Exchange Reactions of Solid Oxides. Part VI. The Reactions of Carbon Monoxide, Carbon Dioxide, and Oxygen on Cuprous Oxide, Nickel Oxide, and Chromium Oxide.*

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The reaction $2CO + O_2 \longrightarrow 2CO_2$ has been studied by using mainly the stoicheiometric mixture of reactants, on NiO, Cr_2O_3, and Cu_2O at pressures of 1—9 cm. and temperatures from 10° to 155°. On the first two oxides the reaction proceeds with an apparent E of 5·5 kcal. mole^{-1} and zero respectively, following the rate law $dP_{CO_2}/dt = kP_{CO}/(P_{CO} + P_{CO_2})$. By using ^{18}O it has been shown that the reaction probably proceeds on only a small fraction (<2·5%) of the surface oxygen sites by an extraction reaction, the carbon monoxide removing a surface oxygen ion which is rapidly replaced by oxygen from the gas phase: evidence is reviewed which suggests that on these two oxides the rate-determining step is the latter, namely, $O_2(\text{gas}) + (e_2/\square^-{}_s)$ † $\longrightarrow O^{2-}{}_{(s)} + O_{ads}$. The oxygen exchange of these three gases with the surface oxygen ions is negligible at temperatures of interest in the oxidation studies.

The oxidation reaction on Cu_2O (formed on precipitated copper powder) probably proceeds by the same mechanism. Here ready exchange of oxygen occurs between the two oxides of carbon and the surface oxygen ions of the catalyst. The oxidation reaction on Cu_2O has an apparent E of 10 ± 2, and the exchange reactions with carbon monoxide and dioxide have E about 10 and 4 kcal. mole^{-1} respectively. The oxidation proceeds on 10—40% of the surface sites, the proportion increasing with rising reaction temperature. By using both ^{13}C and ^{18}O it has been shown that no exchange of carbon occurs between carbon monoxide and carbon dioxide on the catalyst surface.

GARNER and his co-workers (*Proc. Roy. Soc.*, 1949, *A*, **197**, 294; 1952, *A*, **211**, 472; *Discuss. Faraday Soc.*, 1950, **8**, 246) have recently investigated extensively the interactions of various gases (especially oxygen, carbon monoxide, and carbon dioxide) with cuprous oxide and cupric oxide. The techniques used included measurement of heats and rates of adsorption and of semiconductivity, upon oxide films and granular oxide prepared by oxidation of the metal. It appears that this work was necessarily performed at gas pressures of less than 3 mm., and mostly less than 0·1 mm., pressures which are often of little practical interest in the study and application of heterogeneous catalysis. In addition, although new and valuable data have been obtained which have led to significant theoretical advances, the details of the interactions are not established: similar remarks apply to the interactions of the same three gases on nickel oxide, which have been studied recently in a similar fashion by Dell and Stone (*Trans. Faraday Soc.*, 1954, **50**, 501) and from a kinetic viewpoint at higher pressures by Parravano (*J. Amer. Chem. Soc.*, 1953, **75**, 1448).

In an attempt to clarify the position and to provide further information, these systems have been examined with ^{18}O and ^{13}C as tracers: also the catalysed oxidation, $2CO + O_2 \longrightarrow 2CO_2$, has been studied on the two oxides, the mass spectrometer being used to follow the course of the reaction. A similar investigation, with chromium oxide as catalyst, is also reported here. Pressures of 1—9 cm. were used.

EXPERIMENTAL

Materials.—Cuprous oxide was prepared by controlled oxidation of pure copper (Winter, *J.*, 1954, 3342), nickel oxide by heating "AnalaR" nickel carbonate in air at 870° for 24 hr., and chromium oxide by controlled decomposition of "AnalaR" chromic oxide (Bevan, Shelton, and Anderson, *J.*, 1948, 1729).

Oxygen containing 30% of ^{18}O was obtained by thermal diffusion (Winter, *loc. cit.*). Carbon monoxide containing *ca.* 60% of ^{13}C was obtained from A.E.R.E., Harwell. Normal carbon

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* Part V, *J.*, 1954, 1522. † For symbolism, see p. 2734.

monoxide was made by the action of concentrated sulphuric acid on 98% "AnalaR" formic acid; both liquids were thoroughly outgassed before reaction and the product was repeatedly fractionated *in vacuo* until mass spectrometric examination of the final material revealed no detectable impurity at mass 44 or 32. Carbon dioxide containing *ca.* 60% of ^{13}C was made by oxidising ^{13}CO with a slight excess of normal oxygen on a heated platinum filament and fractionating the product *in vacuo.* Normal carbon dioxide was prepared by fractionating the commercial solid *in vacuo.*

Method.—The reactions were followed by the technique employed for studying the isotopic exchange reactions of solid oxides (Winter, *J.*, 1950, 1170): *i.e.*, the oxide, suitably pre-treated (see below), was confined in a Pyrex or Hysil reaction vessel provided with a small leak to the ionisation chamber of the mass spectrometer; on admission of the reactant gas the relevant mass peaks were continuously monitored. Thus the reaction system was essentially static, but no evidence was found that gas-phase diffusion was a rate-limiting factor (cf. Houghton and Winter, *J.*, 1954, 1509). The volume of the reaction system varied between 30 and 80 ml. The mass spectrometer and auxiliary apparatus have been briefly described by Winter (*J.*, 1954, 1522). For work on Cu–Cu_2O two samples, A and B, each of 4 g., were used, the oxide film being first formed to a depth of *ca.* 50 Å with normal oxygen, with four cycles of alternate oxidation and reduction (cf. Garner, Gray, and Stone, *Proc. Roy. Soc.*, 1949, *A*, **197**, 294); at the end of the work the B.E.T. surface areas of the samples, determined with nitrogen at $-193°$, were 2·21 and 0·62 m.^{2} g.$^{-1}$ respectively, an area of 16·2 Å^2 being used for the nitrogen molecule. The experiments were performed in groups, in roughly the order given below, with after-treatment with enriched oxygen as noted: no particular precautions were taken to exclude grease or mercury vapour from the catalyst. Similar remarks apply to NiO, the same 1 g. sample being used for all the work, except in the experiments on $Ni^{18}O$: the B.E.T. (N_2) surface area was 5·48 m.^{2} g.$^{-1}$. For Cr_2O_3 the B.E.T. (N_2) area was 14·2 m.^{2} g.$^{-1}$; the same 1 g. sample was used throughout the work.

Cuprous Oxide—Sample A. (*a*) Exchange reactions of carbon dioxide. The oxide was held at 38° in the presence of 1 cm. of a 1 : 1 mixture of normal oxygen and oxygen containing 30% of ^{18}O, and 1·7 cm. of normal carbon dioxide was then added to the system. In 26 min. the ^{18}O content of the carbon dioxide had risen smoothly to 1·65% but there was no change in the 32 : 34 : 36 mass ratios of the oxygen present. The temperature was rapidly raised to 61°; the rate of exchange of the carbon dioxide increased but again no change occurred in the oxygen mass ratios, although now oxygen was being lost from the gas phase, doubtless owing to oxidation of the underlying copper: the rate of oxygen loss was negligible at 38°. A material balance showed that at 61° the amount of ^{18}O gained by the carbon dioxide was approximately equal to the amount transferred to the oxide surface by oxidation during the experiment.

The exchange of carbon dioxide with an oxygenated surface was then followed at three temperatures, at a pressure of 3·8 cm. The gas was pumped out after each run, *ca.* 3 cm. of 15% ^{18}O were admitted at the reaction temperature, and the whole was left for 30 min.; the oxygen was removed by a Töpler pump and finally the oxide was treated at 76° overnight with 2 mm. of oxygen containing 15% of ^{18}O. In the morning the pressure in the reaction vessel was apparently $\leqslant 10^{-1}$ mm.; vigorous pumping was applied for 10 min. and the vessel cooled, with continued pumping, to the reaction temperature: pumping was continued for at least 1 hr. in each case. The carbon dioxide was then added and the 44/46 peaks were monitored until equilibrium was reached: the equilibrium ^{18}O content was about 1%. These three runs gave good first-order plots. On the assumption that the pre-treatment with enriched oxygen gave a surface containing 15% of ^{18}O in each case, the values of k_0 * and n_s * were calculated, the volume of gas used being known: a plot of log k_0n_s *versus* $10^5/T$ gives an apparent activation energy of $4·7 \pm 1·0$ kcal. mole^{-1}. The results are given in Table 1; the pressure-dependence was not investigated.

It might be argued that the observed exchange is due to reaction with adsorbed oxygen atoms or molecules not removed by reaction with the underlying metal overnight or by the subsequent pumping. To test this, at the conclusion of all the work below on Cu–Cu_2O the above experiment was repeated at 38° with, however, a pre-treatment temperature of 155° (at which the 2 mm. of enriched oxygen was removed from the gas phase in less than 2 min.): no free oxygen should be present the next morning under these conditions, but essentially the same kinetics were observed as before.

(*b*) Exchange reactions of carbon monoxide. The exchange of ^{18}O between the oxygenated

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* The symbols are those used earlier in this series (cf. Houghton and Winter, *loc. cit.*).

surface and 6 cm. of normal carbon monoxide was followed similarly, by using the same procedure to regenerate the ^{18}O content of the oxide surface between each kinetic run. The results are summarised in Table 1; good first-order plots were obtained: the values of log k_0n_s yield $E = 11{\cdot}5 \pm 2{\cdot}0$ kcal. mole^{-1}. As with carbon dioxide, a later run at 38° in which the pre-treatment with ^{18}O was carried out at 155° gave essentially the same rates as those shown in Table 1.

TABLE 1.

Exchange with	$10^5/T$	$10^{-18}n_s$ *	$\log_{10} k_0n_s$	Exchange with	$10^5/T$	$10^{-18}n_s$ *	$\log_{10} k_0n_s$
	Sample A				*Sample B*		
CO_2 at 3·8 cm.	272·5	3·04	17·655	CO_2 at 4·2 cm. ...	329·0	1·96	17·159
	295·9	2·40	17·390		329·0	2·05	17·149
	311·5	1·97	17·250		351·0	1·36	17·018
CO at 6 cm.	295·9	3·78	17·558		351·0	1·25	17·000
	312·5	2·48	17·114	CO at 5·7 cm.	300·3	1·50	17·620
	341·4	1·68	16·437		304·2	1·44	17·600
					317·4	1·30	17·485
					329·0	0·95	17·150
					343·6	0·89	17·060

* n_s = atoms g.$^{-1}$.

While the exchange with carbon monoxide was being investigated, the rate of production of carbon dioxide was measured by observing the rate of increase of the peak at mass 44. Two experiments are shown in Fig. 1, and the initial rates of formation of carbon dioxide give $E \approx 14$ kcal. mole^{-1}. The rate of formation of carbon dioxide on admission of oxygen to the freshly-evacuated surface within 3 min. of the completion of an exchange reaction was measured in two cases: these experiments are also shown in Fig. 1 and yield $E \approx 17$ kcal. mole^{-1} from the initial rates of reaction. It appears from the above experiments that the rate of formation of carbon dioxide by reaction between the oxygenated surface and adsorbed monoxide is slow; thus a pressure of less than 1/30 mm. is produced (in the presence of ~6 cm. of carbon monoxide) at 47° in 40 min.; nevertheless it might be argued that the observed exchange is due, not to a direct exchange of oxygen of the carbon monoxide with surface oxygen, but to exchange of oxygen between $CO_{(ads)}$ and $CO_{2(ads)}$, only the latter species being exchanged directly with surface oxygen. To test this a mixture of 6·5 cm. of normal carbon monoxide and 1·3 cm. of carbon dioxide containing *ca.* 60% of ^{13}C and *ca.* 3% of ^{18}O was introduced into the reaction vessel, the catalyst having been previously exposed to *ca.* 15% of ^{18}O as usual. Both the gases picked up ^{18}O slowly from the surface, but no ^{13}C appeared in the carbon monoxide: this experiment was performed at 18°, 47°, and 68°, and the observations in each case were continued for an hour. It should be noted that introduction of $^{13}CO_2$ into the mass spectrometer produced an *immediate* significant increase in the mass 28 and 29 tube residuals, and a change in their ratio:

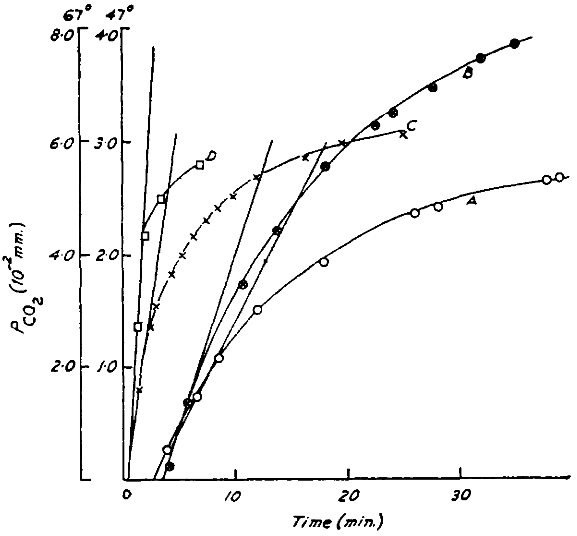


FIG. 1. *Formation of carbon dioxide from carbon monoxide on* Cu_2O *during the exchange reaction at* P_{CO} *6·0 cm. and* (*A*) *47°,* (*B*) *67°. Also formation of carbon dioxide from* $(CO)_{ads}$ *on admission of oxygen to catalyst at* P_{O_2} *2·0 cm. and* (*C*) *46°,* (*D*) *67°.*

this effect became steady in 1—2 min. and is ascribed to CO^+ fragments produced from the carbon dioxide under the relatively high electron-accelerating potential used in the mass spectrometer ion source between filament and trap. (CO^+ is produced from CO_2 by electron bombardment with an accelerating potential of about 20·4 v, according to Stueckelberg and Smyth, *Phys. Rev.*, 1930, **36**, 472; see also Kallmann and Rozen, *Z. Physik*, 1929, **58**, 52; 1930, **61**, 61; Morrison, *J. Chem. Phys.*, 1954, **22**, 1219.) This effect was allowed for in interpreting these three

FIG. 2. *Reaction,* $2CO + O_2 \longrightarrow 2CO_2$, *on* Cu_2O (*stoicheiometric mixture*). *A,* P_T 3·1 *cm.,* 86°; *B,* P_T 2·5 *cm.,* 66°; *C,* P_T 3·3 *cm.,* 48°.

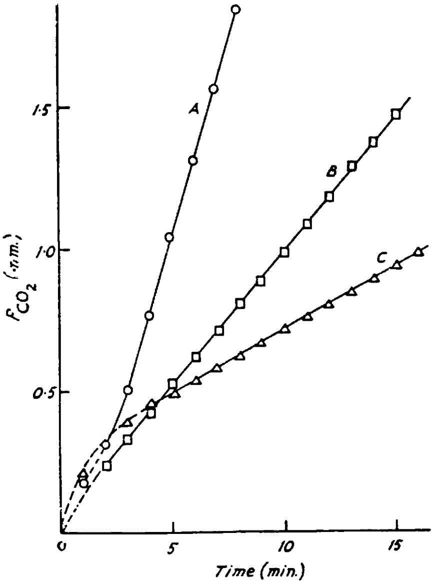
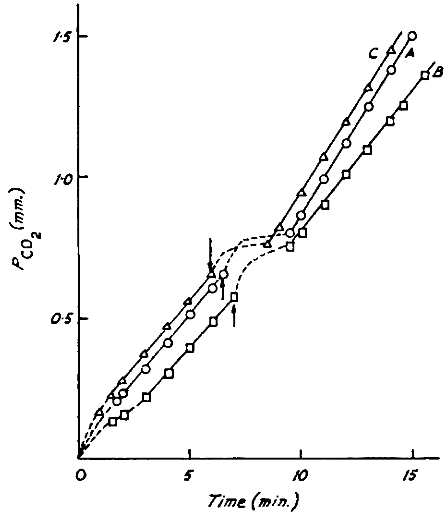
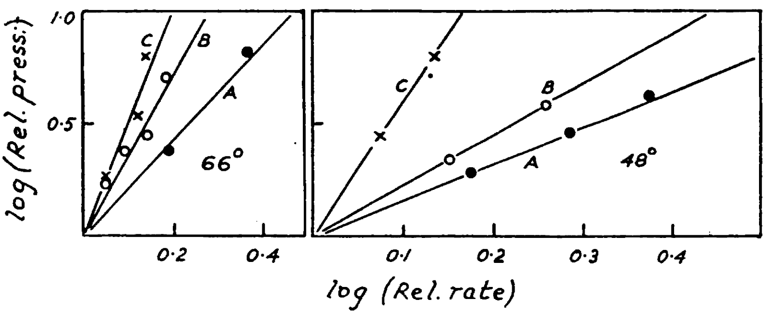


FIG. 3. *Reaction,* $2CO + O_2 \longrightarrow 2CO_2$, *on* Cu_2O; *initially the stoicheiometric mixture; addition of oxygen or carbon dioxide after* 6—7 *minutes, as indicated by arrows.*



Curve	Initial P_T (cm.)	Final P_{O_2} (cm.)	P_{CO} (cm.)
A	2·5	0·83	4·57
B	3·1	1·8	2·1
C	3·3	6·9	2·2

FIG. 4. *Reaction on* Cu_2O *at* 48° *and* 66°.



A, P_T; *B,* P_{CO}; *C,* P_{O_2}.

experiments; the main proof that no reversible formation of ^{13}CO occurred was that after the first 1—2 min. the 28 : 29 ratio remained constant for the remainder of the experiment at a value corresponding to only some 3% of ^{13}C while the 44 : 45 ratio was constant throughout. A more direct proof would be to isolate the carbon monoxide and analyse it separately.

(*c*) The oxidation of carbon monoxide by oxygen. A study was made of the reaction $2CO + O_2 \longrightarrow 2CO_2$, catalysed by the Cu–$Cu_2O$ surface, by following the rate of appearance of mass 44 in the sample bled into the mass spectrometer. The reaction was carried out under static conditions in the same apparatus, and in general the stoicheiometric mixture of reactants was used but in some reactions, once a steady state had been reached, more of one of the reactants was injected into the system and the new steady state determined. In general the value of dP/dt (where P = pressure of carbon dioxide in the system) became constant in the first 2—4 min. and remained so for at least a further 10 min. : this steady value was used in calculating the rate constant. Normally only the initial stages of the reaction were followed, *i.e.*, the first 10—15 min. of the reaction, or the corresponding time after the change of gas composition by injection of more of one of the reactants. Some typical experiments are shown in Figs. 2 and 3, and the results are summarised in Figs. 4 and 5. It is seen from Fig. 5 that the surface gradually became more reactive with use, the rate nearly doubling, at any given temperature, during 20 experiments, while the apparent activation energy fell from 11·5 to ~9·0 kcal. mole^{-1}. We shall assume in the Discussion that $E = 10 \pm 2·0$ kcal. mole^{-1}. The mass spectrometer ion source and the reaction system leak were calibrated at intervals through the work with known pressures of carbon dioxide so that the peak heights could be converted into gas pressures in the reaction vessel. Normally observations of the kinetics were not extended beyond a carbon dioxide pressure of 1·5—2·0 mm., *i.e.*, at most 20% (usually 10%) of the reaction. It was found that the mass spectrometer sensitivity, defined for the present purpose as (mass 44 peak height)/(pressure of CO_2 in reaction system), remained reasonably constant (with fixed electron- and ion-accelerating potentials) and independent of moderate changes in the pressures of the two reactants during the whole of this work. It was, however, noted that at one period, for some days, the admission of oxygen to the mass spectrometer caused an appreciable rise in the mass 44 tube blank : this produced an anomalous rapid rise of the mass 44 peak at the beginning of a reaction but did not alter the steady-state value of dP_{CO_2}/dt. This phenomenon was not studied in detail : it was doubtless caused by some temporary contamination, with carbonaceous material, of the filament region of the mass spectrometer.

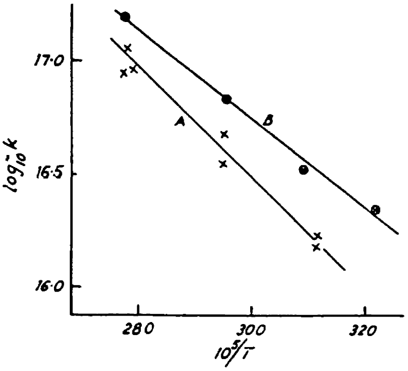


Fig. 5. *Reaction on* Cu_2O ($P_T \approx 3·0$ *cm.*).
A, Early experiments.
B, Experiments after 20 more runs.

After each run the catalyst was heated to 96—100°, and evacuated overnight, then isolated and cooled to the reaction temperature. This procedure was adopted after it had been noted on several occasions that if, after a run, the catalyst was pumped at the reactant temperature for *ca.* 5 min. and a fresh run then started at once at the same temperature but with a gas mixture of different composition, the first 5 min. or so yielded a pseudo-steady state which was the same as that attained towards the end of the previous experiment (cf. also Fig. 3) : this false rate slowly changed to that characteristic of the new conditions : pumping between runs at the reaction temperature for 1—2 hr. yielded intermediate rates.

The initial stages of the desorption from the catalyst into a high vacuum after a kinetic experiment (run to ~20% completion) with the stoicheiometric gas mixture was examined qualitatively at each temperature. The reaction vessel was rapidly evacuated to *ca.* 10^{-3} mm., through the auxiliary vacuum line, and the gas then being evolved from the catalyst was diverted *directly* into the mass spectrometer ion source by means of a tap by-passing the leak. The mass spectrometer showed a small transitory peak at mass 32 which very rapidly dropped to zero (*i.e.*, to the level of the tube residual) but peaks at mass 44 and 28 remained more or less steady at high values for many minutes at all temperatures. The peak at mass 28 was too large to have been caused solely by CO^+ fragments formed from the carbon dioxide molecules in the ionisation process; this was confirmed by following the desorption of masses 28 and 30 after 30% ^{18}O had reacted with normal carbon monoxide.

The effect of pre-treating the surface was studied at 50° : the catalyst was outgassed overnight at 96—100°, isolated, cooled to 50°, exposed to 1 cm. of carbon dioxide for 15 min., and pumped hard for 5 min.; the reaction mixture (3·0 cm.) was then added and the production of carbon dioxide followed as usual. Similar experiments were performed in which pre-treatment was with carbon monoxide and oxygen. Pre-treatments with carbon monoxide and carbon dioxide caused no change in the velocity of the subsequent oxidation reaction, but treatment with oxygen caused the rate during the first 4 min. to be about 3 times that on the untreated catalyst. The run with oxygen pre-treatment showed marked curvature of the P_{CO_2}–time plot after the eighth minute, probably because of exhaustion of the reaction mixture, since the reaction was by then more than 30% complete.

(*d*) The oxidation reaction on an ^{18}O-enriched surface. After the above work the sample was outgassed at 155° for 3 hr. and *ca.* 0·64 ml. (N.T.P.) of 30% ^{18}O added : this was apparently all taken up in less than 2 min. The catalyst was left isolated at 155° overnight to ensure so far as possible the complete utilisation of the oxygen and cooled to 48°. The oxidation reaction was then carried out, at an initial pressure of 2·7 cm. of the stoicheiometric mixture made from isotopically normal gases; and the mass 44, 46, 28, and 30 peaks were monitored. A similar experiment was performed in which the reaction was carried out at 155° with 2·2 cm. of the normal reaction mixture; the two runs are summarised in Fig. 6.

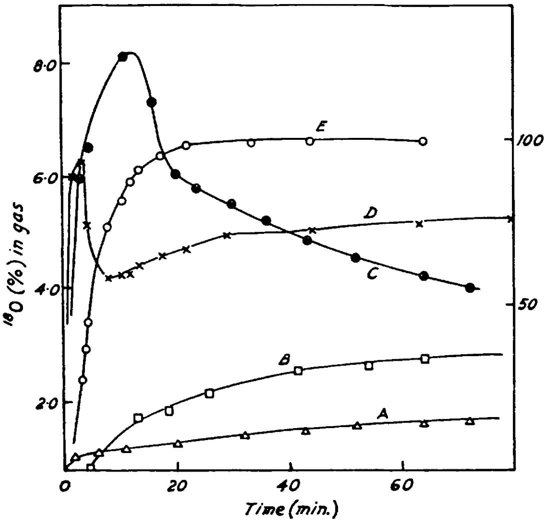


FIG. 6. *Reaction on* $Cu_2{}^{18}O$.
Extent of reaction (right-hand scale), *A* at 48°, and *E* at 155°.
^{18}O content of CO (left-hand scale), *B* at 48°.
^{18}O content of CO_2 (left-hand scale), *C* at 48°, and *D* at 155°.

Sample B. After the above work sample A was accidentally spoilt. It appeared from discussions with Dr. F. S. Stone that there was some risk of the observations' being influenced by the presence on the surface of active adsorbed oxygen (cf. Garner, Gray, and Stone, *loc. cit.*) owing to the relatively low temperatures at which the oxide was outgassed and treated with ^{18}O between experiments. The more important parts of the ^{18}O work were therefore repeated, with a higher outgassing temperature, on a fresh catalyst prepared from the same bulk batch of metallic copper.

(*a*) Exchange reaction of carbon dioxide. The fresh catalyst (previously oxidised to a depth of *ca.* 50 Å with normal oxygen, following several cycles of alternate oxidation and reduction as for sample A) was outgassed at 200° for 24 hr., isolated, and treated with *ca.* 1·5 ml. (N.T.P.) of oxygen containing 30% of ^{18}O. After 24 hr. the system was evacuated for 5 min., isolated, and cooled to room temperature during 24 hr. : this procedure of outgassing, ^{18}O treatment, etc., at 200° was carried out between each run.

The exchange reaction was followed at a pressure of *ca.* 4·2 cm. of normal carbon dioxide in the reaction vessel; the first two runs on the new catalyst were anomalously fast, but subsequent experiments were reproducible and are summarised in Table 1; good first-order plots were obtained. Values of k_0 and n_s were calculated by assuming that the surface oxygen ions contained 30% ^{18}O; a plot of log k_0n_s yields $E = 3{\cdot}0$ kcal. mole^{-1}.

(*b*) Exchange reaction of carbon monoxide. This was studied in the same way with the same pre-treatment procedure; pressures of 5·5—6·0 cm. of normal carbon monoxide were employed. The results are given in Table 1 and yield $E \approx 9{\cdot}0 \pm 2$ kcal. mole^{-1}. During these experiments the rate of formation of carbon dioxide in the reaction system was followed by noting the height of the mass 44 peak from time to time. At temperatures between 12° and 20° the rate was negligible, but at 41° and at 60° it was several times that found on catalyst A : these two runs gave linear plots of P_{CO_2} *versus* time, from the slopes of which an apparent activation energy of 21 kcal. mole^{-1} was obtained.

The effect of active adsorbed oxygen was demonstrated by an experiment in which the catalyst, after being outgassed at 200°, was cooled to 76° and then treated with *ca.* 1·2 ml. (N.T.P.) of 30% ^{18}O and left at 76° for 22 hr.; then the system was evacuated for a short time and the catalyst isolated and cooled to 31° during 24 hr. An exchange reaction with normal carbon monoxide at 5·6 cm. was then performed and at the same time the production of carbon dioxide was followed : the system (reaction volume *ca.* 45 ml.) yielded *ca.* 0·85 cm. pressure of carbon dioxide in 41 min.—a much higher rate of production than was found at 60° on the catalyst treated with oxygen at 200°. This exchange reaction had a k_0n_s about 25% and n_s about twice as great as those for the corresponding reaction on the catalyst treated at 200°.

The influence was studied of pre-adsorbed carbon dioxide on the exchange reaction between the surface and carbon monoxide. After the normal outgassing and ^{18}O treatment at 200° the catalyst was cooled to 31° during 24 hr. and then exposed to 0·8 cm. of normal carbon dioxide for 55 min. : the ^{18}O content of the carbon dioxide at this point was noted. The system was evacuated for 1 min., 5·5 cm. of normal carbon monoxide were admitted, and the exchange reaction followed. The value of k_0n_s found was about 25% of that for the reaction on the clean surface, although n_s was about normal : in the calculations it was assumed that the ^{18}O removed by the carbon dioxide had come uniformly from the cuprous oxide surface, *i.e.*, that the surface oxygen ions were equally accessible to both gases; but if the amount of ^{18}O lost to the carbon dioxide is ignored the above statements regarding k_0n_s and n_s still hold. During the exchange reaction relatively large amounts of carbon dioxide were slowly evolved from the catalyst.

(*c*) The oxidation reaction on an ^{18}O-enriched surface. The catalyst was subjected to the standard outgassing and ^{18}O treatment at 200° and cooled to 15°. The isotopically normal stoicheiometric reaction mixture (2·0 cm.) of oxygen and carbon monoxide was added and the ^{18}O content of the carbon dioxide formed monitored; at the same time a record was taken of the ^{18}O content of the two reactant gases. No ^{18}O was taken up by the oxygen, but the ^{18}O contents of the other two gases changed with time in the same manner as in the two experiments on catalyst A (cf. Fig. 6); at this lower temperature the whole process was slower, and indeed the oxidation reaction appeared almost to stop, being some 50% completed in 1½ hr. and only about 70% completed in 4 hr.

At the end of this series of experiments the B.E.T. (N_2) surface area of the catalyst was found to be 0·62 m.^{2} g.$^{-1}$, approximately 25% of that found for catalyst A. This lower value may well be due to the frequent treatment at 200°, but it is nevertheless interesting that k_0 and n_s for both catalysts were similar (cf. Table 1).

TABLE 2. *Reaction* $2CO + O_2 \longrightarrow 2CO_2$ *on* NiO.

$10^5/T$	$\log_{10} k$	P_T *	$10^5/T$	$\log_{10} k$	P_T *	$10^5/T$	P_{O_2}	P_{CO}	k ‡
206·6	1·87 †	1·5	293·2	0·82	3·2	303·1	6·22	1·78	2·72
212·3	1·76 †	1·4	303·1	0·76	3·4	—	—	—	—
220·8	1·675 †	3·3	310·5	0·765 †	2·0	303·1	1·15	2·25	5·74
235·8	1·62 †	2·0	311·5	0·66	3·0	—	—	—	—
285	0·93	3·3	321·5	0·56	3·2	303·1	2·20	4·40	5·64

* Stoicheiometric mixture. † Reaction on $Ni^{18}O$. ‡ Arbitrary units (multiply by 1·77 × 10^{19} to convert k into mole g.$^{-1}$ min.$^{-1}$). Pressures in cm.

Nickel Oxide.—(a) *Oxidation of carbon monoxide by oxygen.* The reaction was studied in the same way as that on Cu–Cu_2O, with 1 g. of oxide catalyst. The results are summarised in Table 2, and a few typical experiments are plotted in Fig. 7. Values of log k from Table 2 gave a good Arrhenius plot, with E = 5·5 kcal. mole^{-1}. It was found essential to outgas the oxide at 240° for 15 hr. between experiments since, as was proved by direct pumping into the mass spectrometer (cf. above), carbon dioxide was only slowly desorbed from the catalyst and, if not completely removed, acted as a poison.

(b) *Oxidation on an* ^{18}O-*enriched surface.* The oxide was outgassed at 540° for 18 hr., then left for some hours at this temperature in contact with oxygen containing 30% of ^{18}O. The ^{18}O content of the gas was then 5·53% and this figure agreed fairly well with that calculated for complete exchange of the surface oxygen ions of the oxide lattice from data obtained earlier in an examination of the oxygen-exchange reactions of nickel oxide, with oxygen containing only 1·2% of ^{18}O (Winter, unpublished work) and also with that calculated from the B.E.T. (N_2) surface area of the catalyst. The oxide was cooled in contact with the enriched gas and 1-g. lots were outgassed by pumping overnight at 540°, isolated, and cooled to the required temperature; the stoicheiometric reaction mixture prepared from isotopically normal gases was admitted and the course of the reaction followed; at the end of the reaction the ^{18}O content of the carbon dioxide was determined. From this, knowing the exchangeable surface-oxygen content of the oxide from the results of the ^{18}O pre-treatment, and also the final pressure of carbon dioxide produced, it was possible to find the fraction, *x*, of the exchangeable surface-oxygen appearing in the carbon dioxide. These experiments are summarised in Table 3; a pressure of *ca.* 1·3 cm. of the stoicheiometric reaction mixture was used. Insufficient increase in ^{18}O content of the carbon dioxide occurred during the oxidation reaction on $Ni^{18}O$ to make it possible to follow accurately the change of ^{18}O content with time, as was done on $Cu_2{}^{18}O$ (Fig. 6), although it was confirmed that an initial rapid rise took place in ^{18}O content, followed by a slow fall.

TABLE 3. *The oxygen extraction reaction on* $Ni^{18}O$ and $Cr_2{}^{18}O_3$.

	$Ni^{18}O$				$Cr_2{}^{18}O_3$		
$10^5/T$	206·6	235·8	259·7	310·5	233·6	274·7	315·5
$1 + \log_{10} x$	0·53	0·97	1·16	1·35	1·311	1·182	1·311
x	0·34	0·93	1·46	2·28	2·05	1·52	2·05

x = % of surface oxygen taking part in extraction reaction.

After one of the above experiments the 1 g. sample was used as catalyst in ten experiments as recorded in the preceding section (a) at temperatures between 35° and 78°; very small amounts of ^{18}O were picked up by the carbon dioxide in these runs. After the tenth experiment the system was heated to 240° and the carbon dioxide began to take up more ^{18}O—up to 0·4% in 30 min.: the sample was then evacuated and heated, with evacuation, to 525°. After 4 hours' evacuation at this temperature some normal oxygen was added and the uptake of ^{18}O followed. A rapid exchange was observed, the ^{18}O content reaching 1·5% in less than 30 min.

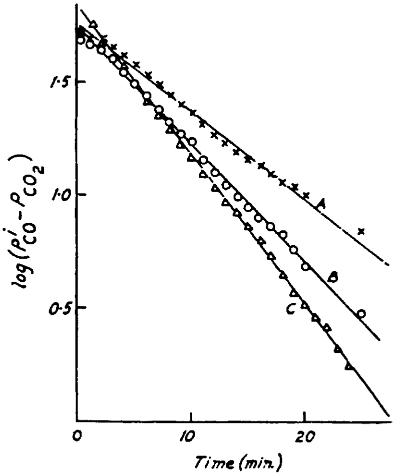


FIG. 7.

(c) *Exchange reactions of carbon dioxide and carbon monoxide.* By using a catalyst surface which had been enriched to ~8% of ^{18}O by exchange with enriched oxygen, it was shown that at temperatures between 30° and 80° the oxygen exchange of these gases with the surface was negligible compared with the rate of oxidation. In another experiment at 57°, with an isotopically normal surface and a reaction mixture prepared from normal carbon monoxide and a 1 : 1 mixture of normal and 30%-^{18}O oxygen, the ^{18}O content of the end product agreed with that calculated from the initial reactants, showing again no appreciable surface exchange (after allowance for the appropriate value of *x*, cf. Table 3); in addition the 32 : 34 : 36 ratios of the reacting oxygen remained constant for at least 75% of the reaction (after this the peak heights became too small for accurate measurement). The latter observation showed that no reversible adsorption of oxygen as atoms occurred during the oxidation reaction.

Chromium Oxide.—(a) *Oxidation of carbon monoxide by oxygen.* When 1 g. of the oxide was used as catalyst, with outgassing at 535° for *ca.* 15 hr. between runs; the results summarised in Table 4 were obtained. They give $E = 0$.

TABLE 4. *Reaction* $2CO + O_2 \longrightarrow 2CO_2$ *on* Cr_2O_3.

$10^5/T$	233·6	257·8	274·7	315·5
$\log_{10} k$ *	1·888	1·861	1·844	1·905
P_T †	3·0	3·0	2·8	3·0

* Arbitrary units (multiply *k* by 8·44 × 10^{16} to convert them into mole g.$^{-1}$ min.$^{-1}$). † Stoicheiometric mixtures. Pressures in cm.

(b) *Oxidation on an ^{18}O-enriched surface.* The oxide was outgassed at 535° for 18 hr. and then left in contact for 24 hr. at this temperature with 30% ^{18}O. The ^{18}O content of the gas was then 8·86% and, as for NiO, this figure agreed with that calculated for complete oxygen exchange of the surface ions. The oxide was outgassed for *ca.* 20 hr. at 535°, isolated, and cooled to the reaction temperature, and the ^{18}O appearing in the carbon dioxide formed during the oxidation reaction followed as before: a pressure of 3 cm. of the stoicheiometric reaction mixture was used. As with the other oxides, the ^{18}O content of the carbon dioxide showed an initial rapid rise, followed by a fall as the reaction proceeded. The value of x, the percentage of the exchangeable surface-oxygen transferred to the carbon dioxide, was found as before from the ^{18}O content of the gas at the end of the reaction. The same 1 g. of oxide was then outgassed at 535° overnight, re-treated with 30% ^{18}O, and outgassed again. The oxidation was studied at other temperatures: values of x so found are given in Table 3.

(c) *Exchange reactions of carbon monoxide and carbon dioxide.* No significant exchange with $Cr_2{}^{18}O_3$ (*ca.* 10% of ^{18}O in surface) occurred with either gas in 1½ hr. at temperatures up to 160° (the highest temperature used in experiments reported in the last section was 155°, where the oxidation required some 20 min. under similar pressure). Finally, the oxide with a surface-^{18}O content of *ca.* 4% was exposed to 3 cm. of normal carbon monoxide, and the temperature was slowly raised. After 2 hr. at 130° there was less than 0·4% of ^{18}O in the gas phase; during the next 35 min. the temperature was increased to 250°, extensive reduction of the oxide occurring; some 20% of the gas was converted into carbon dioxide containing *ca.* 2% of ^{18}O, but the ^{18}O content of the remaining carbon monoxide was only about 0·7%. This experiment may have profoundly altered the catalyst which was therefore abandoned.

(d) *Mobility of surface oxygen ions in chromium oxide at* 535°. The last experiment performed as recorded in the preceding section (b) was at 44°; during this the ^{18}O content of the carbon dioxide formed rose to a maximum of over 2·5% and the final value, when all the carbon monoxide had been oxidised, was 1·47%. The oxide was evacuated for 30 min. and the temperature then rapidly raised, with evacuation, to 535°; occasional checks during this time, by pumping directly into the mass spectrometer, showed that the greater part of the adsorbed carbon dioxide was evolved below 250°. The ^{18}O content of this gas remained below 2%. The oxide was held at 535° while being pumped overnight, isolated, and cooled to room temperature. A further oxidation was then performed at this temperature with the same pressure as before of the stoicheiometric mixture of normal gases; the ^{18}O content of the final carbon dioxide was 1·28%. This procedure was repeated twice more; the product of the last run then contained 0·7% of ^{18}O.

DISCUSSION

(a) *Reactions on Cuprous Oxide.*—Garner, Stone, and others (*Proc. Roy. Soc.*, 1949, *A*, **197**, 294; 1952, *A*, **211**, 472; *Discuss. Faraday Soc.*, 1950, **8**, 246) have provided convincing evidence that, at pressures up to about 1 mm. and at temperatures around 25°, both oxygen and carbon monoxide are very readily chemisorbed, the heat of adsorption being 55 kcal. mole^{-1} for oxygen and 20 kcal. mole^{-1} for carbon monoxide. They concluded that on an oxygenated surface at about room temperature $(CO)_{ads}$ forms a "CO_3 complex," formation of which does not involve lattice oxygen; a similar complex is formed by carbon dioxide on an oxygenated surface with a heat of adsorption of about 20 kcal. mole^{-1}. At the temperatures and pressures used they apparently did not regard the formation of the "CO_3 complex" as reversible with respect to carbon monoxide although they showed that in the presence of excess of carbon monoxide it is decomposed to carbon dioxide. The work reported here, showing the ready exchange of oxygen between surface ions and gaseous carbon monoxide and carbon dioxide, may be interpreted by assuming that a $(CO_3)^{2-}{}_{ads}$ complex involving lattice oxygen is readily formed and decomposed under our conditions of higher pressures and that the observed rates of exchange are controlled by the rates of desorption of the gases, with activation energies roughly equal to the heats of adsorption at high coverage:

$$CO + 2O^{2-}{}_{(s)} \rightleftharpoons (CO_3)^{2-}{}_{ads} + (e_2/\square^-{}_s)$$

$$CO_2 + O^{2-}{}_{(s)} \rightleftharpoons (CO_3)^{2-}{}_{ads}$$

where $(e_2/\square^-{}_s)$ is a surface F′ centre (cf. Rees, "Chemistry of the Defect Solid State," Methuen, 1954, p. 18). This suggestion may be compared with that proposed by Garner

(*J.*, 1947, 1239) for the adsorption of carbon monoxide on oxides of transition elements, where he writes:

$$CO + 2O^{2-} \longrightarrow CO_3^{2-} + 2e$$

or

$$CO + 2O^{2-} + 2M^{2+} \rightleftharpoons CO_3^{2-} + 2M^{+}$$

the two electrons set free being possibly accommodated in the S or D shell of the metal, M.

If we assume that our cuprous oxide surface was energetically very similar to that used by Garner *et al.*, this mechanism requires the heats of adsorption for carbon monoxide and dioxide to decrease at very high coverages to about 10 and 4 kcal. mole^{-1} respectively, these figures being the means of those found by us for the exchange reactions on catalysts A and B; a fall of this magnitude does not appear unreasonable since the coverage of both gases at the pressures used in the heat measurements was certainly less than a half and usually less than one-third of that of oxygen in the same pressure region, and in fact in the case of carbon monoxide Garner, Stone, and Tiley (*Proc. Roy. Soc.*, 1952, *A*, **211**, 472) record a heat of 20·8 kcal. mole^{-1} for 9% coverage, falling to 18·1 at 26% coverage. A linear fall with increasing coverage would, on the basis of these figures, give a value of about 6 kcal. mole^{-1} at saturation. Our experiments, *e.g.*, with ^{13}C, show clearly that, even if the exchange in both cases occurs through the formation of $(CO_3)^{2-}{}_{ads}$, there is not sufficient disproportionation, *i.e.*, formation of carbon dioxide from carbon monoxide, or the reverse, to account for the rates of exchange found; thus we are forced to the conclusion that, although $(CO_3)^{2-}{}_{ads}$ when formed may be essentially the same entity in the two cases, its mode of decomposition is governed by the nature of the gas adsorbed. This is possible since formally the formation of the complex involves four electrons from the surface in the case of carbon monoxide but only two in the case of carbon dioxide: we may regard these as being localised in the immediate vicinity of the complex, possibly as defect structures (F′ centres) of limited mobility in sub-surface layers, as suggested in another connection by Rees (*op. cit.*, p. 125). The amount of charge localised near $(CO_3)^{2-}{}_{ads}$ must determine its mode of decomposition; nevertheless some reduction of the surface does occur, as is shown by the slow formation of gaseous carbon dioxide during the exchange reactions with carbon monoxide (cf. Fig. 1 and similar observations on catalyst B, which should in all cases have been freed from O_{ads} by the treatment at 200°).

Our observations on the oxidation reaction agree in many ways with those of Garner, Stone, and Tiley but exhibit a number of differences. These workers, using a 1 : 1 mixture and a different procedure for attaining a steady surface state, found the rate to be proportional to $P_{O_2}{}^{1\cdot0}$ and to have $E = 11{\cdot}4 \pm 2$ kcal. mole^{-1} between 10° and 36°; they found the reaction course to be represented by $\log P_{(2CO+O_2)} = kt$.

It is probable that our experiments, shown in Fig. 1, in which we followed the initial rate of formation of carbon dioxide on admission of oxygen to a catalyst holding adsorbed carbon monoxide, refer to conditions similar to those in the experiments of Garner *et al.* These workers found under their conditions that θ_{CO} was high and θ_O very low, where θ refers to fractional surface coverage: it is likely that the same holds in our experiments. Too much notice should not be taken of our value of 17 kcal. mole^{-1} for E, since it is based on only two runs, and the rate of reaction at 67° was high: the figure may well be in error by at least 3 kcal. mole^{-1}.

The present kinetic work deals only with the initial stage of the reaction, when the rate is linear for an appreciable time, and the rate constants reported are those calculated from the initial rates or from the new steady state after the injection of one or other of the two gases into a reacting mixture which had reached a steady state. It may be noted that in several cases the results obtained by the injection method were confirmed by an experiment in which was employed only gas of the composition of the mixture after injection. The injection technique is not wholly satisfactory but was used since it speeded the work and also because there was a slow drift in reactivity of the catalyst during this study, and it was felt that the method was probably a more accurate way of determining the effect of changing the partial pressures of the two reactants. Fig. 5 shows that the reactivity of the catalyst roughly doubled during the series of experiments, while the activation energy may have fallen slightly: we conclude that $E = 10 \pm 2$ kcal. mole^{-1} for the stoicheiometric mixture, which is a little lower than that found for the 1 : 1 mixture by Garner *et al.* over a smaller temperature interval. Fig. 4 shows the effects of variation in the pressures of the two reactants at two temperatures: we find Rate $\propto P_{CO}^{0\cdot28}$ and $\propto P_{O_2}^{0\cdot20}$ at 66° in the presence of a constant pressure of the other gas, and in confirmation of this, for the stoicheiometric (1 : 2) mixture, Rate $\propto P_T^{0\cdot48}$, where $P_T = P_{CO} + P_{O_2}$; $P_{CO} = 2P_{O_2} = \frac{2}{3}P_T$ for stoicheiometric case.

Similarly, at 48°, Rate $\propto P_{CO}^{0\cdot45}$ and $\propto P_{O_2}^{0\cdot17}$ and $\propto P_T^{0\cdot63}$. Evidently competition occurs between the two reactants and therefore since the adsorption isotherms for the mixed gases are not known the true activation energy cannot be determined. The experiments (Fig. 2) show there is a time lag between admission of gases to the bare catalyst and attainment of the steady state, of about 3 min. at 86° and 4 min. at 48°; a similar interval occurs after the injection of more of one of the reactants into a system which has reached a steady state (Fig. 3). This time lag is rather greater than that normally taken by the mass spectrometer to recover steady conditions after change of pressure behind the leak leading to the ionisation chamber, and we believe it is associated with the production of steady conditions on the catalyst surface; it is about the same as that found with pure oxygen and carbon monoxide separately at lower temperatures and pressures by Garner *et al.* (*locc. cit.*).

The desorption experiments, on pumping out after a reaction, show that the adsorbed layer during the reaction contains carbon dioxide and carbon monoxide (although no poisoning by the former was found). Oxygen must also be adsorbed, as was clearly shown by Garner, Stone, and Tiley (*loc. cit.*), but either it reacts very rapidly with adsorbed carbon monoxide or it is very strongly held and is eventually consumed by oxidation of underlying copper or in restoration of the oxidation state of a partly reduced surface. In this connection the two experiments displayed in Fig. 6, and the confirmatory one on catalyst B at room temperature, are of considerable interest: the former show that at both temperatures (48° and 155°) the carbon monoxide attacks the surface very rapidly and extracts oxygen from it, the ^{18}O content of the carbon dioxide formed rising to a maximum of 8·2% and 6·24% respectively; on catalyst B at 15° the maximum ^{18}O content was 6·77%. The experiment at 48° shows the slow fall of ^{18}O content in the product as normal oxygen from the gas phase is utilised: the carbon monoxide meanwhile shows a steady rise in ^{18}O content owing to exchange with those parts of the surface not taking part in the catalytic reaction. The curve for ^{18}O content of the latter gas includes some contribution from CO^+ fragments formed from the product, but the error from this cause is not important here. The run at 155° shows the slow rise in ^{18}O content of the carbon dioxide, the rise beginning towards the end of the oxidation reaction and continuing for some time after its completion, owing to exchange with parts of the surface not involved in the reaction: this run was too fast to yield, by manual scanning of the peaks, a record of the ^{18}O content of the carbon monoxide. The high ^{18}O content of the product at the maxima shows that the amount of isotopically normal reactive $(O)_{ads}$ present, derived from the gas phase, is small during the first stages of the reaction. If we assume the B.E.T. (N_2) surface area of the catalyst (2·21 m.^{2} g.$^{-1}$) corresponds to a surface layer of about $2{\cdot}25 \times 10^{19}$ ions of oxygen on the 4 g. of catalyst (cf. Garner, Stone, and Tiley, *loc. cit.*) and that at the maximum ^{18}O content all the ^{18}O in the product then formed has been produced by extraction of ^{18}O from the surface and not by exchange, we calculate that these figures correspond to an extraction of oxygen from 14% (48°) and 33% (155°) of the surface: the subsequent exchange of the carbon dioxide with the surface demonstrates that not all of the surface is active in the extraction reaction. After allowance for the latter exchange, the ^{18}O content of the carbon dioxide at the completion of the reaction at 155° also corresponds to extraction of oxygen from ~35% of the oxide surface. The peak ^{18}O content in the run on catalyst B at 15° corresponds to an extraction of ^{18}O from 10% of the surface.

We suggest that our observations may be interpreted in the following way:

$$CO(gas) + 2O^{2-}{}_{(s)} \longrightarrow (CO_3)^{2-} + (e_2/\square^-{}_s) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

followed by

$$(CO_3)^{2-} + O_2(gas) + (e_2/\square^-{}_s) \longrightarrow CO_2(gas) + 2O^{2-}{}_{(s)} + O_{(ads)} \quad . \quad . \quad (2)$$

The reaction takes place on only a fraction of the surface sites. Reaction (2) is complex and is probably divisible into two steps:

$$O_2(\text{gas}) + (e_2/\square^-{}_s) \longrightarrow O^{2-}{}_{(s)} + O_{(ads)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

followed by

$$(CO_3)^{2-} \longrightarrow CO_2(\text{gas}) + O^{2-}{}_{(s)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

Reaction (2*b*) is probably promoted by the destruction of the neighbouring F′ centre according to (2*a*). The $O_{(ads)}$ formed in reaction (2*a*) reacts as shown in (2*c*) to complete the cycle.

On the above scheme reaction (2*a*) or (2*b*) would be expected to be rate-determining. Garner, Gray, and Stone (*loc. cit.*) record that on admission of oxygen to a surface (of cuprous oxide on copper strip) saturated with carbon monoxide, *ca.* 50% of the latter could be recovered as carbon dioxide on evacuation at room temperature. On the other hand, Garner, Stone, and Tiley (*loc. cit.*), using a granular copper–cuprous oxide catalyst such as ours, found that the complex formed by adsorption of carbon dioxide on to an oxygenated surface was stable at room temperature in the presence of excess of adsorbed oxygen, but was quantitatively decomposed by excess of adsorbed carbon monoxide, giving carbon dioxide. The residual gas pressures in the system during these experiments are not recorded (although they were undoubtedly very low), but it is probable that this is an important factor; we have repeatedly found in the present work that addition of several cm. of oxygen gas to a catalyst holding adsorbed carbon monoxide causes the appearance of gaseous carbon dioxide in the reaction system (cf. Fig. 1; similar observations were made on catalyst B at 20°).

Garner, Stone, and Tiley (*loc. cit.*) suggested, for temperatures between 10° and 36°, at much lower pressures, a reaction between $O_{(ads)}$ and $CO_{(ads)}$, with the adsorption of oxygen

$$O_2(\text{gas}) \longrightarrow 2O_{(ads)} + 55\ \text{kcal. mole}^{-1} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

[which is analogous to reaction (2*a*)] as the rate-determining step; they suggested that extraction of oxygen from the surface would occur at *ca.* 70° and upwards. It is possible that in the present work the latter reaction took place at significantly lower temperatures because of the higher pressures used, but further work in this connection is desirable. The fact that our figure for E (10 ± 2 kcal. mole^{-1}) is very close to that found by Garner, Stone, and Tiley ($11{\cdot}4 \pm 2$ kcal. mole^{-1}) may indicate that both studies were concerned with the same limiting process. They noted that their value for E, if it referred to reaction (3), was not in agreement with their earlier figure of $7 \pm 1{\cdot}5$ kcal./mole for the adsorption of oxygen in the absence of other gases, but suggested that the presence of high concentrations of $(CO_3)_{ads}$ might modify the value of E. Nor for that matter does our value of E agree with that (15·5 kcal. mole^{-1}) found by us for the oxidation of copper powder (Winter, *J.*, 1954, 3342). In any case our ^{18}O results * show that lattice oxygen is largely involved in the reaction under our conditions and thus that the mechanism of the reaction on cuprous oxide is very similar to that proposed by Schwab and Drikos (*Z. phys. Chem.*, 1942, **52**, *B*, 234) for the same reaction on cupric oxide.

The experiment with a 1 : 1 mixture of normal and 30%-^{18}O for the oxidation of carbon monoxide shows that, as in the oxidation of copper (Winter, *J.*, 1954, 3342) any $O_{(ads)}$ formed is strongly adsorbed or rapidly reacts further, and does not take part in a desorption stage $2O_{(ads)} \longrightarrow O_2(\text{gas})$ which would lead to equilibration. It is most likely that any $O_{(ads)}$ formed is labile over the surface (cf. Winter, *J.*, 1954, 1522) and reacts rapidly with a neighbouring $(CO_3)^{2-}$ complex:

$$(CO_3)^{2-} + O_{(ads)} + (e_2/\square^-{}_s) \longrightarrow CO_2(\text{gas}) + 2O^{2-}{}_{(s)} \quad . \quad . \quad . \quad (2c)$$

[This reaction, like (2) above, probably proceeds in two stages, the first being the destruction of the F′ centre.]

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* Cf., in particular, the high proportion of the total reaction (~30%) which has occurred in the experiment at 155° at the maximum ^{18}O content of the carbon dioxide (Fig. 6).

The effect of pre-treating the surface with one or other of the three gases, studied at 50°, shows that neither carbon monoxide nor carbon dioxide poisons the surface appreciably, but that pre-treatment with oxygen causes a marked acceleration. The effect of oxygen is in accord with Garner's finding that $O_{(ads)}$ was very reactive; it also confirms the conclusion drawn from the reaction on a $Cu_2{}^{18}O$ surface that the concentration of $O_{(ads)}$ is low, at least during the early stages of the normal oxidation reaction with the stoicheiometric mixture. Garner, Stone, and Tiley (*loc. cit.*; cf. Dell and Stone, *Trans. Faraday Soc.*, 1954, **50**, 501) have also shown that the desorption of carbon dioxide should not be the slow stage on cuprous oxide.

(b) *Reactions on Nickel Oxide.*—Our work shows this catalyst is much less active than cuprous oxide in promoting oxygen exchange between carbon monoxide and dioxide and the surface; the exchange between oxygen gas and the surface attains a reasonable rate only above 400° (Winter, unpublished work), and thus is rather less easy to achieve than exchange between the surface and carbon dioxide, which is measurable at 250°. The oxygen exchange work gives a value of about 7×10^{19} for n_s, compared with approximately $6{\cdot}3 \times 10^{19}$ calculated from the B.E.T. (N_2) surface area. Analysing the CO-oxidation experiments on $Ni^{18}O$ in the same way as for $Cu_2{}^{18}O$ we find that the ^{18}O contents at the completion of the reaction correspond to an extraction of ^{18}O from 0·34% (49°) and 2·3% (211°) of the nickel oxide surface; all the experiments are summarised in Table **3**. As noted in the Experimental section there is no appreciable exchange between any of the three gases and the surface at temperatures around 50°, but after some ten oxidation experiments in this region the majority of the ^{18}O originally present in the surface is still available for exchange at higher temperatures with oxygen and with carbon dioxide: it is clear that at the lower temperatures the extraction, and probably the whole oxidation of carbon monoxide, occurs only at a small number of very reactive fixed sites. The oxidation experiment in which a non-equilibrated $^{18}O_2$–$^{16}O_2$ mixture was used shows that, as with the reaction on cuprous oxide, no adsorption-desorption, involving dissociation of molecular oxygen, occurs during the reaction.

The oxidation kinetics may be accounted for (cf. Dell and Stone, *loc. cit.*) by assuming competition between carbon monoxide and carbon dioxide for the small number of sites left free by oxygen, which is strongly adsorbed (or for a small number of very active sites, oxygen not competing for these). [The occurrence of appreciable chemisorption of oxygen, at these temperatures and pressures, on another part of this nickel oxide preparation, has been confirmed and measured in work connected with the exchange reactions with gaseous oxygen: similar remarks apply to chromium oxide (Winter, unpublished work).] Then, if the velocity is proportional to the concentration of carbon monoxide on these sites,

$$\text{Rate} = \frac{dP_{CO_2}}{dt} = \frac{kP_{CO}}{(P_{CO} + P_{CO_2})} = \frac{k(P^i_{CO} - P_{CO_2})}{(P_{CO} + P_{CO_2})} = \frac{k(P^i_{CO} - P_{CO_2})}{P^i_{CO}} \quad . \quad (4)$$

where P^i_{CO} is the initial pressure of carbon monoxide, P_{CO} and P_{CO_2} are the pressures of the two gases at any time during the reaction, and $P^i_{CO} - P_{CO} = P_{CO_2}$.

Integration of eqn. (4) yields:

$$kt = -P^i_{CO} \log (P^i_{CO} - P_{CO_2}) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Fig. 7 shows that this equation adequately represents our observations: it may be noted that the equation

$$\log (t - t_0) = \alpha g - \log a\alpha \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

used for this reaction on the same catalyst by Parravano (*J. Amer. Chem. Soc.*, 1953, **75**, 1448), derived from $dg/dt = a \exp \alpha g$, where g is the amount of conversion and α and a are constants, does not give so good a fit as eqn. (5), although it gives fair straight lines when applied to our results. Eqn. (6) has no very clear physical interpretation and in the present instance we prefer (5): the latter equation should, if our assumptions about the mechanism are correct, hold until P_{O_2} becomes so low that the surface begins to be denuded of oxygen, and in fact it appears to hold up to at least 90% conversion.

It is of interest that Parravano found eqn. (6) to hold for the first few runs on a fresh catalyst, but that after a time the activity diminished until a plot of log P_T against time gave good straight lines in the temperature region 100—180°. Over the range 180—240° on the aged catalyst the equation $-\mathrm{d}P_T/\mathrm{d}t = kP_T^{1\cdot25}$ held. (Parravano removed the carbon dioxide continuously from the gas phase and followed the fall of total pressure, P_T.) We did not observe higher activity during the first few runs on any sample and we ascribe this to our practice of heating the catalyst in a high vacuum to at least 240° overnight before each run, which should remove adsorbed gases and provide a surface of standard and reproducible activity.

It should be noted that it can readily be shown that our eqn. (4) and (5) are formally the same as the log P_T–time plot used by Parravano (see his Fig. 3), after allowance for the different experimental conditions (*i.e.*, the product was removed continuously in the earlier work).

The mechanism we propose requires that the velocity constant should be little affected by moderate changes in the initial pressures of reactants, provided the ratio $P_{CO} : P_{O_2}$ is kept constant: Table 2 shows that, with the stoicheiometric mixture ($P_{CO}/P_{O_2} = 2$), a twofold change in initial pressures not change k; on the other hand a 5—6-fold increase in P_{O_2}, coupled with a 25% reduction in P_{CO}, reduces k by half. Again, the catalyst is readily poisoned by carbon dioxide, as is shown by a run at 57° in which the surface was exposed to 1·6 cm. of carbon dioxide for 10 min. and evacuated for 3 min. before addition of 3 cm. of the stoicheiometric reaction mixture; the value of k for this run was 3·2, to be compared with 5·74 for the reaction on the outgassed surface under the same conditions of temperature and pressure (cf. Table 2). Similarly a series of five successive experiments at 57° (not reported in detail here) in which the catalyst was merely evacuated at 57° for 10—15 min. between runs showed a progressive reduction in rate; mass-spectrometric examination of the gas being desorbed between experiments showed it to consist of carbon dioxide (as indeed it should, the runs being carried to completion). The oxide was restored to its original activity by outgassing overnight at 240°. The poisoning by carbon dioxide is in accord with the work of Dell and Stone (*loc. cit.*) who showed from their heat measurements that this gas might be expected to poison nickel oxide, but not cuprous oxide. The experiments in which the oxidation reaction was carried out on a $Ni^{18}O$ surface (Table 3) show that although only a very small fraction of the surface takes part in the extraction reaction, this proportion increases slowly with temperature; a plot of log x against $10^5/T$ (where x is the percentage of the surface taking part in the extraction reaction) gives $E \approx 3\cdot8$ kcal. mole^{-1}, while the oxidation reaction velocity constants calculated by eqn. (5) and shown in Table 2 give $E \approx 5\cdot5$ kcal. mole^{-1}. We find no inflexion point in the Arrhenius plot of the oxidation figures, in contrast to Parravano. This may be due to the different method of catalyst preparation (Parravano prepared his catalyst by igniting the nitrate) or (more probably) to the difference in experimental techniques, in particular to our practice of outgassing the catalyst at an elevated temperature between experiments.

Dell and Stone (*loc. cit.*), discussing Parravano's figures, suggested the reaction proceeds at lower temperatures ($E \approx 3$ kcal. mole^{-1}) *via* adsorbed species and that at higher temperatures (>160°) it proceeds by the extraction reaction with $E \approx 13$ kcal. mole^{-1}. They saw the difficulty in explaining why it occurs all at very low temperatures unless it takes place on a few very reactive sites. Dell and Stone proved that whereas an adsorption complex which they write as $(CO_3)_{ads}$ could be readily formed by the reaction of carbon monoxide or carbon dioxide with adsorbed oxygen, this complex was stable in the presence of excess of either oxygen or carbon monoxide at 20° : they were, however, able to measure the oxidation reaction quite readily at 20° and 2—8 mm.

The facts that the kinetic runs show no inconsistencies, and that each smoothly and accurately follows eqn. (5), particularly at the commencement of the reaction, coupled with the observations on $Ni^{18}O$ (see above), lead us to conclude that, as in the case of cuprous oxide, the reaction $2CO + O_2 \longrightarrow 2CO_2$ occurs, under our conditions at least, almost if not entirely by the extraction mechanism, on only a small fraction of the surface sites, the process being described by equations such as (1) and (2) above.

Since at reaction temperatures carbon monoxide alone shows no exchange on nickel oxide, in spite of the proved presence of up to 2—3% of active sites, we conclude that in the absence of oxygen these sites are *irreversibly* covered by chemisorbed carbon monoxide which is only released as carbon dioxide by subsequent adjacent absorption of oxygen, or on considerable rise in temperature. This favours regarding reaction (2*a*) as rate-determining on this oxide. If the rate equation is written as

$$\text{Rate} = PZ\exp(-E/\boldsymbol{R}T) \qquad \ldots\ldots\ldots \quad (8)$$

where P is a frequency factor, and Z the number of active sites per g., Z increases on change from 49° to 211° by a factor of $\sim 6{\cdot}7$, as shown by the experiments on $Ni^{18}O$; over the same temperature range the rate of oxidation increases by a factor of $\sim 16{\cdot}2$. The number of reaction sites, as shown by experiments on $Ni^{18}O$, increases smoothly by an exponential function

$$Z = Z_0\exp(-E_1/\boldsymbol{R}T) \qquad \ldots\ldots\ldots \quad (9)$$

with $E_1 \approx 3{\cdot}8$ kcal. mole^{-1}; the corrected apparent E for the catalytic reaction is then, P being assumed to be constant, about 1·7 kcal. mole^{-1}.

Similar arguments, applied to the reaction on $Cu_2{}^{18}O$ at 155° and 48°, would reduce the observed value of E for the oxidation from 10 ± 2 to a corrected figure of 8 ± 2 kcal. mole^{-1}.

(c) *Reactions on Chromium Oxide.*—This oxide proved very similar to nickel oxide in its behaviour. Thus we may note: the absence of exchange with carbon monoxide and carbon dioxide until relatively high temperatures are reached; the small number of sites active in the extraction reaction during the oxidation of carbon monoxide; the very low apparent activation energy of the latter reaction; and the negligible increase in the number of active sites with increase in temperature. The oxidation also followed the same kinetic law [eqn. (5)] as on nickel oxide, but the kinetics were not so fully investigated.

The results in Tables 3 and 4 agree in showing that both the rate of the oxidation and the number of active (extraction) sites remain approximately consistent over the temperature range 44—155°, so that, in the eqns. (8) and (9) above, both E and $E_1 \approx 0$. It seems reasonable to think that the oxidation reaction follows the same course as on nickel oxide.

(d) *General.*—The present study amplifies the picture built up as a result of other work on these reactions, but although general agreement is reached on many points there are several divergences, and in particular our proposals for the mechanism of the oxidation reaction ($CO + \frac{1}{2}O_2 \longrightarrow CO_2$) on cuprous and nickel oxides at low temperatures differ fundamentally from those of Garner, Stone, *et al.* A repetition and extension of this work combining our technique with heat measurements similar to those of Garner and Stone would be valuable, since it is not certain that the catalysts used in the two laboratories are energetically similar and therefore detailed correlation of observations may not be justified at present.

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