours, the ninth surface of No. 12. This surface

was probably not more than 25% saturated with oxygen and the heat of adsorption of 23,112 cal. indicates that hydrogen was largely adsorbed on nickel surface. No water could be removed by evacuation at 0°. When the catalyst was slowly heated up to 90° in hydrogen, a decrease in pressure was first noticed between 70 and 80°. Evacuated at 90°, 4.9 mg. of water was obtained, while the 3.211 cc. of adsorbed oxygen is equivalent to 5.1 mg. of water. The catalyst was then evacuated at 400° and the surface so produced about half saturated with oxygen at 0°. Although hydrogen admitted to this surface gave a somewhat higher thermal effect, yet it is probable that little water synthesis was involved. Heating in hydrogen as before indicated that reduction of adsorbed oxygen was occurring well below 60° and was complete at this temperature. Between 60 and 90° hydrogen produced no further effect. Evacuation at 90° gave 9.5 mg. of water whereas the 6.331 cc. of oxygen adsorbed is equivalent to 10.2 mg. of water. The catalyst was again evacuated at 400° and the surface so produced completely saturated at 0° with oxygen, unadsorbed oxygen removed, and hydrogen admitted. The much larger heat of hydrogen adsorption, 66,728 cal., and the definitely greater heat of oxygen adsorption on this surface strongly suggest that it was able to catalyze water formation at 0°. Upon standing overnight at 0°, all but 0.02 cc. of the gas disappeared and when this was removed the system showed no pressure in the manometer. No water could be desorbed by evacuation at 0°. Evacuation at 90, 150, 200 and 300° desorbed 0.5, 1.0, 1.7 and 2.8 mg. of water, respectively, or a total of 6 mg. The total amount of hydrogen which disappeared is equivalent to 5.5 mg. of water. The fourth surface was obtained by a final evacuation at 400° and it showed a quite similar behavior.

These experiments show definitely that oxygen adsorbed at 0° upon a nickel surface, which has been formed by heating relatively large amounts of oxygen previously adsorbed at 0°, *e. g.*, the treatments of No. 12 recorded in Table II, is still activated. That such surfaces should possess catalytic activity is not surprising when the magnitudes of their heats of the oxygen adsorption are considered. In the first two experiments the agreement between the amounts of water desorbed and the amounts of oxygen just previously adsorbed indicates that it is only this oxygen which is catalytically active. The large amounts of oxygen previously adsorbed but transformed by heating take no part in the reaction even at 90°. The increased heat of oxygen adsorption observed in the third experiment indicates that some reduction of nickel oxide by adsorbed hydrogen probably occurred during the evacuation between 90 and 400°. That the more active surfaces are able to catalyze the combination of hydrogen and adsorbed oxygen at 0° is suggested by the magnitudes of the hydrogen thermal effects, which are much too high for the heats of adsorption of this gas on nickel. The

greater difficulty in desorbing water from the last two surfaces also indicates their higher order of activity. Assuming water formation at 0° in the case of the two latter surfaces, heats of adsorption of water of the order of those obtained with platinum black catalysts¹⁰ may be calculated.¹¹

TABLE III
HYDROGEN ADSORPTION ON PREVIOUSLY ADSORBED OXYGEN
Catalyst 12. Weight, 6.982 g.

			Pressure increase, mm.	Volume adsorbed, cc. N. T. P.	Heat evolved, cal.	Heat of adsorption cal./mole
I	Oxygen	1	0.00	3.211	13.010	90,758
	Hydrogen	1	82.70	3.353	3.459	23,112
Adsorbed oxygen removed by reduction, followed by evacuation up to 400°						
II	Oxygen	1	0.00	3.097	12.463	90,142
		2	.00	3.234	12.946	89,671
				6.331	25.409	
	Hydrogen	1	44.50	3.180	3.987	28,085
Adsorbed oxygen removed by reduction, followed by evacuation up to 400°						
III	Oxygen	1	0.00	5.582	23.217	93,167
		2	.00	5.660	23.446	92,796
		3	98.13	2.366	8.196	77,580
				13.608	54.859	
	Hydrogen	1	144.90	1.970	5.869	66,728
Surface evacuated up to 400°						
IV	Oxygen	1	0.00	5.831	23.924	91,896
		2	.00	3.033	12.415	91,688
		3	40.44	4.065	15.472	85,266
				12.929	51.811	
	Hydrogen	1	41.60	1.721	5.239	68,194

D. Work on Copper.—On catalytically active copper oxygen was found to be both rapidly and strongly adsorbed at 0° , and the phenomena were in most respects quite similar to those on the nickel surfaces already studied. Only one marked difference was noted, namely, that the heats of oxygen adsorption on a given surface decreased as the amount of gas adsorbed increased. Therefore, the thermal measurements on copper probably represent more nearly differential heats than is the case with nickel.

¹⁰ G. B. Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, **34**, 799 (1930).

¹¹ Using the value of 57,826 cal. ("International Critical Tables," Vol. V, p. 176) for the heat of formation of water and average values for the heats of oxygen adsorption of 92,981 and 91,792 cal. for the third and fourth surfaces, respectively, values for the heat of adsorption of water of 55,392 and 56,264 cal. are obtained. Such high values may in part explain the difficulty in removing adsorbed water.

The time required to reach thermal equilibrium in the calorimeter after admitting oxygen to a partially saturated surface varied from twenty-five to thirty minutes in the case of copper, whereas fifteen minutes sufficed in the case of nickel. Adsorbed oxygen could not be removed from copper surfaces at temperatures up to 400°. Heat treatments of a catalyst previously saturated with oxygen at 0° resulted in a surface capable of again

TABLE IV
OXYGEN ADSORPTIONS ON COPPER

	Pressure increase, mm.	Volume adsorbed, cc. N. T. P.	Heat evolved, cal.	Heat of adsorption, cal./mole
Catalyst 9. Weight, 14.730 g.				
Original surface				
1	0.00	2.446	8.317	76,164
2	82.94	2.006	5.510	61,527
		4.452	13.827	
Second surface: produced by heating at 170° for three hours				
1	0.00	0.485	1.344	62,100
2	1.16	.453	1.250	61,832
		.938	2.594	
Third surface: produced by heating at 250° for three hours				
1	0.00	0.454	1.403	69,216
2	.00	.470	1.486	70,822
3	.00 ^a	.477
		1.401		
Catalyst 13. Wt. 12.219 g.				
Original surface				
1	0.00	2.025	6.887	76,182
2	5.34	1.776	5.382	67,881
		3.801	12.269	
Second surface: produced by heating at 200° for three hours				
1	0.00 ^b	1.492	4.600	69,061
Third surface: produced by heating at 250° for five hours				
1	0.00	1.520	4.712	69,440
2	18.90	0.958	2.966	69,351
		2.478	7.678	
Fourth surface: produced by heating at 300° for three hours				
1	0.00 ^b	1.548	4.863	70,368
Fifth surface: produced by heating at 400° for three hours				
1	14.90	1.063	3.392	71,478

^a This pressure was obtained only after standing overnight at zero degrees.

^b Pressure diminished slowly but reached zero in about half an hour.

adsorbing oxygen strongly at this temperature. Undoubtedly this is a phenomenon similar to that observed with nickel. Experimental results are given in Tables IV and V. As would be anticipated from the behavior of nickel, the temperature to which an oxygen saturated copper catalyst is heated determines in large part the nature of the new surface formed. Temperatures between 170 and 400° were investigated. Excepting unpromoted copper at 300° and above, it appears that in this temperature range, the higher the temperature employed in heating, the greater the amount of oxygen subsequently adsorbed at 0°. Again excepting original surfaces, the heats of adsorption on the unpromoted catalysts show a marked tendency to increase as the temperature of heating is increased, while the promoted catalysts do not exhibit a definite trend; in fact the initial thermal values remain almost constant on all surfaces of No. 11 after the first.

The copper catalysts were reduced from the oxide at 175°. Catalysts 9 and 13 were of copper alone while 10 and 11 contained 7.5% thoria in each case. If the adsorptive capacities of these preparations are corrected, because of their considerable differences in weight, to the weight of 11, the effect of a promoter in increasing the extent of surface is seen to be very marked. Thus the original surfaces of 10 and 11 would adsorb 13.342

TABLE V
OXYGEN ADSORPTIONS ON PROMOTED COPPER

	Pressure increase, mm.	Promoter, 7.5% thoria Volume adsorbed, cc. N. T. P.	Heat evolved, cal.	Heat of adsorption, cal./mole
Catalyst 10. Weight, 18.149 g.				
Original surface				
1	0.00	4.551	16.844	82,904
2	.00	4.536	15.214	75,130
3	.00	4.478	13.099	65,524
4	75.80	2.356	6.118	58,167
		15.921	51.275	
Second surface: produced by heating at 175° for three hours				
1	0.00	2.498	7.833	70,240
2	.00	2.488	7.366	66,323
3	13.18	2.133	5.275	55,396
		7.119	20.474	
Third surface: produced by heating at 300° for two hours				
1	0.00	2.524	7.676	68,122
2	.00	2.503	7.615	68,148
3	.00	2.514	7.343	65,426
4	22.46	1.861	4.745	57,113
		9.402	27.379	

TABLE V (Concluded)

	Pressure increase, mm.	Promotor, 75% thoria Volume adsorbed, cc. N. T. P.	Heat evolved, cal.	Heat of adsorption, cal./mole
Catalyst 11. Weight, 15.209 g.				
Original surface				
1	0.00	2.482	9.112	82,235
2	.00	2.585	8.814	76,375
3	.00	2.568	8.369	73,000
4	.00	2.559	8.270	72,390
5	.00 ^a	2.520	6.914	61,457
		12.714	41.479	
Second surface: produced by heating at 200° for three hours				
1	0.00	2.466	7.499	68,117
2	.00	2.482	7.501	67,696
3	.00 ^a	2.526	7.257	64,353
		7.474	22.257	
Third surface: produced by heating at 200° for three hours				
1	0.00	2.623	8.064	68,864
2	.00	2.539	7.722	68,128
3	.00 ^a	2.487	6.180	55,662
		7.649	21.966	
Fourth surface: produced by heating at 300° for three hours				
1	0.00	2.603	7.941	68,335
2	.00	2.235	6.795	68,101
3	.00	2.534	7.227	63,881
4	.00 ^b	1.752	4.333	55,400
		9.124	26.296	
Fifth surface: produced by heating at 400° for three hours				
1	0.00	2.740	8.366	68,392
2	.00	2.550	7.800	68,517
3	.00	2.599	7.536	64,950
4	108.20	2.060	5.153	56,032
		9.949	28.855	

^a Pressure diminished slowly but reached zero in half an hour.

^b Pressure reduced to zero by evacuating the catalyst.

and 12.714 cc. of oxygen, respectively, while 9 and 13 would adsorb but 4.597 and 4.731 cc., or approximately a third as much. The first heating has in each case caused a relatively larger decrease in the adsorptive capacity of the unpromoted catalyst, unlike nickel which, however, contained relatively smaller amounts of thoria. The great similarity of the second and third surfaces of 11 indicates that heating at 200° for the three hours is sufficient to maintain the *status quo*, while for promoted nickel a

temperature of 350° is required to do this. Considering the initial values for the heats of adsorption on the original surfaces of these catalysts, namely, 82,904 and 82,235 cal. against 76,164 and 76,182 cal., it is apparent that the promoted catalysts possess original surfaces of definitely higher quality than the unpromoted. After heating, the qualities of all of the surfaces became much more nearly alike.

E. Reaction Velocities.—In an endeavor to obtain information about any relations which might exist between the catalytic activity of a copper surface on the one hand and its capacity for adsorbing oxygen at 0° and the magnitudes of the incident thermal effects on the other, the following experiments were undertaken. As a convenient measure of catalytic activity the well-known ethylene-hydrogen reaction was chosen. Reaction velocity measurements, made by the manometric method, were followed, after thorough evacuation of the surface, by the customary determinations of the heats of oxygen adsorption. Preliminary velocity experiments on No. 10 showed that although a copper surface when saturated at 0° with oxygen possessed a negligibly small catalytic activity at this temperature, if the surface were heated activity returned. When velocity runs were attempted, however, on copper surfaces only partially saturated with oxygen at 0° this oxygen reacted. Ethylene-hydrogen reaction velocity measurements, with alternate oxygen adsorptions and heatings were made, however, on No. 11, a thoria promoted copper, and on No. 13, which was unpromoted. A comparison of reaction velocities with the extents and heats of oxygen adsorption is given in Table VI. The composition of the reaction mixture was always very nearly 1:1. Catalytic activity is taken as proportional to the reciprocal of the half time, and relative activities are calculated by arbitrarily giving the original surface of No. 11 the value of 100. The data in columns 4 and 5 of Table VI are not directly calculable from Tables IV and V because average heats of adsorption have been computed using an extrapolated value for the final thermal effect on a surface.

The experimental results show that whereas the original surface of No. 11 was decreased only about 41% in extent (as measured by the amount of oxygen adsorbed) as a result of heating the oxygen saturated surface at 200° for three hours, its catalytic activity was simultaneously decreased by 80%. The other half of the decrease is probably to be accounted for by the diminished heats of adsorption on the second surface. Relatively small changes in activity were produced by the second and fourth heatings, yet they are accompanied by significant changes in adsorptive capacity and / or heats of adsorption. The very much lower activity observed on the original surface of No. 13 shows thoria to be an effective promoter for copper. While this promoter effect is reflected in the relative extents of the original surfaces of these two catalysts, the average heat of adsorption

on No. 13 appears relatively too high. A comparison of the first thermal value on each original surface in this case seems the more significant. It is hardly to be expected that all of the oxygen adsorbed at 0° will define surface capable of participating in a given surface reaction. Only a certain fraction of the surface so defined will be involved in any particular reaction, and this fraction may well vary with the temperature, pressure and concentrations existing in the reaction system, also perhaps with the chemical composition of the catalyst surface. Pertinent thermal data should be calculated only from adsorption occurring on that fraction of the surface which is really active in catalysis. Thus while the data presented in Table VI indicate that relations exist between the behavior of a copper catalyst toward oxygen and the catalytic activity of the metal, these data are inadequate to define such relations quantitatively. It is considered, however, that they are sufficiently suggestive to justify further experiments with this end in view.

TABLE VI

A COMPARISON OF OXYGEN ADSORPTION CHARACTERISTICS WITH CATALYTIC ACTIVITY

	Surface	Half time, <i>T</i> (min.)	1/ <i>T</i>	Total oxygen adsorption, cc. N. T. P.	Average heat of adsorption, cal./mole	Relative activity
Catalyst 11	Original	3.5	0.284	12.118	75,323	100
	Second	17.4	.058	7.195	67,776	20
	Third	16.0	.063	6.216	68,371	22
	Fifth	15.5	.065	7.530	68,256	23
	Ninth			2.486	55,510	0
Catalyst 13	Original	76.8	.013	3.438	74,874	5
	Second			1.492	69,061	almost 0

Discussion

The experimental work that has so far been carried out seems to substantiate the idea that oxygen is taken up by nickel and copper catalysts with characteristic effects. In the case of both of these surfaces oxygen is rapidly and irreversibly adsorbed at 0°. The relative amounts of oxygen so adsorbed are in line with the known relative activities of these catalysts. Initially nickel adsorbs over four times as much oxygen as an equal weight of copper. Adding thoria as a promoter increases the extent of the surface in the case of nickel more than four times, while the promoted copper shows nearly a three-fold increase. Thus in part the known superior activity of nickel over copper may be explained on the basis of greater surface; also, the function of a promoter in increasing the extent of surface is very clearly brought out.

The heats of oxygen adsorption on the surfaces studied also afford further insight into the relative activities of the catalysts. Thus the highest heats of oxygen adsorption occur on nickel surfaces while copper surfaces, as might be expected, show considerably lower thermal effects. The pres-

ence of thoria as a promoter causes a very definite increase in the heats of oxygen adsorption only on original catalyst surfaces. Regenerated unpromoted copper surfaces show somewhat higher thermal effects than similar regenerated promoted surfaces. In the case of nickel the initial thermal values on the original surface and all of the thermal values on the second surface of No. 8, the unpromoted catalyst, are higher than those on the corresponding promoted surfaces of No. 12. Such phenomena, together with the observed relative constancy of the heats of oxygen adsorption on a given nickel surface and the rapid decrease in these heats, with surface covered, on copper catalysts may be clues to the well-known specificity of catalysts. A maximum in heat of adsorption values has already been observed with very active nickel and hydrogen,¹² yet it is of interest that an irreversibly adsorbed gas like oxygen also shows it. In general, the magnitudes of the heats of oxygen adsorption are in the range of those found for platinum black catalysts.¹³ On the basis of thermal effects alone the catalysts could be rated in the order of decreasing activity as nickel, platinum, copper, the order of their known activities for hydrogenations.

For all the catalysts studied, heating a surface which had been saturated with oxygen at 0°, in a suitable temperature range, caused a fresh unsaturation of surface to develop. It is well known that active nickel and copper surfaces are far from uniform and often highly non-uniform in character. Such surfaces are considered to possess areas of various degrees of unsaturation or catalytic activity (these two terms often, although not always, parallel each other). When oxygen comes into contact with an active surface at 0° it will first be adsorbed and then where the surface is sufficiently active may further react to form oxide at this temperature. On less active surface adsorbed oxygen may change to oxide only upon being heated in a suitable temperature range. Evidence that some oxide formation takes place on the original surfaces of the promoted catalysts at 0° is found in the magnitudes of the higher heats of oxygen adsorption there occurring. Thus values for the heat of formation, per mole of oxygen, of NiO range from 115,800 to 103,000 cal. and those for Cu₂O from 87,600 to 79,826 cal. according to different observers.¹⁴

All surfaces after the first, *e. g.*, the regenerated surfaces, are much less extensive, as measured by oxygen adsorption, and are much less active as indicated both by heats of oxygen adsorption and reaction velocity measurements. The heats of adsorption on such surfaces are distinctly less than those required for oxide formation. Evidence that oxygen is *adsorbed*

¹² Fryling, *J. Phys. Chem.*, **30**, 818 (1926).

¹³ G. B. Taylor, Kistiakowsky and Perry, *ibid.*, **34**, 799 (1930).

¹⁴ Landolt-Börnstein-Roth-Scheel, "Tabellen," 5th ed., Vol. II, pp. 1530, 1531; "International Critical Tables," Vol. V, pp. 187, 192.

on these less active surfaces in activated form is found in the low temperatures required for its removal by reduction. Thus oxygen taken up by a nickel catalyst at 0° has been shown definitely to react with hydrogen below 90° and most probably as low as 0° , while large amounts of known oxide simultaneously present were unattacked. Similarly in the case of copper, oxygen adsorbed at 0° was removed at this temperature by hydrogen, while after heating the surface, such oxygen was inert. The minimum temperatures for the reduction of NiO and Cu_2O are stated to be 220 and 155° , respectively.¹⁵ Unless some activated form of oxide is present, therefore, the presence of *adsorbed* oxygen on the less active areas of the catalysts seems entirely probable. When a surface saturated with oxygen at 0° , is heated in a suitable temperature range, the following processes may occur (a) changes in the oxygen content of adsorption complex and oxides, (b) transformation of adsorption complexes to definite oxides, (c) physical changes such as sintering and the development of cracks or porosity in protective oxide films. Each of these processes conceivably may play a part in the regeneration of active surface during heating. Processes (a) and (b) if leading to combinations more rich in oxygen will cause previously covered surface to be exposed. The increased adsorptive capacities which the active surfaces studied have been found to exhibit toward oxygen at temperatures above 0° lend support to this idea. Evidence for process (b) has already been given, namely, that oxygen taken up at 0° is activated but becomes inactive after heating. Further evidence for this process is forthcoming if its mechanism is examined. The transformation of an adsorption complex to a fully formed oxide molecule must involve the rupture of metal-metal linkages and, therefore, create a fresh unsaturation of the metal surface. Such a surface will be in effect promoted by interspersed groups of oxide molecules. Furthermore, oxygen adsorbed on the more unsaturated metal surface should create a relatively less unsaturated surface upon heating than oxygen, initially adsorbed on more saturated surface, which upon heating to a sufficiently high temperature forms oxide only by the breaking of a greater number of metal-metal bonds. Therefore, it would be expected that within limits, the higher the temperature to which a given surface carrying adsorbed oxygen is heated, the greater the extent and the degree of unsaturation of the resultant surface. In spite of adverse sintering effects, it is experimentally found that with both nickel and copper increasing the temperature of heating has caused an increase in the extent of surface which is usually accompanied by a definite although sometimes small increase in the heats of adsorption. Furthermore, the large decrease in quantity and quality which a catalyst surface suffers as a result of the first oxygen adsorption and subsequent heat treatment is probably due to the relatively high degree

¹⁵ Wright and Luff, *J. Chem. Soc.*, **33**, 540, 26 (1878).

of unsaturation of this surface and the consequent large amount of oxygen taken up as oxide at 0° . By process (c) fresh surface will be opened up if coherent oxide films are formed, but their extensive formation on highly non-uniform surfaces does not seem extremely probable. Process (b), which may be aided by (a), is therefore considered largely responsible for the regeneration of surface. Accordingly, it seems necessary to postulate that in the range of surface which takes up and holds oxygen strongly at 0° , there are combinations between the surface and oxygen varying from metal oxide on the most active areas to strongly *adsorbed* oxygen on the relatively less active portions.

While the alternate reaction velocity and heat of oxygen adsorption measurements are here confined to copper and a single reaction, it is not believed that the behavior found is limited to this particular combination. Further work is, therefore, being undertaken under different conditions, with other catalysts, and with other reactions in the hope of developing more completely the indicated relations and of obtaining a better insight into the mechanism of the regeneration of oxygen poisoned surfaces.

Summary

1. The adsorption of oxygen at 0° on catalytically active nickel and copper surfaces has been studied. Relatively large amounts of this gas are rapidly and irreversibly taken up with a considerable evolution of heat. Molar heats of oxygen adsorption of the order of 98,000 cal. and higher, and 82,000 cal., have been obtained for promoted nickel and promoted copper, respectively.

2. A catalytically active surface, capable of again adsorbing relatively large amounts of oxygen at 0° with only moderately reduced thermal effects, is obtained simply by heating in a suitable temperature range a surface previously poisoned by saturation with oxygen at 0° . Evidence is advanced indicating that heating causes a change of *adsorbed* oxygen to stable oxide.

3. The amounts of oxygen taken up and the magnitudes of the heats of oxygen adsorption classify nickel and copper both promoted and unpromoted in their proper relative positions as catalysts. Additional light is thrown upon the function of a promoter of the irreducible oxide type.

4. Evaluation of the activity of copper catalysts on the one hand by reaction velocity measurements, and on the other by heats of oxygen adsorption and oxygen adsorbing capacity, indicates that definite relations exist between these properties.