The rate of dissociation of CO$_2$ on nickel has been studied by means of the $^{14}$CO$_2$-CO exchange reaction. For pure polycrystalline nickel between 500 and 1240°C the forward rate constant, in mole cm$^{-2}$ s$^{-1}$ atm$^{-1}$, is given by:

$$\ln k_f = -\frac{7300}{T} - 2.57.$$ 

This is shown to be closely consistent with ideal chemisorption kinetics. Lower apparent rate constants when Ni$_S$$_2$ is added to the surface or at bulk saturation with sulfur are consistent with a surface blockage mechanism by chemisorbed sulfur which shows a Langmuir adsorption isotherm. The adsorption coefficient of sulfur, in at. pct $^\circ$, is deduced to be given by the equation:

$$\ln K_S = \frac{29,100}{T} - 15.82.$$ 

Results from associated Auger electron spectroscopic studies are in good accord with an ideal Langmuir adsorption isotherm for sulfur on polycrystalline nickel.

**ISOTOPE** exchange methods have been widely used for the determination of reaction paths and the rates of elementary steps in the heterogeneous catalysis of gas reactions, and much of this work has recently been reviewed by Ozaki. These methods have not been widely used in studies of high temperature reactions of metallurgical interest except by Grabke, who has studied the rates of reaction of carbon dioxide with several metal, oxide, and carbon surfaces by measurement of the rate of the overall exchange reaction:

$$^{14}$$CO$_2$(g) + $^{12}$CO(g) = $^{14}$CO(g) + $^{12}$CO$_2$(g).  

[1]

For the high temperature metal surfaces (Au, Ag, Pd, Cu, Ni, Co, Fe, and W) reaction [1] may be assumed to occur by the two partial reactions:

$$^{14}$$CO$_2$(g) = $^{14}$CO(g) + O(ad)  

[2]

and,

$$^{12}$$CO(g) + O(ad) = $^{12}$CO$_2$(g).  

[3]

Thus, a measurement of the rate of formation of $^{14}$CO gives the rate of reaction [2] on the metal surface, provided that the homogeneous gas reaction and reaction at other surfaces of the apparatus can be neglected. If the metal surface is in chemical equilibrium with the particular CO$_2$-CO mixture, this gives the exchange velocity and, by deduction, the rate constant of the untagged reaction:

$$\text{CO}_2(g) = \text{CO}(g) + O(ad)$$  

[4]

since the isotope effect which results from the difference in mass of carbon-12 and the radioactive carbon-14 is negligible.

Reactions [2] and [4] can be further broken down to the elementary steps:

$$\text{CO}_2(g) = \text{CO}_2(ad)$$  

[5]

$$\text{CO}_2(ad) = \text{CO}(ad) + O(ad)$$  

[6]

$$\text{CO}(ad) = \text{CO}(g).$$  

[7]

Grabke was able to rule out step [7], the desorption of CO, as rate determining but it is not possible by these methods to distinguish between [5] and [6] as the rate determining step, since each would yield the same rate law. Accordingly, the rate determining step is best considered as the dissociative chemisorption of CO$_2$, represented by Eq. [4].

A knowledge of the rate constant of reaction [4] is particularly important in understanding more complex metallurgical reactions. It has been concluded, for example, that reaction [4] is the rate determining step in the interfacial reaction for the decarburization of $\gamma$-iron and liquid iron by CO$_2$ and there is some evidence that it controls the initial rate of oxidation of solid iron in CO$_2$. The present work was initially undertaken to extend the temperature range of Grabke's study of reaction [4] on nickel in order to substantiate or deny a similar interpretation of the rates of decarburization of liquid nickel which were being concurrently studied in this laboratory.

Exploratory experiments at about 1000°C gave exchange velocities about 300 times higher than those reported by Grabke. Accordingly, the rates have been remeasured over the wide temperature range of 500 to 1240°C and the influence of sulfur on the rates has been investigated. As will be shown in this paper, interference by strongly chemisorbed sulfur is the most likely explanation for the large difference in rates.

**EXPERIMENTAL DETAILS**

**Gas Circuit and $^{14}$C Counting**

Purified CO$_2$ was first partially converted to CO and
$^{14}\text{CO}$ by passing through an alumina furnace tube held at 850 to 1000°C and containing about 40 g of powdered carbon which initially contained approximately 1 mCi of $^{14}$Cl. The CO was then oxidized to CO$_2$ by passing the gas through a column of CuO held at approximately 300°C. The resulting labelled CO$_2$ was then stored in a glass reservoir through displacement of dibutyl phthalate by a controllable peristaltic pump. The total activity of the stored gas was usually about 10 $\mu$Ci in 23 l (STP) and this activity could be roughly controlled by adjustment of the temperature of the carbon furnace.

During an experiment the desired CO$_2$-CO mixture was prepared by calibrated capillary flowometers, the labelled CO$_2$ being displaced from the reservoir by pumping in the dibutyl phthalate. An additional circuit permitted the same gas mixture to be prepared without radioactive CO$_2$. After passing over the nickel surface, the gas was passed through a molecular sieve (Linde, type 13X) and Ascarite to strip out the CO$_2$. The CO$_2$ was then oxidized to CO$_2$ in a column of CuO at about 300°C and passed through a 1 l vessel to waste. This vessel could be bypassed and isolated to permit drawing a sample of CO$_2$ from it by freezing into a gas bottle in a liquid nitrogen trap. By this means, samples could be obtained without significantly disturbing the gas flow. A similar method was used to obtain samples of the ingoing CO$_2$.

Counting of the $^{14}$C content of the CO$_2$ was by a lead sheathed internal Geiger-Müller tube (Twentieth Century Electronics Ltd., type GA26), essentially using the methods of Brown and Miller.$^{10}$ Counting was carried out at room temperature and at 100 mm Hg of CO$_2$ with 20 mm Hg of CS$_2$ to suppress the avalanche caused by CO$_2$ ions. Electronic quenching was by a circuit based on that of Neher and Pickering$^{11}$ but utilizing a 6BK4C vacuum tube. The appearance potential for the Geiger-Müller regime was typically 2500 V and counting plateaux of 250 to 300 V with slopes of 2 to 4 per 100 V were obtained. The count at 100 V above appearance was taken for the rate calculation after deduction of the background count obtained with natural CO$_2$.

**Experimental Arrangement and Materials**

The experimental arrangement was substantially the same as that described earlier, i.e., the gas was passed to the surface of the metal, which was held in an alumina crucible (1.6 to 2.1 cm ID), through a co-axially held alumina or silica tube of 5 to 7 mm ID, held 2 to 5 mm above the surface of the metal. Three different heating systems were used: a long resistance furnace of about 60 cm length, a short resistance furnace of about 30 cm length, and inductive heating in a water-cooled chamber. Temperature measurement was by noble metal thermocouple in the resistance furnaces and by two-color pyrometry (Millertron Inc. Therm-O-Scope) of the surface of the inductively heated sample.

High purity carbonyl nickel (International Nickel Co.) was used for specimen preparation. The typical impurity content of this material (in wt. pct.) is: S, 0.0003, Fe, 0.0015, Cu, 0.0001, and C, <0.01. Specimens were prepared by several methods: melting, surface grinding, and remelting into crucibles under CO$_2$/CO atmospheres; reusing decarburized samples from the concurrent study of decarburization kinetics, and metallographically polishing the upper surface of some of the specimens.

**Procedure**

The specimen was initially brought to temperature and held under a desired CO$_2$/CO ratio for several h. Labelled CO$_2$ was introduced, the CO$_2$/CO ratio being maintained at the same value. Samples for counting were then taken after a period of about 15 min with, usually, a second sample being taken after a further 10 to 15 min to confirm that a steady-state had been achieved. The temperature, gas composition, or flow-rate was then changed and samples again taken after 15 to 30 min. During periods when the labelled CO$_2$ was being prepared, or overnight, the specimen was kept under the CO$_2$/CO ratio required for the next experiment. When specimens were changed, blank experiments were carried out to confirm that significant exchange was not occurring on the refractory surfaces in the furnace tube.

For most of the experiments with added sulfur, a small pellet of NiS$_2$ (=10 mg) was dropped to the surface of the nickel through the gas delivery tube. Gas samples were then taken until successive samples, separated by at least 15 min, gave the same count. In other sulfur experiments, samples containing a bulk concentration of approximately 0.1 wt. pct S were used. These had been prepared by dissolving the NiS$_2$ in liquid nickel and then rapidly freezing.

**RESULTS**

If $k'$ is defined as the forward rate constant of reaction [2] for a bare surface, the rate per unit area can be formally written as:

$$\frac{dn_{14\text{CO}}}{dt} = k'(1 - \Sigma \theta_i)P_{14\text{CO}_2} - k''P_{14\text{CO}} \theta_O \tag{8}$$

where $\theta_i$ represents the fractional coverages of adsorbed species $i$ which can prevent dissociation of CO$_2$ by adsorption on reaction sites, $\theta_O$ is the fractional coverage by oxygen, $k''$ is the reverse rate constant, and $n$ and $P$ represent number of moles and partial pressure, respectively. Noting that for isotope exchange equilibrium,

$$\frac{P_{14\text{CO}_2}}{P_{14\text{CO}}} = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}/ \frac{k''\theta_O}{k'(1 - \Sigma \theta_i)} \tag{9}$$

and considering the exposure of a volume of gas $V$, at temperature $T$, to an area of metal surface $A$, we obtain,

$$\frac{V}{ART} \frac{dP_{14\text{CO}}}{dt} = k'(1 - \Sigma \theta_i)[P_{14\text{CO}_2} - P_{14\text{CO}} (P_{\text{CO}_2}/P_{\text{CO}})] \tag{10}$$

Integrating this expression from $t = 0$ to $t = t$ with the initial conditions that $P_{14\text{CO}} = 0$ and $P_{14\text{CO}_2} = P_{14\text{CO}_2}$, we obtain:

$$k'(1 - \Sigma \theta_i)t = \frac{V}{ART} \left( \frac{1}{1 + B} \right)$$