The Interfacial Kinetics of the Reaction of CO_2 with Nickel. Part I: The $^{14}CO_2$-CO Exchange Reaction and the Influence of Sulfur

A. W. CRAMB, W. R. GRAHAM, AND G. R. BELTON

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:

$$\ln k_f = -7300/T - 2.57.$$

This is shown to be closely consistent with ideal chemisorption kinetics. Lower apparent rate constants when Ni_3S_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^{-1}, is deduced to be given by the equation:

$$\ln K_S = 29,100/T - 15.82.$$

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.[1] 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,[2,3] oxide,[4] and carbon[5] surfaces by measurement of the rate of the overall exchange reaction:

$$^{14}CO_2(g) + {}^{12}CO(g) = {}^{14}CO(g) + {}^{12}CO_2(g). \quad [1]$$
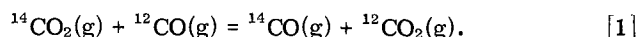
For the high temperature metal surfaces (Au, Ag, Pd, Cu, Ni, Co, Fe, and W) reaction [1] may be assumed[3] to occur by the two partial reactions:

$$^{14}CO_2(g) = {}^{14}CO(g) + O(ad) \quad [2]$$

and,

$$^{12}CO(g) + O(ad) = {}^{12}CO_2(g). \quad [3]$$
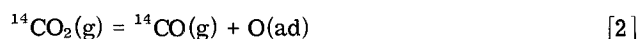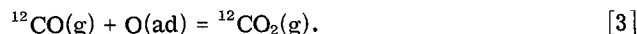
Thus, a measurement of the rate of formation of ^{14}CO gives the rate of reaction [2] on the metal surface, provided that the homogeneous gas reaction and reaction at other surfaces of the apparatus can be neglected. If the metal surface is in *chemical equilibrium* with the particular CO_2-CO mixture, this gives the exchange velocity[6] and, by deduction, the rate constant of the untagged reaction:

$$CO_2(g) = CO(g) + O(ad) \quad [4]$$

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:

$$CO_2(g) = CO_2(ad) \quad [5]$$

$$CO_2(ad) = CO(ad) + O(ad) \quad [6]$$

$$CO(ad) = CO(g). \quad [7]$$

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[6] 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 γ-iron[2] and liquid iron[7] by CO_2 and there is some evidence[8] 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[3] 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.[9]

Exploratory experiments at about 1000°C gave exchange velocities about 300 times higher than those reported by Grabke.[3] 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

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Manuscript submitted May 26, 1978.

^{14}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 m Ci of ^{14}C. 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 μCi in 23 1 (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 flowmeters, 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 was then oxidized to CO_2 in a column of CuO at about 300°C and passed through a 1 1 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 avalanching 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 pct/100 V were obtained. The count at 100 V above appearance was taken for the rate calculations 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,[7] *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 coaxially 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,[9] 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 flowrate 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 Ni_3S_2 ($\simeq$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 Ni_3S_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:

$$\frac{dn_{14CO}}{dt} = k'(1 - \Sigma_i\theta_i)P_{14CO_2} - k''P_{14CO}\,\theta_O \qquad [8]$$

where θ_i represents the fractional coverages of adsorbed species i which can prevent dissociation of CO_2 by adsorption on reaction sites, θ_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,

$$\left(\frac{P_{14CO_2}}{P_{14CO}}\right)_{eq} = \frac{P_{CO_2}}{P_{CO}} = \frac{k''\theta_O}{k'(1 - \Sigma_i\theta_i)} \qquad [9]$$

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

$$\frac{V}{ART}\frac{dP_{14CO}}{dt} = k'(1 - \Sigma\theta_i)[P_{14CO_2} - P_{14CO}(P_{CO_2}/P_{CO})]. \qquad [10]$$

Integrating this expression from $t = 0$ to $t = t$ with the initial conditions that $P_{14CO} = 0$ and $P_{14CO_2} = P^*_{14CO_2}$, we obtain:

$$k'(1 - \Sigma_i\theta_i)t = \frac{V}{ART}\left(\frac{1}{1+B}\right)$$
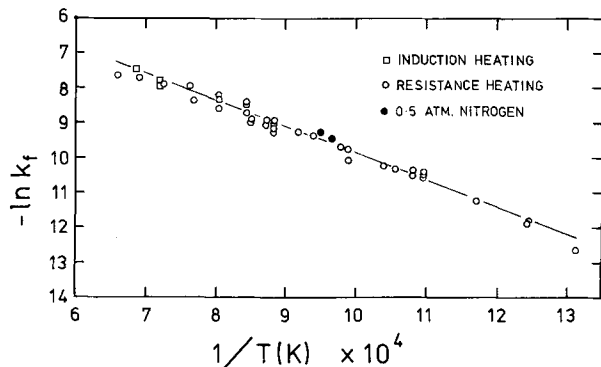
Fig. 1—Logarithm of the apparent rate constant for the dissociation of CO_2 on the pure nickel specimens as a function of reciprocal temperature.

$$\times \ln\left[\frac{P^*_{14CO_2} - P_{14CO}(1 + B)}{P^*_{14CO_2}}\right] \qquad [11]$$

where B refers to P_{CO_2}/P_{CO}. Taking the first equality from Eq. [9] and noting that at any instant,

$$P_{14CO_2} + P_{14CO} = P^*_{14CO_2} \qquad [12]$$

this becomes,

$$k'(1 - \Sigma_i\theta_i) = \frac{\dot{V}}{ART}\left(\frac{1}{1+B}\right) \ln\left[\frac{1}{1 - P_{14CO}/(P_{14CO})_{eq}}\right] \qquad [13]$$

where $\dot{V}$ is V/t, the volume flow rate of the gas mixture, and $(P_{14CO})_{eq}$ is the partial pressure of tagged CO if complete isotope equilibrium were to be achieved. The term in square brackets on the right hand side of Eq. [13] is related to the counting rate of the ingoing CO_2, N', and that of the CO_2 which results from conversion of CO, N, by the expression:

$$P_{14CO}/(P_{14CO})_{eq} = N(1 + B)/N'B. \qquad [14]$$

For convenience in presenting the results we will represent the apparent forward rate constant on the left hand side of Eq. [13] by the symbol k_f, i.e.,

$$k_f \equiv k'(1 - \Sigma_i\theta_i). \qquad [15]$$

Derived values for k_f, in units of mole cm^{-2} s^{-1} atm^{-1}, for the exchange reaction on nickel are presented in Arrhenius form in Fig. 1. No significant trends could be detected with flowrate, which was varied between 6.7 and 26.7 cm^3 s^{-1} (STP), addition of 0.5 atm N_2, or with CO_2/CO ratio, which was generally varied between 0.5 and 2. A slightly wider variation in the CO_2/CO ratio (0.5 to 3) was used at the low temperature of 913 K, and these results are shown in Fig. 2. The CO_2/CO ratio at 1 atm total pressure which is in equilibrium with graphite is approximately 1.3 at this temperature. Accordingly, the results for the two lowest ratios are at supersaturation with respect to graphite, as are the results for the three lowest temperatures with a CO_2/CO ratio of 2. No graphite particles were found on the surfaces of quenched samples.

The best straight line through the data in Fig. 1 (45 points) is given by the equation
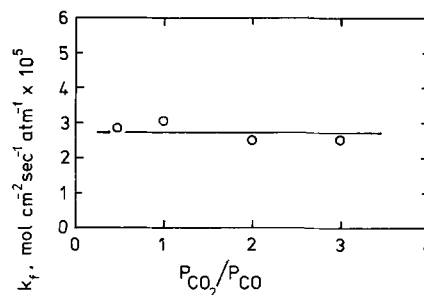

Fig. 2—Apparent rate constant as a function of CO_2/CO ratio for pure nickel at 913 K.

$$\ln k_f = -\frac{7300\ (\pm300)}{T} - 2.57\ (\pm0.31) \qquad [16]$$

where the uncertainties represent two standard deviations. No significant difference occurs in this equation if the results at thermodynamic supersaturation with respect to graphite are not included.

On making the initial addition of Ni_3S_2 to the surface of the specimen at 906°C (1179 K), the apparent rate constant decreased steadily from an original value of 1.6×10^{-4} to less than 3×10^{-6} mole cm^{-2} s^{-1} atm^{-1}, the lowest value which could be measured with reasonable accuracy, in a period of about 3.5 h. Accordingly, the experiments were confined to temperatures above 1050°C. Under these conditions, steady values of the apparent rate constant were reached in periods of 1 to 3 h after changes in temperature or specimen. After long periods, typically 30 to 40 h, the apparent rate constant began to increase. A second addition of Ni_3S_2 reduced the apparent rate constant back to the steady value within the time needed to perform a measurement (20 to 25 min). The steady-state results of 13 experiments with 3 specimens and with CO_2/CO ratios of 1, 2, and 3 are presented in Fig. 3. As with the results for pure nickel, there is no detectable dependence of the rate constant on the CO_2/CO ratio.

Two experiments were carried out on specimens with a bulk concentration of approximately 0.1 wt pct S with no further addition of Ni_3S_2 to the surface. Steady values of the apparent rate constant were reached within 20 min after reaching temperature. The close accord of these results with the others is also shown in Fig. 3.
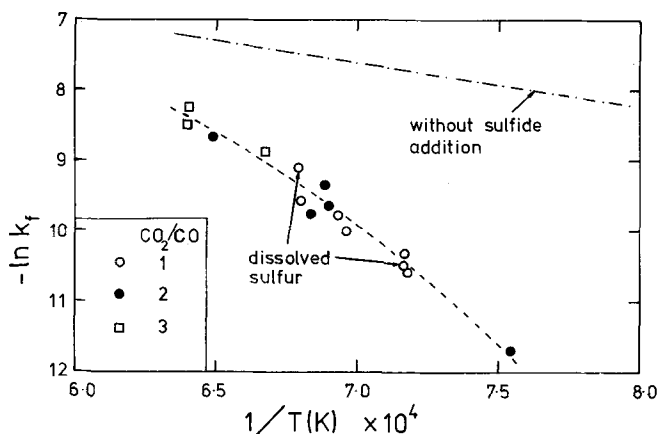

Fig. 3—The effect of Ni_3S_2 additions or bulk saturation by sulfur on the apparent rate constant.

DISCUSSION

As considered in more detail in the Appendix, the independence of k_f on the total pressure of CO_2 and the CO_2/CO ratio is consistent with Eq. [4] as the rate determining step, in accord with the deductions of Grabke.[3] The independence of k_f on CO_2/CO ratio also indicates that the equilibrium coverage by adsorbed oxygen is small, i.e., $\theta_O \ll 1$, under the conditions of the experiments. In view of this and the very high purity of the undoped nickel we may tentatively assume that the apparent rate constant k_f can be identified with the bare surface rate constant k'.

Recasting Eq. [16], we obtain:

$$k' = 0.076 \exp\,(-14{,}500/RT) \qquad [17]$$

where the activation energy is expressed in cal mole^{-1}. The preexponential factor in this equation is near to the classical collision frequency for CO_2 at the average temperature (1100 K) of the experiments, namely, 0.2 mole cm^{-2} s^{-1}. Accordingly, the data are reexamined in Fig. 4 in terms of ideal chemisorption kinetics for a gas molecule of mass M, for which,

$$k' = (2\Pi MRT)^{-1/2} \exp\,(-E/RT) \qquad [18]$$

or

$$RT \ln\,[k' \, (2\Pi MRT)^{1/2}] = -E \qquad [19]$$

for either classical collision theory or the activated complex theory for a mobile complex.[12] Within the experimental scatter there is no significant trend with temperature, indicating a close adherence of the rate constant to Eq. [18]. Thus, the dissociative chemisorption of CO_2 on a high temperature pure polycrystalline nickel surface appears to follow "ideal" chemisorption kinetics, with an activation energy of 16.6 ± 0.7 kcal mole^{-1}.

The Effect of Sulfur

If it is assumed that the sites for the adsorption of sulfur and the reaction of CO_2 are identical, that there are no other interfering species, and that the rate of reaction of CO_2 on a covered site is negligible, we may rewrite Eq. [15] as:

$$k_f = k'(1 - \theta_s). \qquad [20]$$

Assuming a Langmuir isotherm of the form,

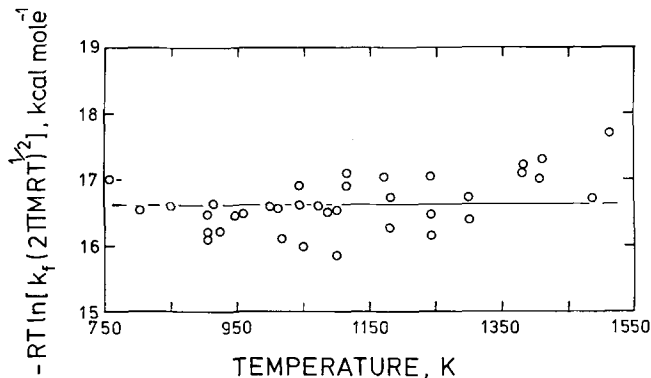$$\theta_s/(1 - \theta_s) = K_s \, a_s \qquad [21]$$

Fig. 4—Rate constants for the dissociation of CO_2 on the pure nickel, plotted in accordance with ideal chemisorption kinetics, Eq. [19].
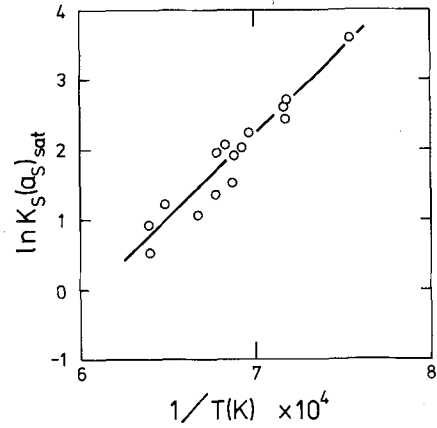
Fig. 5—Logarithm of the product of the adsorption coefficient and the concentration of sulfur at bulk saturation, assuming Eq. [23] to hold, as a function of reciprocal temperature.

where K_s is the adsorption coefficient and a_s is the bulk activity of sulfur, we obtain

$$k_f = k' \, [1/(1 + K_s \, a_s)]. \qquad [22]$$

There is good accord between the results obtained with specimens containing 0.1 wt pct S, which is above bulk saturation (see Fig. 7), and the results obtained by adding particles of Ni_3S_2 to the surface. Accordingly, the activity of sulfur can be taken to be that at bulk saturation of nickel by sulfur. Rearranging Eq. [22], we obtain:

$$K_s \, (a_s)_{sat} = (k' - k_f)/k_f. \qquad [23]$$

Values of the logarithm of this function for the experimental results are shown plotted vs reciprocal temperature in Fig. 5. The best straight line is given by:

$$\ln K_s \, (a_s)_{sat} = \frac{24{,}400 \, (\pm 3900)}{T} - 14.88 \, (\pm 2.68) \qquad [24]$$

where the uncertainties represent two standard deviations.

The expected apparent Arrhenius activation energy for the dissociation of CO_2 on sulfur-saturated nickel when $K_s \, (a_s)_{sat} \gg 1$ is readily calculated from Eqs.
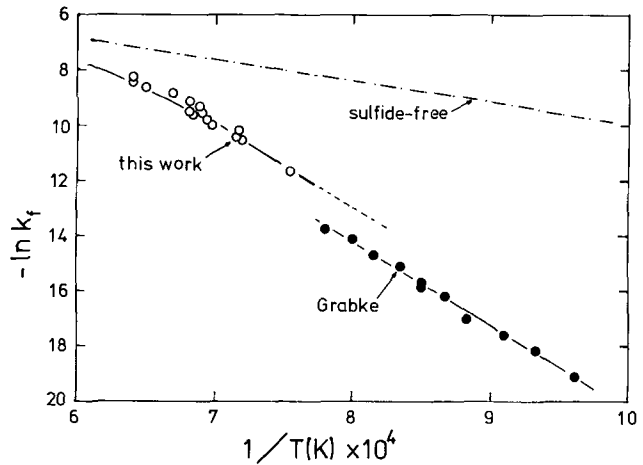
Fig. 6—Comparison of the apparent rate constants for the dissociation of CO_2 on sulfur saturated nickel with those of Grabke[3] on nickel foils.

[22], [24], and [17] to be 63 ± 8 kcal mole^{-1}. This is in experimental agreement with the value of 61.2 ± 0.3 kcal mole^{-1} which was obtained by Grabke[3] from his studies with nickel foil.

The reasonable quantitative agreement (within a factor of about 3) between Grabke's results and the extrapolation of the present results for sulfur-saturated nickel is shown in Fig. 6. This strongly suggests that his foils were similarly saturated with sulfur. Whether the source of the sulfur could be in the preparation of the foils, which was by Kersten's method[13] of electrolysis of nickel sulfate-sodium citrate solutions, or in the reaction gases cannot be answered by the present work.

The Adsorption Isotherm for Sulfur on Nickel

The solubility of sulfur in solid nickel has most recently been examined by Meyer[14] who established the solidus by combining his careful measurements of the activity of sulfur in liquid Ni-S melts with those of Brigham et al[15] for the activity of sulfur in solid Ni-S alloys. His results, which are in reasonable accord with the earlier work of Barbouth and Oudar,[16] are presented in Fig. 7. Up to about 1200°C, his results are closely described by the equation:

$$\ln (\text{at. pct S}) = -\frac{4700}{T} + 0.94. \qquad [25]$$

Assuming Henry's Law and taking the standard state for dissolved sulfur to be the 1 at. pct solution, Eqs. [25] and [24] can be combined to give an expression for K_S in units of (at. pct)$^{-1}$:

$$\ln K_S = \frac{29,000}{T} - 15.82. \qquad [26]$$

Assuming an ideal adsorption isotherm for sulfur at all bulk compositions clearly cannot be justified from the kinetic measurements alone, since all were carried out at bulk saturation. Accordingly, studies of the surface segregation of sulfur from low bulk concentration were carried out by high temperature Auger electron spectroscopy. The in situ heating technique, instrumentation, and experimental procedure were essentially identical to those which have been previously described in detail.[17] The sample was prepared by sectioning and metallographically polishing a carbonyl nickel pellet of well established low sulfur concentration: 3 ± 0.5 ppm (0.0005 at. pct).
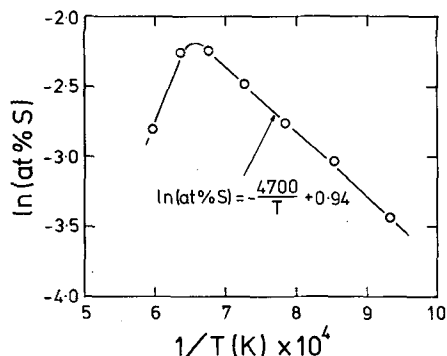The Auger peak height ratio S(152 eV)/Ni (848 eV)

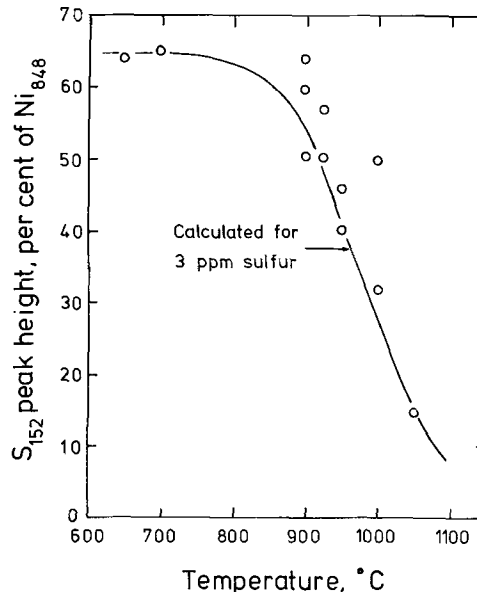Fig. 7—Results of Meyer[14] for the solubility of sulfur in solid nickel.

Fig. 8—Comparison of calculated coverages by sulfur with those determined by Auger electron spectroscopy of a specimen containing 3 ppm (0.0005 at. pct) S. Calculations are based on Eqs. [26] and [27] and assuming a peak height ratio of 65 pct for $\theta_s \rightarrow 1$.

was measured as a function of time at temperatures from 650 to 1050°C. Constant values (± 3 pct) were reached in 250 min at 650°C and in 10 min at 1050°C. The final values at all temperatures are presented in Fig. 8. The reproducibility is considerably poorer than in the previous work on segregation in iron-phosphorous alloys[17] and this is attributed to the severe surface roughening which occurred during the experiments because of the "onion skin" structure of carbonyl nickel pellets.

In view of the large difference in escape depths of 152 and 848 eV electrons, the surface concentration of sulfur may be taken to be directly proportional to the peak height ratio. Figure 8, therefore, is equivalent to a plot of the relative surface coverage of Ni by S, with $\theta_s = 1$ at a peak height ratio of approximately 65 pct, i.e., where the ratio becomes independent of temperature. Rearranging Eq. [21], we obtain:

$$\theta_S = \frac{K_S a_S}{1 + K_S a_S}. \qquad [27]$$

Substituting values for K_S from Eq. [26] and converting θ_S to the equivalent peak height ratio yields the continuous curve in Fig. 8. The agreement is surprisingly good and is strong evidence that the adsorption isotherm for sulfur on polycrystalline Ni is near to ideal, in that, within experimental error, the same value of K_S describes the adsorption at both bulk saturation and 0.0005 at. pct S. At 1000°C, this represents more than a hundred-fold change in bulk composition.

CONCLUDING COMMENTS

The accord between the temperature dependence of the rate constant for the dissociation of CO_2 on the undoped, high purity nickel and ideal kinetics of chemisorption, Eqs. [18] and [19] and Fig. 4, suggest that the assumption that these experiments were carried out with a clean surface is correct. This leads to an

apparent inconsistency in that the sulfur concentrations of these specimens were approximately the same as that of the sample used in the Auger studies. From the data in Fig. 8, adsorption of sulfur and interference with the rates might be expected at the temperatures of the kinetic studies. However, the calculated equilibrium pressure of COS under the conditions of the experiments is significant. Taking the available thermodynamic data[15,18] the calculated pressure is about 1.6×10^{-6} atm at 900 K and about 8×10^{-7} atm at 1500 K for 0.5 atm CO and 3 ppm S in Ni. There is thus a mechanism for cleaning sulfur from the surface. The rate of replenishment by solid state diffusion at low bulk concentration would be expected to be slow. The attenuation of the effect of sulfur after long periods when Ni_3S_2 was added to the surface is consistent with such a cleaning mechanism.

It is concluded that Eq. [17] gives the rate constant for the dissociation of CO_2 on a clean, polycrystalline nickel surface and that the interference by sulfur is by a simple site blockage mechanism. The adsorption of sulfur on polycrystalline nickel follows an essentially ideal adsorption isotherm, with a standard Gibbs energy of adsorption given, from Eq. [26], by,

$$\Delta G^O = -241,900 \ (\pm 33,000) + 13.15 \ (\pm 22.3)T \ \text{J} \qquad [28]$$

where the standard state for dissolved sulfur is the 1 at. pct solution and the uncertainties (two standard deviations) do not include any contribution from uncertainty in the solubility of S in Ni.

APPENDIX

The Rate Determining Step

The forms of Eqs. [8] to [13] resulted from taking the dissociative chemisorption of CO_2 (Eq. [4]) as the rate limiting step, in accord with the conclusions of Grabke.[3] It is important to examine if other mechanisms could reasonably be justified.

The principle of isotope exchange experiments[1] is that the measured rate of isotope exchange is a statistical fraction of the total exchange (labelled and unlabelled reactants) occurring in the system. Accordingly, the dependence of the rate of isotope exchange on the total partial pressures of reactants can be used to help establish the rate determining step. Since, by design, the experiments are carried out over long periods, chemical equilibrium may be reasonably assumed at the gas-metal interface, at least at the higher temperatures. Activities of, say, oxygen and carbon can then be expressed in terms of the gas composition, i.e., P_{CO_2}/P_{CO} and P^2_{CO}/P_{CO_2}, respectively.

Grabke[3] found the apparent rate constant to be independent of the CO_2/CO ratio between values of 0.2 and 10 at 1273 K and 1 atm total pressure. This represents a 460-fold change in the activity of carbon. A smaller variation was used in the present work, but no trend was found for the CO_2/CO ratio varying between 0.5 and 2 over the bulk of the temperature range. This represents an 8-fold variation in carbon activity. At 1273 K, the equilibrium activity of carbon with respect to graphite[18] would vary between about 0.001 and 0.009, whereas at 1073 K the variation would be between about 0.022 and 0.18. The work of Blakely

and his coworkers[19-21] on the adsorption of carbon on several crystallographic surfaces of nickel shows that at these activities and temperatures, the adsorption of carbon would be a strong function of composition or activity. Accordingly, we may conclude from the linear dependence of the rate on P_{CO_2} alone that reactions of the type,[6]

$$CO_2(g) + C \rightarrow 2CO(g) \qquad [29]$$

where the carbon is considered to be either dissolved or adsorbed, may be neglected.

The independence of the apparent rate constant on the CO_2/CO ratio is also consistent, as discussed in more detail by Grabke,[3] with chemisorption of oxygen being small under the conditions of the experiments, i.e., $\theta_O \rightarrow 0$. This might well be expected for oxygen potentials which are much lower than those necessary to form the first oxide. In the present work, the CO_2/CO ratio was typically two orders of magnitude lower than that which would be in equilibrium with Ni and NiO.

The possible influence of site coverage by chemisorbed CO on the form of the rate law can be ruled out by the work of Klier, Zettlemoyer, and Leidheiser.[22] Extrapolating their adsorption isotherm data for the (110) and (100) planes by means of their own or other heat of adsorption data[23] leads to negligibly small coverages at the pressures and elevated temperatures of the present experiments. Klier, et al, also measured the rate of exchange of CO on nickel surfaces at room temperature (298 K). The very high rates (10^{-10} moles cm^{-2} s^{-1} at 10^{-6} atm CO) are strong evidence that the desorption of CO cannot be an important rate determining step at elevated temperatures, in accord with Grabke's conclusions.[3]

Elementary steps involved in the carburization of the specimen, e.g.,

$$CO(g) \rightarrow C(ad) + O(ad) \qquad [30]$$

must also be occurring at dynamic equilibrium. Labelled CO which results from the exchange reaction must transfer some ^{14}C to the surface and, by diffusion, to the bulk of the specimen. Since, however, the experiments were continued until successive measurements gave the same net exchange, we may reasonably conclude that the final measurements were under conditions where the rate of diffusive transfer of ^{14}C to the bulk of the specimen was negligible in comparison to the $^{14}CO_2$-CO exchange.

Thus, the evidence is very strong that the dissociative chemisorption of CO_2 is the rate limiting step. This is further supported by the close accord between the pre-exponential factor in the rate equation and the classical collision frequency of CO_2 molecules with the surface.

REFERENCES

1. A. Ozaki: *Isotopic Studies of Heterogeneous Catalysis,* Kodansha Ltd., Tokyo, and Academic Press, Inc., New York, 1977.
2. H. J. Grabke: *Proc. 3rd Int. Congr. Catalysis,* pp. 928-38, 1964.
3. H. J. Grabke: *Ber. Bunsenges. Phys. Chem.,* 1967, vol. 71, pp. 1067-73.
4. H. J. Grabke: *Ber. Bunsenges. Phys. Chem.,* 1965, vol. 69, pp. 48-57.
5. H. J. Grabke: *Ber. Bunsenges. Phys. Chem.,* 1966, vol. 70, pp. 664-74.
6. C. Wagner: *Advances in Catalysis,* vol. 21, pp. 323-81, 1970.
7. D. R. Sain and G. R. Belton: *Met. Trans. B,* 1976, vol. 7B, pp. 235-44.
8. E. T. Turkdogan and J. V. Vintners: *Met. Trans.,* 1972, vol. 3, pp. 1561-74.
9. M. Byrne: MS Thesis, University of Pennsylvania, 1978.
10. S. C. Brown and W. W. Miller: *Rev. Sci. Instr.,* 1947, vol. 18, pp. 496-500.
11. H. V. Neher and W. H. Pickering: *Phys. Rev.,* 1938, vol. 53, p. 316.
12. S. Glasstone, K. J. Laidler, and H. Eyring: *The Theory of Rate Processes,* McGraw-Hill Book Co., New York, 1941.
13. H. Kersten: *Rev. Sci. Instr.,* 1931, vol. 2, pp. 649-53.
14. G. A. Meyer: Ph.D. Thesis, Columbia University, 1972.
15. R. J. Brigham, H. Neumeyer, and J. S. Kirkaldy: *Can. Met. Quart.,* 1971, vol. 9, pp. 525-29.
16. N. Barbouth and J. Oudar: *Compt. Rend.,* 1969, Ser. C, vol. 269, pp. 1618-21.
17. A. C. Yen, W. R. Graham, and G. R. Belton: *Met. Trans. A,* 1978, vol. 9A, pp. 31-34.
18. *JANAF Thermochemical Tables, 2nd ed., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.,* 37, U.S. Govt. Printing Office, Washington, D.C., 1971.
19. J. C. Shelton, H. R. Patil, and J. M. Blakely: *Surface Sci.,* 1974, vol. 43, pp. 493-520.
20. L. C. Isett and J. M. Blakely: *Surface Sci.,* 1975, vol. 47, pp. 645-49.
21. L. C. Isett and J. M. Blakely: *J. Vac. Sci. Tech.,* 1975, vol. 12, pp. 237-41.
22. K. Klier, A. C. Zettlemoyer, and H. Leidheiser: *J. Chem. Phys.,* 1970, vol. 52, pp. 589-602.
23. G. Wedler, private communication to Ref. [22].