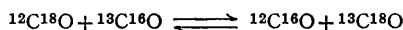## 1104. *Exchange Reactions of Oxides. Part VIII.*[1] *The Homomolecular Exchange of Carbon Monoxide.*

By E. R. S. WINTER.

The homomolecular exchange reaction

$$^{12}C^{18}O + {}^{13}C^{16}O \rightleftharpoons {}^{12}C^{16}O + {}^{13}C^{18}O$$

occurs readily at around room temperature or below on many oxides. Refractory oxides (Nb_2O_5, SiO_2, Al_2O_3) and also Na_2O, TiO_2, and GeO_2 are of low or zero activity but many others are highly active. The activity of NiO depends on the method of its preparation and upon the lithium or chromium content; superficial films of oxide upon the metal, *e.g.*, Ni–NiO, Cu–Cu_2O, or Fe–Fe_2O_3, are abnormally active. The metals Ag, Cu, Pd, Pt, Fe, and Ni have been studied: the first two are inactive and the activity of the others increases in the order given: nickel is rapidly poisoned by formation of $Ni(CO)_4$. Finely-divided sodium chloride is inactive, as are Cu–CuCl, ZnF_2, and graphite. The amount of carbon monoxide adsorbed under reaction conditions is reported for all active oxide catalysts.

A small amount of ^{18}O-exchange between the carbon monoxide and the surface occurs with the active oxides: in general this takes place at the same speed as the homomolecular reaction and stops when that reaction has reached equilibrium: the two reactions are accounted for by postulating a small number of immobile sites where the basic reaction is

$$CO(g) + nO^{2-}(s) \rightleftharpoons CO_{n+1}{}^{2n-}(s)$$
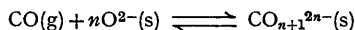
THE exchange of oxygen between $^{13}C^{16}O$ and $^{12}C^{18}O$, catalysed by Fe formed by reducing Fe_2O_3, was first observed by Webb and Eischens[2]; Eischens earlier[3] studied the exchange of ^{14}C between the gas phase and ^{12}CO adsorbed on the same catalyst. Winter[4] also noted the exchange of oxygen between $^{13}C^{16}O$ and $^{12}C^{18}O$ on Cu–Cu_2O at $-78°c$ but in this case there was also some exchange of ^{18}O with the Cu_2O surface. Because of the importance of this reaction in indicating the intimate nature of the interaction between adsorbed molecules of carbon monoxide, and as much work has been done on the infrared spectra of carbon monoxide adsorbed upon various metals and oxides, it is very surprising that no further studies have been made.

The present study records the widespread power of finely-divided metallic oxides to catalyse this intermolecular exchange reaction at or below $300°K$. Some observations upon metal surfaces are included: several metallic halides and also graphite are inactive.

[1] Part VII, Winter, *J.*, 1955, 3824.
[2] Webb and Eischens, *J. Amer. Chem. Soc.*, 1955, **77**, 4710.
[3] Eischens, *J. Amer. Chem. Soc.*, 1952, **74**, 6167; *J. Chem. Phys.*, 1951, **19**, 377.
[4] Winter, in "Chemisorption," ed. W. E. Garner, Butterworths, London, 1957, p. 195.

EXPERIMENTAL

Method.—The reaction was studied at 10^{-1} mm. and at 2 cm. pressure of CO. The experimental approach at 2 cm. was essentially that used extensively in earlier studies of the exchange of ^{18}O between gaseous molecular oxygen and the surface of metallic oxides.[5] The reaction vessel was of silica suspended vertically so that it could be surrounded by a furnace or by a thermostat operating around room temperature or by a Dewar flask containing a freezing mixture. The reaction vessel was connected by a graded seal to a T-junction, in one arm of which was sealed a drawn-out capillary leading to the ionization region of a mass spectrometer. The other arm of the T-junction led through a U-trap to a mercury manometer and to a 3-way tap leading to the gas-dosing burette and to the main high-vacuum pumping line. All connecting tubing was 8 mm. internal diameter; the volume of the reaction system, with the trap at $-78°c$, was about 130 ml. The U-trap was kept at $-78°$ throughout, so that the catalysts were always protected from tap grease and mercury and water vapour. The electrically heated furnace used for the preliminary outgassing of the catalysts was electronically controlled to $\pm 1·0°$ overnight.

The catalyst (bulk oxides) was weighed into the reaction vessel which was then sealed on to the apparatus. A convenient amount was 0·2—5 g., depending on the reactivity. The furnace was placed around the specimen and the temperature raised to about 250—300°. The reaction vessel was evacuated slowly and pumped hard for 10—15 min. and the catalyst treated with two doses of 1-cm. pressure of pure oxygen, each being left in contact for 10 min., pumping to 10^{-3} mm. for some minutes between doses. The furnace was raised to the outgassing temperature, usually 450°c, and the catalyst pumped overnight; in the morning the pressure was usually less than 5×10^{-6} mm. The sample was then isolated from the pumps and cooled to the reaction temperature, which in most cases was 0—30°c. This treatment with oxygen followed by overnight outgassing was, except where otherwise noted, repeated between each run when several experiments were performed on the same catalyst.

A measured quantity of carbon monoxide containing a non-equilibrium mixture of the four isotopic species, $^{12}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{16}O$, and $^{13}C^{18}O$, was added through the 3-way trap to the reaction vessel containing the outgassed catalyst at the reaction temperature, and a continuous record taken of the change in the (mass 30: mass 31) ratio with time, by analysing the sample bled off continuously to the mass spectrometer through the capillary leak. Several times during each run the values of the 28 and 29 peaks were measured in order to confirm that the ^{18}O-content of the gas did not change. In general a pressure of 1—2 cm. of CO was maintained in the reaction vessel; the rate of loss of gas to the mass spectrometer was in all cases negligible during the time taken for an experiment. During each experiment measurements were taken of the rate of appearance of carbon dioxide in the gas phase; oxygen was also looked for but never found.

A few experiments were done in the same way with non-equilibrated nitrogen; these are dealt with briefly later: in these experiments the oxides were merely outgassed beforehand, no pretreatment with oxygen being given.

For work at 10^{-1} mm. of carbon monoxide, roughly the same weights of catalyst as those for 2 cm. were taken: the pretreatments were also the same. In this series of experiments the reaction vessel was connected to the gas-dosing system and to an automatic recording–control system[6] which kept the pressure constant throughout the adsorption and also recorded the rate of adsorption. This reaction system also led to a Töpler pump by means of which most of the gas phase could be removed when necessary and transferred to small sample tubes, each provided with a break seal for mass-spectrometric analysis. After pretreatment, pumping, and cooling to room temperature, the adsorption of non-equilibrated carbon monoxide was allowed to proceed at 10^{-1} mm. for some 3—4 hr., with a known quantity of gas. At the end of this time adsorption was usually complete: whether or not this was so, most of the gas phase was recovered for analysis, which as before included a check on mass numbers 32, 44, and 45. The amount of gas recovered for analysis was between 0·005 and 0·03 ml. at s.t.p. A few experiments were performed on double quantities of oxide and gas: here a second sample of gas was taken for analysis about 18 hr. after the first.

The pretreatment was varied in the case of the metals and for a few less stable oxides and for the halides; details are given briefly.

(*a*) Metals, halides, Na_2O, and graphite: no oxygen treatment, outgassing temperatures, Pt, Pd (both on Cabosil): 350°c; Fe, 470°; Ni, 390°; Cu, 200°; NaCl, 220° for 1 hr., after 18 hr. at 22°; ZnF_2, 250° for 18 hr.; Cu–CuCl, 90°; Graphite, 500°; Na_2O, 480°.

[5] Winter, *Adv. Catalysis*, 1958, **10**, 196—241.
[6] Winter, *J. Sci. Instr.*, 1961, **38**, 345.

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(*b*) Ag_2O: no oxygen treatment, fresh sample used for each experiment, pumped at 22°.

(*c*) Ni–NiO: pumped 20 min. at 250° after each run, then sufficient oxygen added to form *ca.* 5 more monolayers of NiO; when all the oxygen had reacted, the temperature was raised to 400° and the catalyst pumped overnight.

(*d*) $Cu-Cu_2O$: similar treatment to Ni–NiO but at lower temperatures, 150° and 200°, respectively. CuO pumped at 230°; no oxygen treatment.

(*e*) NiO from $Ni(OH)_2$: pumped at 200°; no oxygen treatment.

(*f*) CoO: pumped at 700°; oxygen treatment at 500°.

(*g*) PdO and PtO_2: pumped at 90° and 130°, respectively; oxygen treatment at 80°.

(*h*) Graphite: pumped at 500°.

(*i*) V_2O_3, MnO, reduced Cr_2O_3: no oxygen treatment, outgassed as indicated under *Materials* later.

After use those catalysts whose areas were not known from earlier work were transferred to another vessel and, after outgassing at the temperature obtaining before the catalytic reaction, their B.E.T. areas were measured with nitrogen at $-193°$: an area of $16 \cdot 1$ Å^2 was assumed for the nitrogen molecule. Excellent B.E.T. plots were obtained in all cases.

Some measurements were also made of the amount of carbon monoxide adsorbed upon these materials at 1 cm. and 2 cm. At the end of the adsorption samples of the gas phase were taken and analysed for carbon dioxide content.

Materials.—MgO, ZnO, α-Fe_2O_3, Cr_2O_3, NiO, and NiO doped with various amounts of Li_2O and fired at 650° were mainly materials used in earlier work.[7] Where this was not so, the method of preparation was exactly as before. In Table 1, Cr_2O_3 "oxidized" and "reduced" are mentioned: the former was material made as described and merely outgassed for 18 hr. at 520°; the reduced material was the same preparation heated for 18 hr. in hydrogen (3 cm.) at 360° and then outgassed for 4 hr. at 440° before isolating and cooling to room temperature for use. ZnO(Zn) refers to the material used in ref. 7*b* and $ZnO(CO_3)$ to oxide made by decomposing $ZnCO_3$ (from pure Zn) at 600°.

Na_2O with a B.E.T. area of $1 \cdot 12$ m.^{2} g.$^{-1}$ was made by heating together the theoretical amounts of NaN_3 and $NaNO_3$ in an evacuated apparatus until the reaction was complete: the temperature was raised very slowly during several days from 200° to 480°. Nickel metal was prepared from the oxalate, and subsequently oxidised to Ni–NiO.[8] Copper was made as before, and subsequently oxidised to $Cu-Cu_2O$.[4] CuO was B.D.H. AnalaR powder. NiO from the hydroxide, written as NiO(OH), was made by decomposing the hydroxide below 210° *in vacuo*.[9] Ag_2O was prepared according to Riley and Baker,[10] and dried for 6 weeks in a vacuum desiccator over quicklime: the product had a B.E.T. area of $2 \cdot 67$ m.^{2} g.$^{-1}$ Silver was made by reduction of the Ag_2O with hydrogen at 230°: it had an area of $16 \cdot 1$ m.^{2} g.$^{-1}$. TiO_2 was in the anatase form prepared by hydrolysis of $TiCl_4$.[11] γ-Al_2O_3 was B.D.H. AnalaR grade.

SiO_2 was a sample of Cabosil: after the activity of this material had been examined, and its B.E.T. area measured (136 m.^{2} g.$^{-1}$) the sample was divided into two: one portion was coated with about 40% w/w of platinum by mixing into a thick paste with the requisite amount of the chloride, drying at 100° and reducing in pure hydrogen at 240°. The other portion was similarly coated with 70% w/w of palladium, the chloride paste being reduced at 300°. The heavy loadings of these metals were an attempt to cover all the silica surface and ensure that any activity found would be due solely to the metals.

GeO_2, La_2O_3, Sc_2O_3, Y_2O_3, Ho_2O_3, Dy_2O_3, and Nb_2O_5 were Specpure grade (Johnson Matthey & Co.). CaO was prepared *in situ* by thermal decomposition of very pure $CaCO_3$ *in vacuo* at 650°.

PtO_2 was prepared by heating chloroplatinic acid with $NaNO_3$ and extracting with water;[12] the well-washed product was dried in a vacuum desiccator over CaO and had a B.E.T. area of $91 \cdot 6$ m.^{2} g.$^{-1}$. PdO was made in a similar fashion from $PdCl_2$;[13] area 15·1 m.^{2} g.$^{-1}$ CoO was made by heating Co_3O_4 (B.D.H. "low in Fe and Ni") to 700° in a high vacuum. Iron was prepared by reducing Fe_2O_3[7*c*] with pure hydrogen at 400—450° followed by pumping for 18 hr. at 480°. The

⁷ (*a*) Houghton and Winter, *J.*, 1954, 1509; (*b*) Barnard, Winter, and Briscoe, *J.*, 1954, 1517; (*c*) Winter, *J.*, 1955, 3824; (*d*) Winter, *Discuss. Faraday Soc.*, 1959, **28**, 183; (*e*) Winter, *J.*, 1955, 2726.
⁸ Dell and Stone, *Trans. Faraday Soc.*, 1954, **50**, 501.
⁹ Teichner and Morrison, *Trans. Faraday Soc.*, 1955, **51**, 961.
¹⁰ Riley and Baker, *J.*, 1926, 2510.
¹¹ Kennedy, Ritchie, and Mackenzie, *Trans. Faraday Soc.*, 1958, **54**, 119.
¹² Voorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397.
¹³ Shriner and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1683.

product was pyrophoric in air and was transferred to the B.E.T. apparatus after use in an atmosphere of dry nitrogen. Fe/Fe_2O_3: when work upon iron was complete the sample was outgassed at 400° and cooled to room temperature; 1 cm. of pure helium was introduced and then sufficient pure oxygen to form first *ca.* $1\frac{1}{2}$—2, and later *ca.* 25 monolayers. The powder remained cold during this oxidation, which was performed very slowly by small increments. V_2O_3 was made by reduction of V_2O_5 with hydrogen at 950°, and outgassed for 18 hr. at this temperature (B.E.T. area, 0·83 m.² g.⁻¹). MnO was made by reducing "Mn_2O_3" with H_2 at 500° and out-gassing for 18 hr. at 530°: the "Mn_2O_3" was made by the action of ammonia upon "AnalaR" $Mn(NO_3)_2$, filtering, and washing and drying *in vacuo.* Graphite was a finely-powdered very pure rod used for spectrographic analysis (area 5 m.² g.⁻¹).

Sodium chloride was made in a finely-divided state by passing a rapid stream of dry nitrogen over the molten salt, and collected in dry nitrogen by electrostatic precipitation.[14] The powder was transferred to the reaction vessel by means of a thin glass septum punctured when required by a breakseal, without exposure to air, tap grease, mercury vapour, or moisture (area 37 m.² g.⁻¹). Cu–CuCl: freshly-reduced copper metal, as used for the preparation of Cu–Cu_2O, was exposed at 20° to sufficient pure dry chlorine to form approximately 100 layers of CuCl; heat was generated and the gas was added in small increments at low pressure. ZnF_2: the laboratory reagent-grade tetrahydrate was dried in air at 200° for 48 hr., and then outgassed for 18 hr. at 250°.

The enriched carbon monoxide used for most of this work was a sample obtained in 1949—1950 from A.E.R.E., containing about 60% of ^{13}C and 6% of ^{18}O. The concentration of oxygen-17 was negligible for present purposes. This gas was part of the enriched fraction made by distilling liquid carbon monoxide at low temperatures. Before use the gas was passed through a trap at −78° and condensed in a pumped nitrogen trap: the solid was pumped briefly and expanded into a storage bulb, the last 5% being rejected. Mass-spectrometric analysis revealed no impurities. The oxygen-18 was distributed in a non-equilibrium manner between the two carbon isotopes, so that the ratio (mass 30 : mass 31) was about 12·5, whereas the equilibrium value was 0·68.

A second sample of enriched carbon monoxide was prepared and used to confirm a selection of the results obtained with the main stock. This was made by mixing equal volumes of $^{13}C^{16}O$ containing the normal abundance of ^{18}O and 60% of ^{13}C, and $^{12}C^{18}O$ containing 6% of ^{18}O and the normal abundance of ^{13}C. The two samples of carbon monoxide were prepared from the corresponding dioxide by reduction with zinc-dust–asbestos catalyst at 420°c. The $^{13}CO_2$ was prepared from $Ba^{13}CO_3$ and $^{12}C^{18}O_2$ by burning pure graphite heated by a platinum spiral in oxygen containing 6% ^{18}O made by thermal diffusion. All gases were rigorously purified by vacuum-distillation at each stage.

The carbon monoxide used for adsorption measurements was made by the action of concentrated sulphuric acid on formic acid; the product was purified by passage through a tube packed with potassium hydroxide pellets and a trap cooled to −78°, and condensed at −193°. It was further purified by distillation *in vacuo* and contained no impurities detectable by mass spectrometry between masses 17 and 50. Oxygen, carbon dioxide, and nitrous oxide were all similarly pure gases prepared and fractionated *in vacuo* by standard procedures. Hydrogen was made from coal-gas by diffusion through a heated palladium thimble.

The enriched non-equilibrated nitrogen was prepared by mixing equal volumes of normal nitrogen and of nitrogen containing 31-atom-% excess of nitrogen-15. The enriched sample was made by the action of NaBrO on $^{15}NH_4NO_3$ and purified by vacuum distillation: the normal sample was made in the same way from normal NH_4NO_3. Mass-spectrometric analysis revealed no impurities between mass 16 and mass 90.

Kinetics at 2 cm. Pressure.—The reaction being studied is:

$$^{12}C^{16}O + {}^{13}C^{18}O \rightleftharpoons {}^{12}C^{18}O + {}^{13}C^{16}O \tag{1}$$
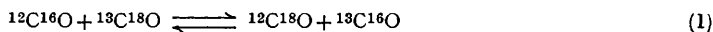
It is to be noted that in all this work at 2 cm. pressure there was no detectable loss of oxygen-18 from the gas phase during the course of any kinetic run, except in the case of NiO prepared from the hydroxide (*q.v.*). With the samples of enriched carbon monoxide available it was most convenient (and most accurate) to follow the course of the reaction by monitoring the ratio of mass 30 to mass 31; as noted above for the main stock of carbon monoxide, this fell from an initial value of 12.5 to *ca.* 0·68 at equilibrium and with the isotope-abundances present could be followed accurately (to ±1—2%) over 90% of the reaction.

[14] Young and Morrison, *J. Sci. Instr.*, 1954, **31**, 90; 1955, **32**, 325.

We will neglect isotope effects and assume the forward and backward reactions to have the same velocity, k_1.

Let n_1, n_2, n_3, and n_4 be the numbers of molecules of $^{12}C^{18}O$, $^{13}C^{16}O$, $^{12}C^{16}O$, and $^{13}C^{18}O$, respectively, in the system at any time, t, after the start of the reaction. Then, making the following substitutions:

$$\left.\begin{array}{c} n_1+n_2+n_3+n_4 = n_g \\ (n_1+n_3)/n_g = \alpha \\ (n_2+n_4)/n_g = \beta \\ n_1/n_4 = R_t; \quad \alpha/\beta = R_\infty \end{array}\right\} \quad (2)$$

where R_∞ is the value of R_t at the end of the reaction, then the velocity of reaction is:

$$v = -\frac{dn_1}{dt} = \frac{A_1 k \phi}{n^2_g}[n_1 n_2 - n_3 n_4] \quad (3)$$

where A is the area in cm.^{2} of catalyst surface, ϕ the number of occupied active sites/cm.^{2}, and k_1 is the rate constant.

By means of equations (2) this transforms into:

$$-\frac{dn_1}{dt} = \frac{A_1 k \phi n_4 \beta}{n_g}[R_t - R_\infty] \quad (4)$$

Now
$$-dn_1/dt = dn_4/dt \quad (5)$$

and we wish to measure

$$-dR_t/dt = -d(n_1/n_4)/dt \quad (6)$$

$$= -\left(\frac{n_1+n_4}{n_4^2}\right)\frac{dn_1}{dt} \quad (7)$$

$$= \frac{A k_1 \phi \beta}{n_g}(1+R_t)(R_t - R_\infty) \quad (8)$$

Integration of equation (8) gives

$$\frac{A k_1 \phi \beta}{n_g}(1+R_\infty)t = \ln\left[\frac{R_0 - R_\infty}{1+R_0}\right] - \ln\left[\frac{R_t - R_\infty}{1+R_t}\right] \quad (9)$$

so that a plot of $\log\{(R_t - R_\infty)/(1+R_t)\}$ against time should give a straight line, the slope of which will give the experimental rate constant, k_e where:

$$k_e = \frac{A k_1 \phi \beta}{n_g}(1+R_\infty) \quad (10)$$

Under the present experimental conditions, α, β, and R are constant and

$$\beta(1+R_\infty) = 1$$

so that finally

$$k_1 \phi = k_e n_g/A \text{ (molecules min.}^{-1}\text{ cm.}^{-2}) \quad (11)$$

This equation shows the composite nature of k_e; in particular it indicates that unless ϕ is dependent upon the pressure of carbon monoxide, P_{CO}, in the reaction vessel, the product $k_e n_g$ should be independent of pressure. On the other hand if ϕ increases with increasing P_{CO} then $k_e n_g$ should similarly increase. Note that an increase in the amount of carbon monoxide adsorbed does not necessarily imply an increase in ϕ since ϕ is not necessarily a fixed fraction of the total amount of carbon monoxide adsorbed.

A few experiments which have been made at different pressures of carbon monoxide are given

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in Table 6 and show no important change of $k_1\phi$ with pressure: the experiments at 10^{-1} mm. do not permit the evaluation of rate constants.

TABLE 1.

Substance	$10^{-13}k_1\phi$	E (kcal. mole^{-1})	Substance	$10^{-13}k_1\phi$	E (kcal. mole^{-1})
Na$_2$O	0	—	NiO(CO$_3$)	$1\cdot65 \times 10^{-2}$	—
MgO	1·61	0	NiO(NO$_3$)	2·07	0
CaO	2·38	0	(A)NiO(OH)	4·68	0
γ-Al$_2$O$_3$	$1\cdot77 \times 10^{-2}$	0	CuO	4·82	0
Sc$_2$O$_3$	3·47	0	ZnO(CO$_3$)	8·28	0
Y$_2$O$_3$	9·07	0	ZnO(Zn)	4·48	0
La$_2$O$_3$	39·0	0	Ga$_2$O$_3$	9·25	0
Dy$_2$O$_3$	27·0	0	GeO$_2$	0	—
Ho$_2$O$_3$	62·8	0	Nb$_2$O$_5$	0*	—
SiO$_2$	6×10^{-2}	—	PdO†	$4\cdot4 \times 10^{-1}$(P)*	—
TiO$_2$	$3\cdot09 \times 10^{-1}$	3·5	PtO$_2$	0	—
ZrO$_2$	2·68	0	Ag$_2$O	1·5(P)	0·6
V$_2$O$_3$	0	—	Ni–NiO	22·5	0·8
Cr$_2$O$_3$ (oxidised)	0*	—	(A)Fe–Fe$_2$O$_3$	3·46	0
			(A)Cu–Cu$_2$O†	3·4	0
Cr$_2$O$_3$ (reduced)	5·34	3	(B)Cu–Cu$_2$O†	71·0	0
MnO	2·46	0	Ni	27(P)	—
α-Fe$_2$O$_3$	1·4	0	(A)Fe	1·87	—
CoO	3·12	3	(B)Fe	$1\cdot12 \times 10^{-1}$	—
(A)Cu	$2\cdot7 \times 10^{-1}$	—	Graphite	0*	—
(C)Cu	0	—	NaCl	0*	—
Pd–SiO$_2$	$3\cdot9 \times 10^{-1}$	—	ZnF$_2$	0*	—
Pt–SiO$_2$	1·1	—	Cu–CuCl	0	—
Ag	0	—			

* No reaction up to 100°.   † Measurements at $-78°$.   (P) Denotes rapid poisoning.

The above analysis assumes rapid exchange of molecules between the gaseous and adsorbed states so that neither adsorption nor desorption is rate-determining, *i.e.*, the slow stage occurs on the surface. Should this not be so then the same kinetic form results but the physical significance of $k_s n_g/A$ will be changed in an obvious way. Plots of $\log\{(R_t - R_\infty)/(1R_t +)\}$ against time gave excellent straight lines over at least 85% of the reaction, from which k_s could be found: the results are given in the Tables in the form of $k_1\phi$, defined by equation (11). Tests on several catalysts showed that the values of $k_1\phi$ were independent of the method of preparing the enriched carbon monoxide and were also independent of the initial composition (R_0, α, β,) of the gas, as should be the case from equations (9)—(11). Further experiments (see Table 6) showed that $k_1\phi$ was independent of the weight of catalyst used, in agreement with equation (11).

The Reaction at 10^{-1}mm. of Carbon Monoxide.—These experiments were designed as a much more sensitive test than was possible in the reactions at 2 cm. of carbon monoxide of the extent, if any, of ^{18}O-exchange with the oxide surface: in fact some exchange was found almost always.

In the following treatment we define γ_0 as $(n_1 + n_4)/n_g$, γ_s as the original ^{18}O content of the oxide surface ($= 0\cdot2\%$), and γ_∞ as (12) the ^{18}O content of the gas phase when sampled. Assume that each active site contains two surface oxygen ions able to exchange with the enriched oxygen of the carbon monoxide (the reason for this will be evident from the Discussion section), and also that the number of active sites per cm.^{2}, ϕ, is the same as at 2 cm. pressure, and that isotopic equilibrium is reached between gas and the $A\phi$ surface sites by the time the sample is taken for analysis. Then, since the ^{18}O content of the reacting system remains constant,

$$n_g\gamma_0 + 2A\phi\gamma_s = (n_g + 2A\phi)\gamma_\infty \tag{13}$$

or

$$\phi = \frac{n_g(\gamma_0 - \gamma_\infty)}{2A(\gamma_\infty - \gamma_s)} \tag{14}$$

Results so obtained are presented in Table 3 which also records values of k_1 calculated from equations (11) and (14). The extent of the adsorption, n_a molecules cm.$^{-2}$, at 10^{-1} mm., and of the equilibration reaction are also noted in the Table, where P means partial and C complete.

The Homomolecular Reaction of Nitrogen.—Experiments with non-equilibrated nitrogen showed that this reaction was very difficult to realise on oxide surfaces. Thus at 2 cm. pressure no reaction was detectable on Dy$_2$O$_3$ after 26 hr. at 650° while on MgO no reaction was found after 6 hr. at 450°.

DISCUSSION

Dealing first with carbon monoxide adsorption, it should be noted that the figures in Table 4 were obtained with materials pretreated in the same way as for the corresponding homomolecular exchange run. Almost all isotherms were measured from *ca.* 10^{-4} mm. to 2—3 cm. and after *ca.* 10^{-1} mm. a plot of θ against log(pressure) was generally roughly linear [θ is the amount of carbon monoxide adsorbed at a given pressure, expressed as a fraction of the B.E.T. (N_2) monolayer]. Of most interest here are the values quoted for θ at 1 and 2 cm. These generally do not show much dependence on pressure, but the pressure-dependence of the homomolecular reaction was not studied in detail (see Table 6; some indication of pressure-dependence is evident from the third column of Table 3). Where θ is given as less than a certain value, that value is the limit of the experimental accuracy under the conditions used. Comparison of Tables 4 and 1 brings out some interesting points, notably the small amount of adsorption on the highly active oxides Y_2O_3, Dy_2O_3, and Ho_2O_3. The quantities of carbon dioxide recorded in the last column were determined at the end of the isotherm, usually after the gas had been in contact with the solid for 4—6 hr.; this is very much longer than the time required for the gas in the adsorption system to reach equilibrium in the homomolecular reaction and it is likely that, except as indicated below, the formation of carbon dioxide plays no significant part in the mechanism of that reaction.

The gases carbon monoxide, nitric oxide, nitrogen, and oxygen present an interesting contrast: the bond strengths are respectively[15] about 256, 162, 225, and 118 kcal. mole.$^{-1}$. Nitrogen is a symmetrical molecule containing a stable triple bond, whereas the electronic structures of the unpaired-electron molecules nitric oxide and oxygen resemble that of carbon monoxide with the addition of one and two electrons, respectively, to the anti-bonding orbitals. All four gases undergo the homomolecular reaction, but not with the same ease. Thus $^{15}N^{16}O$ and $^{14}N^{18}O$ interchange oxygen as soon as mixed at *ca.* 2 cm. at room temperature[16], the rate falling off as the pressure is reduced: the rate is not increased (at low pressure) by freezing out solid nitric oxide and re-volatilizing. Some increase might be expected when it passes through the solid state, since there is *X*-ray diffraction evidence[17] that solid nitric oxide is mainly the head-to-tail cyclic dimer (although most of the infrared data have been interpreted in terms of the monomer mixed with *cis*- and *trans*-dimers[18]). It seems most likely that the reaction in nitric oxide occurs by the formation of head-to-tail dimers by binary or possibly ternary collisions in the gas phase: it may well be that some excitation is required, and is provided by transformation of translational energy into vibrational energy on collision: this need may be the reason why no reaction occurs on freezing out. In particular it is necessary to bring the N---O distance (2·4 Å) much nearer to the normal N–O distance (1·12 Å) for exchange of partners to be possible. The effect of temperature and of different diluent gases on the homomolecular reaction in nitric oxide should make a most interesting study. In complete contrast to nitric oxide, pure samples of the other three gases, non-equilibrated, have been kept in these laboratories in bulbs of Pyrex glass for at least twelve years at room temperature and exposed to ordinary daylight (not direct sunlight), without detectable equilibration; as might be expected, successive freezing out and re-volatilization, up to 20 times, caused no reaction with any of the three gases.

We thus have the following series: CO-homomolecular exchange occurs rapidly on the surface of many oxides around room temperature, with small or zero activation energy; NO-reaction occurs very readily in the gas phase; reaction complex almost certainly consists of two molecules; O_2-reaction occurs with greater difficulty than with carbon monoxide requiring higher temperatures and significant apparent activation energies: in most cases

[15] Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958.
[16] Spindle and Stern, *J. Chem. Phys.*, 1960, **32**, 1579.
[17] Dulmage, Meyers, and Lipscomb, *J. Chem. Phys.*, 1951, **19**, 1432; *Acta Cryst.*, 1953, **6**, 760.
[18] Smith, Keller, and Johnstone, *J. Chem. Phys.*, 1951, **19**, 189; Fately, Bent, and Crawford, *J. Chem. Phys.*, 1959, **31**, 204.

full dissociation of the oxygen molecule is involved and the measured kinetics refer to the slow desorption stage. N_2-reaction occurs with very great difficulty, if at all, on oxides, certainly requiring much higher temperatures than are required with oxygen: it is, of course, catalysed by metals.

The foregoing suggests that a possible mechanism would involve the formation of a head-to-tail square complex of two molecules: by analogy with nitric oxide it is likely this complex would be associated with two (or possibly only one) electrons, derived from, and shared with, the solid catalyst, thus becoming very similar in its electronic structure to the bimolecular nitric oxide complex. π-bonding with the surface would then be involved, the shared electrons probably entering the antibonding $2p_z$ orbits, and thus weakening the C–O bonds and promoting the possibility of exchange of partners in the reaction complex. Suitable places for the formation of such complexes would be dual or quadruple surface vacancies with one or two trapped electrons. By a dual vacancy or vacancy pair we mean a surface Shottky–Wagner anion vacancy adjacent to a similar cation vacancy: a quadruple vacancy is two dual vacancies side by side so as to make a more or less square 4-fold surface aggregated defect. In the notation suggested by Rees[19] a dual vacancy with two trapped electrons for an MO oxide, such as MgO, is $(\square_s{}^+\rlap{\diagup}{\times}e_2|\square_s{}^-)$ or, in atomic notation like that of Kroger and Vink[20] $(V_{\text{Mg}^{2+}}\rlap{\diagup}{\times}V_{\text{O}^{2-}}{}^{2-})$. There appears to be no evidence from other techniques which unequivocally points to the widespread presence of surface defects of the nature we postulate. It is, however, clear from the discussions of Kroger and Vink[20] and of Seitz,[21] and the review by Symons and Doyle[22] that dual electron-excess centres are possible in general in bulk crystalline solids, and have been adduced in certain cases, particularly in the alkali halides, which have been studied most. It is possible that the two carbon monoxide molecules could stand out more or less at right angles to the surface at a dual vacancy but they could be accommodated in the surafce at a quadruple vacancy. Since surface defects with two trapped electrons are likely to be much less common than those with one, it is possible that an exact electronic analogy with nitric oxide is not needed and that one electron only is donated by the solid. However, this cannot be the mechanism on most of the oxides examined since it does not account for the localized small but definite ^{18}O-exchange between gas and surface. A square dimeric complex could be invoked to explain any homomolecular reaction catalysed by non-oxide solids, for instance halides, but it is significant that none has so far been found (cf. Table 1); on ionic solids the evidence so far is that oxygen must be present in the surface lattice. Metallic catalysts are discussed later.

The main kinetic results are summarized in Tables 1 and 2. They show values of $k_1\phi$ at about 2 cm. pressure of carbon monoxide and measured at 20—22°, with certain exceptions

TABLE 2.

Nickel oxides.

Substance	$10^{-13}k_1\phi$	E (cal. mole^{-1})	B.E.T. (m.^{2} g.$^{-1}$)	CO adsorbed* 1 cm.	2 cm.	CO$_2$, %
NiO(CO$_3$)	$1\cdot65\times10^{-2}$	—	5·48	0·049	0·058	5·5
NiO(OH)	4·68	0	115	0·18	0·39	7·8
NiO(NO$_3$)	2·07	0	6·04	0·15	0·17	0
NiO(NO$_3$) +0·01 M% Cr$_2$O$_3$	1·49	0	3·22	0·082	0·095	0
+0·01 M% Li$_2$O	2·98	1·5	8·96	0·06	0·068	0
+0·10 M% Li$_2$O	6·21	4·5	7·0	0·35	0·38	0
+1·0 M% Li$_2$O	12·6	0	2·59	0·65	0·78	0
Ni–NiO	22·5	0·8	1·08	0·076	0·083	0

* Expressed as a fraction of the B.E.T. (N$_2$) monolayer coverage.

[19] Rees, "Chemistry of the Defect Solid State," Methuen, 1954.
[20] Kroger and Vink, *Solid State Physics*, 1956, **3**, 307.
[21] Seitz, *Rev. Mod. Phys.*, 1954, **26**, 7.
[22] Symons and Doyle, *Quart. Rev.*, 1960, **14**, 62.

which are noted. Table 3 gives the results of the experiments at 10^{-1} mm. and lists values of ϕ and k_1 calculated by means of equations (11) and (14).

Referring first to the reaction upon oxides, Table 3 shows that in all the cases examined, which include most of the active oxides, there is a small amount of ^{18}O-exchange between the carbon monoxide and the surface. A few active oxides were not examined at low pressures SiO_2 (Cabosil) through lack of material; PdO and Ag_2O because of poisoning effects noted at 2 cm.; Ni–NiO, Fe–Fe_2O_3, and Cu–Cu_2O because of variation in the activity of successive preparations which made it meaningless to attempt to evaluate ϕ for these materials by the use of equations (11) and (14). It was confirmed, however, that all three metal–metal oxide

TABLE 3.

Substance	Adsn.	Reaction	k_1 (min.$^{-1}$)	Molecules cm.$^{-2}$	
				ϕ (sites cm.$^{-2}$)	n_a (mol. cm.$^{-2}$)
MgO	C	C	$2 \cdot 6 \times 10^2$	6×10^{10}	$2 \cdot 9 \times 10^{11}$
CaO	C	C	$2 \cdot 5 \times 10$	$9 \cdot 6 \times 10^{11}$	$1 \cdot 5 \times 10^{12}$
γ-Al_2O_3	C	C	$3 \cdot 3$	$5 \cdot 3 \times 10^{10}$	$9 \cdot 8 \times 10^{10}$
Sc_2O_3	C	C	$> 2 \times 10^3$	$< 1 \cdot 8 \times 10^{10}$	$7 \cdot 2 \times 10^{11}$
Y_2O_3	C	C	$1 \cdot 5 \times 10^3$	6×10^{10}	$1 \cdot 6 \times 10^{13}$
La_2O_3	P	C	$4 \cdot 2 \times 10$	$9 \cdot 2 \times 10^{12}$	$2 \cdot 1 \times 10^{13}$
Dy_2O_3	C	C	$9 \cdot 3 \times 10^2$	$2 \cdot 9 \times 10^{11}$	$6 \cdot 2 \times 10^{12}$
Ho_2O_3	C	P	$2 \cdot 1 \times 10^3$	3×10^{11}	$1 \cdot 7 \times 10^{13}$
TiO_2	C	P	$> 6 \times 10^2$	$< 5 \times 10^9$	$1 \cdot 3 \times 10^{11}$
ZrO_2	C	C	$2 \cdot 9 \times 10^2$	$9 \cdot 3 \times 10^{10}$	$5 \cdot 7 \times 10^{12}$
Cr_2O_3 (reduced)	C	P	$4 \cdot 3 \times 10$	$1 \cdot 2 \times 10^{12}$	$1 \cdot 9 \times 10^{14}$
MnO	C	C	$6 \cdot 15 \times 10$	4×10^{11}	4×10^{11}
α-Fe_2O_3	P	C	$4 \cdot 7 \times 10$	3×10^{11}	$1 \cdot 9 \times 10^{13}$
CoO	P	C	7	$4 \cdot 5 \times 10^{12}$	$7 \cdot 5 \times 10^{13}$
$NiO(CO_3)$	P	P	$> 3 \cdot 3$	$< 5 \times 10^{10}$	$3 \cdot 7 \times 10^{12}$
$NiO(NO_3)$	C	C	3×10	$6 \cdot 6 \times 10^{11}$	$1 \cdot 3 \times 10^{13}$
$+0 \cdot 01\% Li_2O$	C	C	$2 \cdot 3$	$1 \cdot 3 \times 10^{13}$	$6 \cdot 2 \times 10^{13}$
$+0 \cdot 10\% Li_2O$	P	C	$7 \cdot 2$	$8 \cdot 6 \times 10^{12}$	$2 \cdot 7 \times 10^{13}$
$+1 \cdot 0\% Li_2O$	P	C	$8 \cdot 4 \times 10$	$1 \cdot 5 \times 10^{12}$	$1 \cdot 4 \times 10^{13}$
CuO	C	C	$2 \cdot 1$	$2 \cdot 3 \times 10^{13}$	$2 \cdot 3 \times 10^{13}$
$ZnO(CO_3)$	C	C	$4 \cdot 1 \times 10$	2×10^{12}	$4 \cdot 9 \times 10^{12}$
$ZnO(Zn)$	C	C	$4 \cdot 5 \times 10$	1×10^{12}	$4 \cdot 9 \times 10^{11}$
Ga_2O_3	C	P	$1 \cdot 5$	$6 \cdot 2 \times 10^{10}$	$3 \cdot 8 \times 10^{11}$
Cu–$Cu_2O(-20°c)$*	C	C	—	$2 \cdot 3 \times 10^{13}$	$1 \cdot 44 \times 10^{14}$
Cu–$Cu_2O(-78°c)$*	C	C	—	$1 \cdot 5 \times 10^{13}$	$1 \cdot 23 \times 10^{14}$

* Work reported in ref. 4.

systems suffered a small amount of ^{18}O-exchange, similar in extent to the bulk oxides. With four oxides—$ZnO(Zn)$, $NiO(NO_3)$, Ho_2O_3, and La_2O_3—a further experiment was performed in which carbon monoxide at low pressure was left in contact with the solid for 24 hr. instead of the normal 3—4 hr. No increase in ϕ as calculated from equation (14) was found. These last experiments show that exchange is confined to a small part of the oxide surface, at rates comparable with those of the equilibration reaction, the rest of the surface oxygen being inert. When considering the values for ϕ in Table 3 it should be remembered that the number of O^{2-} ions at the surface of a metallic oxide is about 10^{15} cm.$^{-2}$. Continuing exchange occurred only with NiO(OH) of high surface area prepared from $Ni(OH)_2$; here the rate of exchange was negligible (at 2 cm.) compared with the rate of equilibration. Thus in two experiments at 2 cm. on this catalyst the homomolecular reaction was virtually complete in 20 min.; when the total ^{18}O content of the carbon monoxide had fallen from the initial value of $6 \cdot 0$ atom-% to $5 \cdot 87$. The ^{18}O content continued to fall slowly and approximately linearly with time, reaching $4 \cdot 15\%$ after 4 hr. Complete exchange with all the surface O^{2-} ions would have reduced this figure to $1 \cdot 55\%$. Klier[23] has also recorded this exchange for NiO prepared in this fashion: the greater lability of the surface oxygen ions of this preparation is undoubtedly due to the very open unsintered structure of the solid.

[23] Klier, *Proc. 2nd Inter. Congr. on Catalysis*, 1960, Technip., Paris, 1961, p. 323.

The present results could be explained by postulating the presence on the surface of the active oxides of a small percentage of active sites at which the carbon monoxide is reversibly dissociated, the adsorbed oxygen-atoms then exchanging with one or more of the neighbouring surface oxygen-ions. By repetition of this process at fixed sites with successive molecules from the gas phase both the limited surface-^{18}O exchange and the equilibration reaction can be accounted for. It is true that, considering first an NiO surface, the formation of $O_{ads.}$ or $O^{-}_{ads.}$, whether by the dissociation of oxygen or by the decomposition of N_2O,[7d] in our experience always leads to exchange with the surface ions, the extent of this exchange depending on the temperature. Similarly on other oxides, we have reasonable grounds for assuming that if ^{18}O or $^{18}O^{-}$ were formed, exchange of ^{18}O with the surface ions would result: the evidence is as follows. We have studied the homomolecular reaction in oxygen:

$$^{18}O_2 + {}^{16}O_2 \rightleftharpoons 2^{16}O^{18}O$$

and the oxygen exchange between O_2 and the surface O^{2-} ions upon NiO, Fe_2O_3, Cr_2O_3,[7c] ZnO, and MgO.[5] In addition in unpublished work we have studied these two reactions upon a large number of other oxides, including most of those used in this paper. In all cases except ZnO and MgO the two reactions are not separable and occur at the same speed, with the same activation energy, and we consider the rate-determining step to be the desorption of oxygen: Boreskov[24] has recently reported similar work with the same general conclusions.

However, these reactions with gaseous oxygen all require elevated temperatures (100 to 600°) and involve activation energies > 12 kcal. mole.$^{-1}$. They are therefore much more difficult to achieve than the carbon monoxide equilibration, although the bond strength in carbon monoxide is nearly twice that of the oxygen molecule. Complete dissociation of carbon monoxide might be expected to lead to the formation of either some oxygen or carbon dioxide and/or to the poisoning of the surface owing to a carbiding reaction:

$$2CO \longrightarrow C + CO_2$$
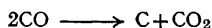
The gas passing to the mass spectrometer was in all cases carefully examined several times during each experiment for the presence of carbon dioxide and oxygen, and the ^{18}O content was measured similarly: no oxygen was found in any experiment and carbon dioxide was detected at 2 cm. of monoxide only with Cu–Cu_2O and Ag_2O, when an ^{18}O-balance showed clearly, as expected, that the carbon dioxide was produced by reduction of the oxide; a trace of dioxide was found in the experiments at 10^{-1} mm. only on $ZnO(CO_3)$. No falling off in rate during a reaction run was noticed with any of the active oxides, good straight lines being obtained from the plot of equation (9) over at least 85% of the reaction: deviations after this were random and due to analytical errors as $R_t \rightarrow R_\infty$. Furthermore a number of catalysts [MgO, Al_2O_3, Y_2O_3, ZnO, Cr_2O_3 (reduced), $NiO(NO_3)$, and Ho_2O_3] were tested for poisoning effects by performing a run at 20° and then pumping for 2—18 hr. at 20° and repeating the run at 20°. This process was performed two or three times, outgassing for varying times up to 18 hr., and the same rate constant was obtained as in the first, standard, run to within 5%. These results are given in Table 5. We conclude that the homomolecular reaction with carbon monoxide on oxides does not involve complete dissociation of the carbon monoxide molecule; the reaction must involve a resonating complex of one or more CO molecules with one or more of the surface oxygen ions.

We think that the general mechanism on oxides at room temperature and below is basically that already suggested for the surface–gas oxygen-exchange reaction with carbon monoxide on Cu–Cu_2O, NiO, or ZnO:

$$CO + 2(O^{2-}/\square_s{}^{-}) \rightleftharpoons (CO_3{}^{2-}/\square_s{}^{-})(e_2/\square_s{}^{-}) \qquad (15)$$
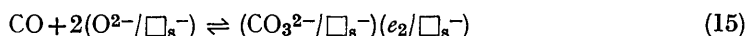
More correctly this equation should be written so as to allow for the interaction of the carbon monoxide with n surface O^{2-} ions, where n is a small number, probably lying between 1 and 3.

[24] Boreskov and Popovskii, *Kinetika i Kataliz*, 1961, **2**, 657; Dzizyak, Boreskov, and Kasatkina, *Kinetika i Kataliz*, 1962, **3**, 81.

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The value of n undoubtedly depends on the crystalline structure of the oxide involved and on the geometry of the active site in each case. For the preparation of Table 3, n has been taken as 2 throughout (cf. derivation of equation 14 above): the adjustment to ϕ involved in the choice of any other value for n is obvious. Thus for an oxide of the rock-salt structure, such as NiO, it is possible that an active site on the (100)-face might consist of a surface vacancy pair ($\square_s^- + \square_s^+$) associated with 2 positive (surface) holes and perhaps underlying

TABLE 4.

Adsorption of carbon monoxide at 20°.

Substance	B.E.T. ($m.^2 g.^{-1}$)	CO adsorbed*		CO_2 (%)
		1. cm.	2 cm.	
MgO	65	0·00015	0·00015	3·7
CaO	25·5	0·025	0·027	1
γ-Al_2O_3	102	0·002	0·003	0
Sc_2O_3	14·25	<0·004	—	0
Y_2O_3	3·64	<0·01	—	0
La_2O_3	2·41	<0·02	—	0
Dy_2O_3	1·5	0·033	0·036	10
Ho_2O_3	0·4	<0·04		0
TiO_2	226	0·0005	0·0005	0
ZrO_2	10·45	0·012	0·013	0
Cr_2O_3 (oxidised)	14·2	—	0·048	0
Cr_2O_3 (reduced)	14·2	—	0·447	0
MnO	8·35	<0·004	—	0
α-Fe_2O_3	33·5	0·039	0·058	0
CoO	2·29	0·27	0·32	3·7
CuO	0·22	0·40	0·60	7·9
$ZnO(CO_3)$	3·89	0·084	0·101	15·5
ZnO(Zn)	5·4	0·0055	0·007	2
Ga_2O_3	14·2	<0·0035	—	0
$(C)Cu-Cu_2O$†	3·18	0·044	0·044	22
$Fe-Fe_2O_3$	11·9	0·038	0·038	0
$Pt-SiO_2$	75	0·081	0·088	7
$Pd-SiO_2$	76	0·056	0·060	8
Fe	8·64	0·017	0·024	0

* Expressed as fractions of the B.E.T. (N_2) monolayer.   † Measurements at $-78°$.

TABLE 5.
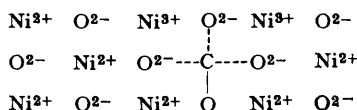
Tests for catalyst poisoning.

Oxide	Pumping time* at 20° (hr.)	$10^{-13}k_1\phi$	Oxide	Pumping time* at 20° (hr.)	$10^{-13}k_1\phi$
MgO	—	1·61	Cr_2O_3 (reduced)	—	5·34
	2	1·65		2	5·46
	18	1·60	$NiO(NO_3)$	—	2·07
γ-Al_2O_3	—	$1·77 \times 10^{-2}$		18	2·00
	4	$1·85 \times 10^{-2}$	Y_2O_3	—	9·07
ZnO	—	4·48		2	9·10
	2	4·30		18	9·25
	16	4·53	Ho_2O_3	—	62·8
				4	64·0

* The first run on each oxide had the normal high-temperature pumping.

TABLE 6.

Substance	Wt. (g.)	P_{CO} (cm.)	$10^{-13}k_1\phi$	Substance	Wt. (g.)	P_{CO} (cm.)	$10^{-13}k_1\phi$
MgO	1	2·0	1·61	Ho_2O_3	0·4	2·0	60·0
	2	2·0	1·60		5·0	2·0	62·8
	1	0·5	1·73	α-Fe_2O_3	1·0	1·0	1·51
	1	4·0	1·65		1·0	2·0	1·40
$NiO(NO_3)$	0·3	2·0	2·20		1·0	4·0	1·82
	1·0	2·3	2·00				
	3·0	2·0	2·07				
	1·0	4·0	2·32				

vacancies which help to stabilize and localize the complex. The carbon monoxide molecule may then align itself above or in the surface vacancy pair with the carbon atom over or in the cation vacancy and the oxygen atom over or in the anion vacancy: a resonating charge complex could then be set up, involving three surface O^{2-} and the oxygen atom from the carbon monoxide molecule, in which event $n = 3$, thus:

$$
\begin{array}{ccccccc}
Ni^{2+} & O^{2-} & Ni^{3+} & O^{2-} & Ni^{3+} & O^{2-} & \\
O^{2-} & Ni^{2+} & O^{2-}\text{---}C\text{----}O^{2-} & & Ni^{2+} & \\
Ni^{2+} & O^{2-} & Ni^{2+} & O & Ni^{2+} & O^{2-} &
\end{array}
$$

Surface complexes of this size are not readily described by any of the notations so far suggested,[19,20] as the resulting equations are somewhat cumbersome. Thus for NiO we might write, in the notation of Rees:[19]

$$CO(g) + (O^{2-}/\square_s^-)_3(Ni^{3+}/\square_s^+)_2(\square_s^-)(\square_s^+) \rightleftharpoons (C/\square_s^+)(O^-/\square_s^-)_4(Ni^{2+}/\square_s^+)_2 \quad (16)$$
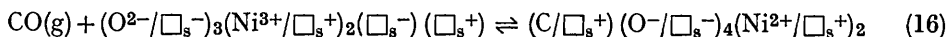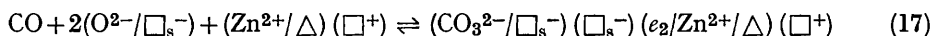
This neglects any associated, possibly sub-surface, defects needed to stabilize and localize the catalytic centre, and of course does not indicate the geometry involved.
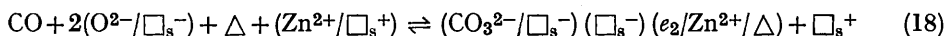
The dependence of the reactivity of NiO upon positive holes is partly supported by the results upon doped NiO given in Table 2, and is discussed later. The total surface reaction (exchange of carbon monoxide with a substantial part of the surface O^{2-} ions) at higher temperatures is probably governed by the formation and/or mobility of positive holes in the surface which would permit the random formation of complexes such as those shown in the left-hand side of equation (16), and their slow migration once formed.

This reaction, equation (15) or (16) or the equivalent, occurring on relatively few stable and immobile catalytic sites, will account for both the localized surface exchange shown in Table 3 and the homomolecular exchange reaction (Tables 1 and 2). A clear distinction must be drawn here between the present work and the earlier[4,5,7e] surface–gas oxygen-exchange experiments with carbon monoxide: the latter were designed to detect and measure a gross effect—the exchange of ^{18}O between the gas (at pressures of 2—6 cm. in a reaction system of roughly the same volume as that used here) and the majority of the O^{2-} ions lying in the oxide surfaces. Not unexpectedly, higher temperatures and activation energies are needed for the latter. We postulate the widespread occurrence on oxides of non-mobile reactive centres on which reactions essentially equivalent to (15) or (16) readily and reversibly occur around room temperature: these centres will be stabilized and activated by associated defects, the nature of which may well vary with the oxide. They may be located at geometric irregularities in the lattice—defect pairs, slip planes, or screw dislocations—or at the boundaries of micro-domains.[25]

To consider an oxide of a different type from NiO, we may take ZnO. Here an interstitial metal ion might be thought necessary, in somewhat the following way:

$$CO + 2(O^{2-}/\square_s^-) + (Zn^{2+}/\triangle)(\square^+) \rightleftharpoons (CO_3^{2-}/\square_s^-)(\square_s^-)(e_2/Zn^{2+}/\triangle)(\square^+) \quad (17)$$

The general surface reaction at higher temperature being written, roughly as before:[4]

$$CO + 2(O^{2-}/\square_s^-) + \triangle + (Zn^{2+}/\square_s^+) \rightleftharpoons (CO_3^{2-}/\square_s^-)(\square_s^-)(e_2/Zn^{2+}/\triangle) + \square_s^+ \quad (18)$$

Equations similar to (16) and (17) can of course be written for other oxides.

An alternative is to regard the active centres as being due to the presence of altervalent ion impurities which lead to point defects in the surface essentially the same in function as those written in equations (16) and (17); probably none of the oxides used was sufficiently pure for this possibility to be excluded. Thus e.s.r. measurements[26] have shown the presence of tervalent cation impurities in high-purity MgO, and similar paramagnetic effects associated

[25] Anderson, *Proc. Chem. Soc.*, 1964, 166.
[26] Wertz, Auzins, Griffiths, and Orton, *Discuss. Faraday Soc.*, 1959, **28**, 136.

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with altervalent metallic impurities have been detected at low temperatures in high-purity irradiated CaO.[27]

It is to be noted that the reactive sites are special areas with unusual properties. Equation (15) is formally the same as that suggested many years ago by Garner to explain the chemisorption of carbon monoxide upon transition metal oxides. The important distinction is that Garner did not regard the reaction as readily reversible: he thought it was responsible for the measured heats of adsorption. This argument has been maintained by the Bristol school, and Stone has recently[28] adduced reasons, based on his calorimetric data, why reaction (15) cannot be readily reversible on Cu–Cu$_2$O, particularly at low temperatures ($-78°$) and so cannot explain our earlier observations[4] of some limited ^{18}O-exchange between carbon monoxide and Cu–Cu$_2$O surfaces at $-78°$ and 10^{-1}—10^{-2} mm. He prefers a purely geometric explanation based on the unusual cuprite oxide structure, and uses this reason to explain the difference in reactivity which we found between Cu–Cu$_2$O and Ni–NiO (*sic*) in the general surface oxygen-exchange of carbon monoxide and these oxides. On this we must comment, first that our earlier work was not upon nickel oxide films on nickel metal but, as is clearly stated,[7e] upon NiO made from the carbonate: reference to Tables 1 and 2 shows that metal–metal oxide systems are for some reason very active (and the activity is difficult to reproduce, cf. Cu–Cu$_2$O) while it so happens that NiO(CO$_3$) is by far the least active nickel oxide we have examined: this was part of the preparation used in the earlier work. Again the other oxide of the cuprite structure, silver oxide, is not particularly active. We conclude that, although simple geometric considerations must have some part to play and may be of greater importance when dealing with the general CO–surface oxygen-exchange, they are not the most important factor.

Since readily reversible carbon monoxide adsorption upon Cu–Cu$_2$O does occur at $\sim 10^{-1}$ mm. involving both localized ^{18}O-exchange with the surface and the homomolecular exchange at $-78°$, the thermochemical argument must be in error.

We believe the reason to be that Stone, for processes occurring on a small part of the surface at lower temperatures, makes use of heats derived from room-temperature measurements of bulk reactions and of processes which take place on an appreciable fraction of the surface. These surfaces obviously possess some heterogeneity, and it is not unreasonable to assume that at the catalytic centres, which our work at 10^{-1} mm. of carbon monoxide (Table 3) shows to exist in small numbers on many oxide surfaces, the energies involved are different from those elsewhere on the surface. The extrapolation from room temperature to $-78°$ may also introduce some error. Our observations[5, 7e] of a more general exchange around room temperature between carbon monoxide and Cu–Cu$_2$O surfaces at pressures of 2—6 cm., involving 30% and upwards of the surface O^{2-} ions, depending upon the activity of the preparation, may, as we have already pointed out,[7e] be due to the fall in the calorimetric heat of adsorption of CO with coverage. Our present experimental arrangements do not permit an examination of the carbon monoxide equilibration reaction at 10^{-1} mm. and at 2 cm., followed by a B.E.T. determination, all in succession upon the same specimen without any intervening exposure to air in transferring from one apparatus to another. Such work is planned. Nevertheless recalculation of our earlier[4] experimental results at $-20°$ and $-78°$ and 10^{-2} to 10^{-1} mm. from equation (14) gives reasonable values for ϕ, as the last two entries in Table 3 show: comparison of n_a with ϕ shows that the catalytic centres may be concerned with 10% or so only of the adsorption that might occur under the conditions of the heat measurements.

We believe that the reaction rates, k_e, we have obtained at *ca.* 2 cm. are correctly related to $k_1\phi$ by equation (11), that is, that we have measured the true surface reaction, neither adsorption nor desorption being rate-determining. Thus we have established by special experiments during the measurements of the adsorption isotherms summarized in Tables 2 and 4 that, at least above 0·5 mm., adsorption equilibrium was attained within a few

[27] Shuskus, *J. Chem. Phys.*, 1963, **39** (i), 849.
[28] Stone, *Adv. Catalysis*, 1962, **13**, 13.

seconds on raising or lowering the pressure: the kinetic experiments at *ca.* 2 cm. lasted from 15 min. to 3 hr. or more. The calculation of k_1 and ϕ separately from equations (11) and (14) is open to some criticism, since it is possible that ϕ will change between 10^{-1} and 20 mm. because of the effect that increasing coverage of carbon monoxide may have upon the surface: it is impossible to assess the importance of this. Certainly in most cases the values of n_a in Table 3 at 10^{-1} mm. correspond to very much smaller coverages than those observed at 1 or 2 cm. (Table 4). Nevertheless, except for ZnO(Zn) the data of Table 3 are at least self-consistent, in that $\phi < n_a$: also if we assume an area, A_c, of 10 Å^2 for each catalytic site, the bombardment rate at 2 cm. from simple gas kinetic theory appears sufficient on all catalysts to account for the observed rate of reaction. Thus at 2 cm. and 300°K the bombardment rate, σ, is $7\cdot7 \times 10^{21}$ molecules cm.$^{-2}$ sec.$^{-1}$: from Table 3 it may be readily established that the product $\sigma\phi A_c$ is in all cases at least 3×10^3 greater than $k_1\phi$ when both quantities are expressed in molecules cm.$^{-2}$ sec.$^{-1}$; in some cases (Al$_2$O$_3$, Cr$_2$O$_3$) the factor reaches 10^5 or even 10^6. Unless the accommodation coefficients are very small, adsorption, *i.e.*, the formation of the correct reaction complex, should not be rate-determining. It may be remarked that Table 3 provides evidence for at least two types of adsorption of CO on some oxides: adsorption was still proceeding on La$_2$O$_3$, α-Fe$_2$O$_3$, CoO, and NiO+0·10% Li$_2$O and +1·0% Li$_2$O when the gas phase was sampled, but in spite of this the equilibration reaction was complete. A second experiment on La$_2$O$_3$, Ho$_2$O$_3$, ZnO(Zn), and NiO(NO$_3$) in which the carbon monoxide was left in contact at 10^{-1} mm. for *ca.* 18 hr. after adsorption equilibrium was attained, showed that ϕ did not change once the equilibration reaction was finished.

It seems convenient to review the values of k_1 and of ϕ presented in Table 3 and then to consider Tables 1 and 2. With Sc$_2$O$_3$, TiO$_2$, and NiO (CO$_3$) the amount of ^{18}O-exchange with the surface was too small to detect. For these oxides ϕ was calculated on the assumption that $(\gamma_0 - \gamma_\infty)$ was just equal to the experimental error of the isotope-abundance measurements (taken as $\pm 1\%$ on the ratio being measured): this gives an upper value for ϕ (which is stated) and therefore from equations (11) and (14) a corresponding minimum value for k_1. If the mechanism we suggest is broadly correct we might expect either k_1 or ϕ or both (or $k_1\phi$) to show some regularity with reference to oxide-type or the position of the metal in the Periodic Table. The results of Table 3 are somewhat disappointing in this respect: this, as mentioned above, may be because of irregular changes in ϕ between 10^{-1} and 20 mm.; owing to the method of calculation, any error in ϕ will also affect k_1. Unfortunately, ϕ cannot be determined from the amount of ^{18}O-exchange with the surface at higher pressures, as $(\gamma_0 - \gamma_\infty)$ is then too small, whilst the determination of equilibration rates at 10^{-1} mm. is not possible owing to the small amount of carbon monoxide used. We can say that the M$_2$O$_3$ oxides, except for γ-Al$_2$O$_3$, V$_2$O$_3$, and (possibly) reduced Cr$_2$O$_3$, have in general high intrinsic reactivity (large k_1) while the MO oxides from Mn to Zn are of somewhat lower activity. The low activity of Ga$_2$O$_3$ is an exception; on the other hand, the activity of MgO is notably high, as is that of TiO$_2$ and ZrO$_2$.

The regular increase of k_1 in the series La–Dy–Ho may be significant; further work is in hand upon other rare-earth oxides and comment is reserved.

Turning to ϕ, there seems no particular regularity to note, except that ϕ does increase with the addition of 0·01% Li$_2$O to NiO and then falls progressively as the Li content increases. The influence of the method of preparation of ZnO upon ϕ and the invariance of k_1 are interesting; electron-microscopy shows the oxide from the carbonate to be a somewhat amorphous powder while ZnO(Zn), which was made by burning the metal in air, is much more crystalline: this difference is reflected in the B.E.T. areas (Table 4). The difference in ϕ is presumably another reflection of the more disordered nature of the former material.

The results in Table 1 show a number of interesting features: the general very low or zero activation energies, together with the reproducibility shown in Tables 5 and 6, indicate a simple, readily reversible reaction. It appears that highly refractory oxides (SiO$_2$, Al$_2$O$_3$, Nb$_2$O$_5$, and TiO$_2$) are of low activity, possibly owing to small values of ϕ (cf. TiO$_2$ in Table 3, although the low activity of Al$_2$O$_3$ appears to be due to a low k_1); the inactivity of GeO$_2$

is unexpected in view of the values found for the other Group IV dioxides, SiO_2, TiO_2, and ZrO_2. Passing across the first long Period from Ca to Ge no obvious regularity emerges: a similar remark applies to the few observations in the series Y to Ag. Doubtless any basic regularities are overshadowed by the variations in metal ion valency and in crystal structure: the activities may also be affected by traces of impurities which could act as electron traps or alternatively help to promote the reaction by stabilizing the catalytic centres. The materials used were generally of high purity but, except for NiO, no study has yet been made of the effect of altervalent ions upon the activity. However, with oxides of the same valency type, and the same or similar crystal structure, the activity often increases regularly as the sub-groups of the Periodic Table are traversed. Thus MgO–CaO; MgO–ZnO; Al_2O_3–Sc_2O_3–Y_2O_3–La_2O_3; Al_2O_3–Ga_2O_3; SiO_2–TiO_2–ZrO_2; and the rare-earth series La_2O_3–Dy_2O_3–Ho_2O_3. In these cases the activity as measured by $k_1\phi$ increases with atomic number (except for La–Dy) but the significance of this is probably related to changes in k_1, as is apparently the case with the rare earths. It is curious that, if the values of ϕ in Table 3 are reliable, k_1 often changes in the opposite direction to $k_1\phi$.

A similar regularity is found in the series of doped NiO samples prepared from the nitrates, the results for which are collected in Table 2. If we assume that the reactivities reflect the increasing concentration and mobility of positive holes as we go from Cr- to Li-containing materials, the series falls into the expected pattern, and the positions of NiO prepared from the hydroxide and of the superficially-oxidized Ni(Ni–NiO) relative to this series are interesting and suggestive. It would appear that the NiO(OH) sample is disordered and labile, as is to be expected from its method of preparation and high surface area, while the $NiO(CO_3)$, possibly because of its higher temperature of preparation (800°), is almost inactive. The disordered state of NiO(OH) is also reflected in the fact that this is the only oxide examined, where, under the conditions of the reaction at 2 cm., the carbon monoxide suffered exchange with the lattice oxygen of the catalyst surface: this point is further discussed under Cu–Cu_2O. The Ni–NiO similarly appears highly disordered, again as expected: the activity here is associated with the presence of nickel ion vacancies in the growing lattice—cf. equation (16).

The change in activity of the NiO preparations with nature and concentration of dopent is similar to the changes in other properties. For example the amount of carbon monoxide adsorbed (Table 2) and of oxygen chemisorbed[7d] and of carbon dioxide absorbed[29] and the semiconductivities of these preparations also show analogous regularities.[7d] All these properties are related to the ability of the solid to provide mobile positive holes at the surface (the semiconductivity measurements were d.c. and thus relate only to the surface conductivity). The small energies of activation found for the samples containing 0·01% and 0·1% Li_2O may be indicative of the increasing difficulty of the desorption step or may be due to poisoning by carbon dioxide; in any case the zero figure for the 1·0% sample is by comparison unexpected.

Various preparations of NiO have been the subject of much study because of their importance in theories of the solid state and of catalyst action. For this reason attempts were made to discover more about the nature of the catalytically-active centres on the NiO prepared from the nitrate and on the Ni–NiO sample. The activity of both catalysts at 20° and 2 cm. of carbon monoxide remained unaffected by pre-adsorption of up to 1/10 a B.E.T. monolayer of oxygen or carbon dioxide at 20°; similarly the decomposition of up to 1/30 of a monolayer of nitrous oxide at 20° was without effect. In both cases however saturation of the surface with carbon dioxide at 20° (10 min. exposure to 2 cm.) followed by pumping for 15 min. at 20° completely poisoned the surface; no carbon dioxide was subsequently found in the carbon monoxide passing to the mass spectrometer.

The pre-adsorption of oxygen was nearly sufficient to saturate the surfaces with respect to this gas; the adsorbed species at this temperature is likely to be a mixture of O_2^- and O^-. The decomposition of N_2O forms first O^-;[7d] no oxygen was detected in the gas phase after

[29] Winter, *Discuss. Faraday Soc.*, 1959, **28**, 217.

this decomposition and the surface was probably approaching one-third to one-half saturation with respect to O^-, assuming that the same sites are active in promoting the N_2O-decomposition as are used in oxygen-chemisorption. These experiments give no direct information on the nature of the sites active in the homomolecular reaction; we can say only that they are probably few in number and that the experiments provide further evidence that these surfaces are heterogeneous, different sites being active in different reactions—a fact that we have already demonstrated for the nitrous oxide decomposition and the CO–O_2 reaction by measurements of the ^{18}O-exchange between gas and surface.[5]

The high activity of Ni–NiO may be a general phenomenon of metal–metal oxide systems, prepared by controlled oxidation to a few tens of atomic layers of a finely-divided pure powdered metal at room temperature or thereabouts. Thus the superficial oxidation of iron powder at room temperature probably produced a surface film consisting mainly of γ-Fe_2O_3;[30] this has a significantly greater activity than the powdered α-Fe_2O_3, although

TABLE 7.

Experiments on Fe–Fe_2O_3.

Run No.	Pretreatment; outgassing		$10^{-13}k_1\phi$	Run No.	Pretreatment; outgassing		$10^{-13}k_1\phi$
1	18 hr.	320°	1·83	8	$1\frac{1}{2}$ Monolayers O_2 at 20°:		0
2	18 hr.	320°	1·87		2 hr. at 20°		
3	$\frac{3}{4}$ hr.	21°	1·60	9	18 hr.	320°	1·40
4	$\frac{3}{4}$ hr.	20°	1·22	10	22 Monolayers O_2 at 21°:		0
5	1 hr.	20°	0·76		2 hr. at 21°		
6	18 hr.	320°	2·00	11	18 hr.	320°	3·46
7	18 hr.	320°	1·92	12	18 hr.	320°	3·46

of course the increase here could be due to the change of oxide type. Cu–Cu_2O also appears exceedingly active but no comparison has been made with bulk Cu_2O. It appears that the activity of these finely-divided preparations of metals and that of the metal–metal oxide systems made from them by careful superficial oxidation, are critically dependent upon minor differences in the preparation procedure; thus neither of the two Cu–Cu_2O preparations used here was as active as that made some years ago.[4] All three catalysts were prepared from the same master batch of copper prepared by reduction with hydrazine and kept sealed in a glass tube after it was washed and dried. Similarly the two samples of iron prepared from the batch of Fe_2O_3 used in this (and earlier) [7c] work differ in activity by a factor of 16. It is not known whether the bulk oxides which form the major object of the present study are equally sensitive since duplicate preparations of these materials have not been tested. It is probable that the method of preparation of the metal–metal oxide catalysts ensures the incorporation of a relatively large number of lattice vacancies which would be expected to lead to high activity.

In similar experiments to those on Ni–NiO it was found that exposure of Cu–Cu_2O to 1 mm. of oxygen at $-78°$ completely poisoned the surface for the homomolecular carbon monoxide reaction: some carbon dioxide was formed but the reactivity was only restored by pumping for 2 hr. at 190°. Treatment with oxygen at 20° followed by addition of the carbon monoxide 24 hr. later at $-78°$ produced a similar poisoning but no formation of carbon dioxide. In the first case the chemisorbed oxygen was presumably held on or near the surface as O_2^- or O^- owing to the slow movement of defects through the solid at low temperatures: some of the oxygen was then able to oxidise the carbon monoxide but no sites were available for the homomolecular exchange. At 20° the chemisorbed oxygen was all incorporated but sufficient movement had not occurred to redistribute the defects through the solid and reactivate the surface. Similarly, when the finely-divided iron preparation had been oxidised at room temperature to a depth of about $1\frac{1}{2}$ and later 25 atomic layers and then pumped for 4 hr. at 20° it was in both cases quite inactive; these results are recorded in Table 7: the activity recorded in Table 1 for Fe–Fe_2O_3 was only achieved after this preparation had been pumped

[30] Wyn Roberts, *Trans. Faraday Soc.*, 1961, **57**, 99.

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for 18 hr. at 320°. In contrast to the lack of reproducibility between duplicate samples, both the Cu–Cu$_2$O and the Fe–Fe$_2$O$_3$ preparations were very reproducible in reactivity when outgassed between runs for 2 hr. at 160° and 320°, respectively. This poisoning by oxygen of metal–metal oxide surfaces around room temperature may alternatively be due to the formation of neutral ion-pairs[31] which are destroyed by incorporation of oxygen at higher temperatures: these ion-pairs could poison the reaction either by acting as deep traps for the electrons from the right-hand side of equation (15), thus preventing its reversal or simply occupying the active sites.

Though the activity of Cu–Cu$_2$O may be anomalously high, that of CuO appears normal when compared with the neighbouring MnO, CoO, NiO, and ZnO. In this series there is no great difference in reactivity and certainly not the dependence that might perhaps have been expected from the d-band structure of the metal ions: CuO and ZnO are of different crystal types from the other three. The high apparent energy of activation found for CuO may be due to a small amount of chemisorbed carbon dioxide acting as a poison: some carbon dioxide was desorbed from this catalyst on raising the temperature to 100° after pumping for 10 min. at 20°. The normal activity of Ag$_2$O is interesting in view of the great activity of Cu–Cu$_2$O, and has already been commented upon. The reaction with Ag$_2$O at 20° was rapidly poisoned by the formation of carbon dioxide —50% of the monoxide was oxidised in 15 min. There was no exchange of ^{18}O between the unoxidised monoxide and the Ag$_2$O detectable at 2 cm. pressure in spite of this extensive oxidation. At −45° the formation of carbon dioxide was much less rapid, but even so the homomolecular reaction stopped in 12 min. after proceeding to less than 10% of completion.

Poisoning by formation of carbon dioxide was also found with PdO at room temperature, with considerable adsorption of carbon monoxide: at −78° the homomolecular reaction proceeded quite rapidly but was poisoned in 10 min., although no dioxide was found in the gas phase. The adsorption of carbon monoxide at −78° was very much less than at room temperature but was still continuing after 3 hr. On the other hand, PtO$_2$ did not catalyse the homomolecular reaction at either temperature; it exhibited strong and very rapid adsorption of carbon monoxide at −78° (*ca.* 2·6 ml. at s.t.p. on 83 m.^{2}), *ca.* 80% being desorbed on warming to 20°: no carbon dioxide was formed. It may be noted that McKinney[32] observed induction periods of between 20 and 132 min. when dry PtO$_2$ was exposed to carbon monoxide at 76 cm. and 25°: the delay was followed by an explosion and the PtO$_2$ was autocatalytically reduced to metal. It is probable that the homomolecular reaction on this oxide is prevented by the formation of a strongly chemisorbed layer of carbon monoxide on all the active sites.

V$_2$O$_3$ is totally inactive, which may be due to sintering during preparation: the reduction of V$_2$O$_5$ by hydrogen took over 200 hr. at 950° and the product had a relatively small surface area. The difference in reactivity between Cr$_2$O$_3$ in the oxidized and in the reduced states is most striking and parallels that found for these preparations in the H$_2$–D$_2$ reaction.[33,34] In the present work it was found that the oxidized form adsorbed less than 0·05 of a monolayer of carbon monoxide whereas the reduced form under the same conditions rapidly took up 0·45 of a monolayer (Table 4). Very long periods of outgassing of the oxidised form (100 hr. at 520°) produced a small degree of activity in the homomolecular reaction but this was poisoned in less than 4 min. at 20°; no carbon dioxide was found in the gas phase in any experiment with Cr$_2$O$_3$. There is no doubt that the difference in reactivity is due to tenaciously held oxygen; there is much evidence from earlier work for this. Thus the reduced form is weakly n-type and the oxidized a p-type semiconductor[35] while on continued evacuation at high temperature the conductivity falls and the activation energy associated with semiconduction rises from 11 to 35 kcal.[7c] The excess of oxygen has been determined chemically[34] and reduction is associated with a distinct colour change towards the blue.

[31] Grimley and Trapnell, *Proc. Roy. Soc.*, 1956, *A*, **234**, 405.
[32] McKinney, *J. Amer. Chem. Soc.*, 1934, **56**, 2577.
[33] Dowden, Mackenzie, and Trapnell, *Proc. Roy. Soc.*, 1956, *A*, **237**, 245.
[34] Weller and Volz, *J. Amer. Chem. Soc.*, 1953, **75**, 5227; 1954, **76**, 4695.
[35] Chapman, Griffiths, and Marsh, *Proc. Roy. Soc.*, 1954, *A*, **224**, 419.

Cr_2O_3 also appears anomalous in its low power to catalyse the N_2O decomposition,[36] but this is true only of the oxidized form:[37] the reduced form is very active until sufficient N_2O has been decomposed to re-form the poisoning layer of oxygen.[5]

The method by which oxygen poisons Cr_2O_3 is not clear. Below the Néel temperature of *ca.* 45° the solid is antiferromagnetic with the antiparallel spins of nearest-neighbour Cr^{3+} ions coupled;[38] this should be the structure of the bare (reduced) surface. Recent work[39] upon the e.p.r. spectrum of the Cr_2O_3–Al_2O_3 system has confirmed this and shown that the oxidized form is characterized by a spectrum due to single uncoupled electrons, trapped either by the chemisorbed oxygen or by higher-valency chromium ions. An aqueous extract of the oxidized form gives a strong reaction for chromate.[7c] It may be, as suggested by Davis,[40] that an array of coupled Cr^{3+} ions is peculiarly suited to the promotion of certain types of weak chemisorption, such as that of hydrogen and, as we now find, carbon monoxide. Alternatively the oxygen may merely occupy particularly active sites, of the type we have postulated earlier, on to which the carbon monoxide would otherwise go: or it may be chemisorbed elsewhere on the surface, trapping the electrons required for the catalysis.

The metals examined, as seen from Table 1, fall into the following series in order of increasing activity: Ag, Cu, Pd, Pt, Fe, and Ni. The two platinum-group metals were supported on Cabosil and the others were in the form of powder or sinter. It is seen that the iron and copper preparations varied considerably in activity from batch to batch so that the exact order of reactivity may not be significant; it may be noted, however, that silver and copper are also very poor in promoting many reactions involving hydrogen, probably because of lack of holes in the *d*-band.[41] It is significant that the magnetic properties of this series of metals divide sharply between Cu and Pd, Cu and Ag being diamagnetic and the other four para- or ferro-magnetic. Also the outstanding but transient activity of nickel may be associated with the ready reaction between nickel and carbon monoxide to form $Ni(CO)_4$, the first stage of which must involve extensive adsorption of the gas which, if even partly reversible, would be expected to lead to homomolecular exchange, at least until the surface was poisoned by the carbonyl. As noted, reaction did occur but it was rapidly poisoned; as the rate slowed down increasing amounts of $Ni(CO)_4$ were detected in the gas phase by mass-spectrometry.

Some recent work[42] on evaporated Ni films has failed to reveal the homomolecular reaction at 0°, possibly because of the low pressures of carbon monoxide used; however, Yates[43] confirms our results.

The observations on iron require special consideration. This was the first catalyst found to promote[2] the homomolecular reaction in carbon monoxide and the interaction between it and carbon monoxide has been the subject of much investigation by Eischens.[2,3] By the use of isotopic molecules Eischens has demonstrated the heterogeneous nature of the iron surface and has also shown that not all the carbon monoxide adsorbed at low temperatures is readily removed by pumping; the last traces are only desorbed by pumping at higher temperatures and appear as dioxide in isotopic equilibrium with carbon monoxide desorbed at the same time, although there is no exchange between the two gases in contact with iron at 25°. Our sample of iron was prepared in the same way as that used by Eischens and in a series of similar experiments we have confirmed his observations. We have also found that the last traces of carbon monoxide are only removed from Pd–SiO_2 and Pt–SiO_2 as carbon dioxide at higher temperatures (*ca.* 200°). In view of the widespread activity of oxides the question therefore naturally arises whether the activity of metals is due to the formation of

[36] Dell, Stone, and Tiley, *Trans. Faraday Soc.*, 1953, **49**, 201.
[37] Schwab and Schultes, *Z. phys. Chem.*, 1930, *B*, **9**, 265.
[38] Brockhouse, *J. Chem. Phys.*, 1953, **23**, 961.
[39] O'Reilly, *Adv. Catalysis*, 1960, **12**, 99.
[40] Davis, in "Chemisorption," ed. W. E. Garner, Butterworths, London, 1957, p. 227.
[41] Couper and Eley, *Discuss. Faraday Soc.*, 1950, **8**, 172.
[42] Suhrmann, Heyne, and Wedler, *J. Catalysis*, 1962, **1**, 208.
[43] Yates, *J. Phys. Chem.*, 1964, **68**, 1245.

small amounts of oxide by decomposition of carbon monoxide or whether clean metal surfaces themselves possess activity.

A succession of homomolecular exchange experiments was performed upon a batch of iron; these are summarized in Table 7. It is evident that prolonged exposure to carbon monoxide slowly poisons the surface, probably owing to a carbiding reaction, the oxygen thereby produced being partly used to form small amounts of carbon dioxide if the surface is cleaned up by pumping at high temperature, and possibly partly incorporated to form surface oxide. The addition of oxygen before experiments 8 and 10 was performed slowly in small increments at room temperature, in the presence of 1 cm. of helium. The B.E.T. area of the sample was measured at the beginning and at the end of this series of 12 runs, and it increased by 30%. In calculating the rate constants it was assumed that this change occurred during the formation of the thicker oxide layer before experiment 10. Run 9 shows that a thin oxide layer is significantly less active then the clean metal, while the last two experiments indicate that a thicker oxide film is much more active. The lack of activity in experiments 8 and 10 has already been commented upon. We conclude that the clean iron surface possesses an activity of its own and that the formation of small amounts of surface oxide (or carbide) reduces this activity.

We consider that the homomolecular reaction upon Fe, Ni, Pd, and Pt probably occurs by the method suggested by Webb and Eischens [2] for the reaction on iron which assumes lines or chains of carbon monoxide molecules, adsorbed in the "linear" form with the carbon atoms nearest the metal, the molecules undergoing lateral interaction with their neighbours, thus leading to a mixing of the oxygen atoms. But there is no reason to limit the many-molecule complex to linear chains. Two-dimensional arrays might be involved, limited by the topology or defect structure of the surface; or the square dimer discussed earlier could be the active species, as it possesses the correct C–O bond-stretching characteristics to account for the shifts of some of the infrared bands with increasing interaction as the coverage is increased.[44,45] The heterogeneity of the surface, readily shown by isotopic tracer experiments, is evidenced by the tenacious retention of some of the carbon monoxide, by our finding that iron is slowly poisoned, and also by the appearance of some dioxide when the last traces of adsorbate are removed.

The inactivity of graphite and of the three halides we have examined is not unexpected in view of our other findings. It is possible that the sample of ZnF_2 possessed a partial surface layer of oxide due to the tenacious retention of water as OH^- followed by decomposition *in vacuo* at high temperature (cf. de Boer [46])

$$2OH^- \longrightarrow H_2O + O^{2-}(s)$$
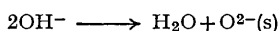
but if so it was not sufficient to give any detectable activity. The NaCl and Cu–CuCl were very pure.

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[44] Eischens, Francis, and Pliskin, *J. Phys. Chem.*, 1950, **60**, 194.
[45] O'Neill and Yates, *J. Phys. Chem.*, 1961, **65**, 901.
[46] de Boer, *Adv. Catalysis*, 1956, **8**, 67.