

# Kinetic Study of Nickel Carbide Oxidation\*

BY J. FREEL † AND A. K. GALWEY

Chemistry Dept., The Queen's University of Belfast

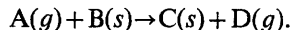
Received 4th July, 1966

Nickel carbide reacted with gaseous oxygen to yield nickel oxide and carbon dioxide as main products. The carbon dioxide formation reaction was deceleratory throughout and obeyed the equation

$$[1 - (1 - \alpha)^{\frac{1}{2}}]^2 = kt,$$

$0.1 < \alpha < 0.8$ , where  $\alpha$  was the fractional reaction at time  $t$ . The activation energy was 30 kcal mole<sup>-1</sup> and the index of oxygen pressure dependency of reaction rate was  $\sim 0.15$ . Both carbidic and non-carbidic forms of carbon were oxidized in the reaction; relatively small changes in rate were caused by removal of the carbidic phase by (i) reduction with hydrogen or (ii) thermal decomposition. The kinetic characteristics of oxidation of the nickel-carbon mixtures resulting from nickel phthalate decomposition were closely similar to those found for a sample which was largely nickel carbide. Carbon oxidation occurs at an interface, between product nickel oxide and the metallic phase, which progresses through the reactant particles. Carbon dioxide formation shows some similarity with the nickel oxidation reaction; oxidation of both elements occurs at a single interface.

The present paper reports a kinetic study of reaction of the type:



It has been shown that different characteristic types of kinetic behaviour occur with different reactants. For example, nickel oxide reduction by hydrogen proceeds through nucleation and growth of the product metallic phase,<sup>1</sup> but the rate of reaction between nickel metal and oxygen is deceleratory throughout,<sup>2</sup> since it is progressively opposed by an increasing thickness of nickel product layer. The rate of methane formation on nickel carbide hydrogenation is controlled by the concentration of carbon at the metallic phase surface.<sup>3</sup> The kinetic characteristics of reactions of nickel carbide vary with different reactants.<sup>4</sup>

Since the rate-controlling processes in nickel oxidation and for nickel carbide reduction are different, it was of interest to determine which of these mechanisms operated during the oxidation of nickel carbide or whether reaction proceeded by a different route. Moreover, since preparations of nickel carbide<sup>3, 4</sup> and of intimate nickel-carbon mixtures were available, comparisons between the behaviour of the different solid reactant systems might yield information about the factors which influence the course of gas-solid reactions.

Nickel carbide has the formula Ni<sub>3</sub>C; it crystallizes in a hexagonal close-packed lattice<sup>5</sup> and decomposes to the elements on heating<sup>6</sup> above about 350°. The free energy<sup>7</sup> of nickel carbide formation is 7,127 cal at 500°K and 4,653 cal at 600°K. Methods used for nickel carbide preparation have been given by Hofer,<sup>5</sup> but the

\* A part of the results and discussion contained in this article were presented at the International Symposium on *Reaction Mechanisms in Inorganic Solids* held in the Department of Chemistry, Aberdeen University, Aberdeen, Scotland, 11-16 July 1966.

† present address: Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada.

products obtained often contain free carbon.  $\text{Ni}_3\text{C}$  is the only nickel-carbon compounds which has been unambiguously identified, though claims for the existence of other substances have been put forward.<sup>5</sup> No kinetic investigation of nickel carbide oxidation was found in the literature, though a study of the oxidation of a solid solution of carbon in nickel has been reported.<sup>8</sup>

## EXPERIMENTAL

The apparatus used for kinetic measurements has been described<sup>3</sup>; equal doses of oxygen at known pressures were admitted to the reaction vessel for known times and subsequently removed for analysis using a Toepler pump. Product gases were identified and quantitatively measured using gas-solid chromatography with a katharometer detector. Reactant and solid product phases were identified from patterns obtained on X-ray diffraction powder photographs.

Kinetic measurements were made using three different samples of solid reactant (preparations A, B, and C). Preparation A was the same sample of reactant as used previously<sup>3, 4</sup>; it was prepared by reduction of nickel hydroxide pellets with hydrogen followed by carburization with hexane. This substance contained 12.8 % (by weight) carbon, which is greater than the theoretical value for  $\text{Ni}_3\text{C}$  (6.38 %) showing the reactant to contain free carbon. Carbon, amounting to 3.9 % of the sample weight, was removed as methane by reaction with hydrogen; this probably represents the carbidic carbon.<sup>3</sup> The surface area of preparation A, measured by the B.E.T. method from nitrogen adsorption at 77°K, was  $45 \pm 5 \text{ m}^2 \text{ g}^{-1}$ . Total carbon contents of all solids were measured by combustion analyses. Oxygen was prepared by decomposition of potassium permanganate in vacuum and purified by distillation at 77°K before use.

Unless otherwise stated, reactions were carried out in  $50 \pm 2 \text{ mm}$  oxygen. Solid samples were weighed  $\pm 0.1 \text{ mg}$  (normally  $\sim 10 \text{ mg}$  for preparation A and  $\sim 5 \text{ mg}$  for preparations B and C) before oxidation. The reactant was outgassed for 2-3 h at reaction temperatures before kinetic measurements were started.

## RESULTS

### OXIDATION OF PREPARATION A

Carbon dioxide was the only significant gaseous product from the reaction of preparation A with oxygen 250-340° and was formed by a rate process which was deceleratory throughout. Typical  $\alpha$ (fractional reaction)-time plots are shown on fig. 1. Carbon monoxide was detected in the early stages of reaction, but the volumes were sufficiently small ( $< 1.5 \%$ ) to be neglected. The total volumes of carbon dioxide (300-340°) showed variations of *ca.* 10 % between different samples, but the maximum volumes corresponded to the total (i.e., carbidic + non-carbidic) weight of carbon contained in the reactant (12.8 %). In one experiment, which was continued for 72 h at the relatively low reaction temperature of 280°, the total volume of carbon dioxide formed was greater than that corresponding to carbidic carbon only.

Nickel oxide was the only solid phase detected by X-ray diffraction measurements made on the non-volatile material remaining after completion of the oxidation reactions ( $\alpha = 1.0$ , for the carbon dioxide formation) at 300 and 320°. This phase was the only product detected after 3 h oxidation at 330° ( $\alpha = 0.95$ ). The diffraction line, attributed<sup>3</sup> to graphite in the reactant, was present in the oxidation products from preparation A. The reactant, after 25-min oxidation at 320° ( $\alpha = 0.5$ ) contained both nickel oxide and nickel metal but the nickel carbide phase could not be detected. After 5-min oxidation at 300° ( $\alpha = 0.17$ ), nickel carbide was the main solid constituent but the pattern indicated that small amounts of metal and oxide were also present.

This evidence shows that (i) carbon dioxide formation is accompanied by nickel oxidation and (ii) both reactions occur at comparable rates, so that a single mechanism may control the oxidation of both elements. Since carbon dioxide formation is deceleratory throughout, this reaction does not involve a process of nucleation followed

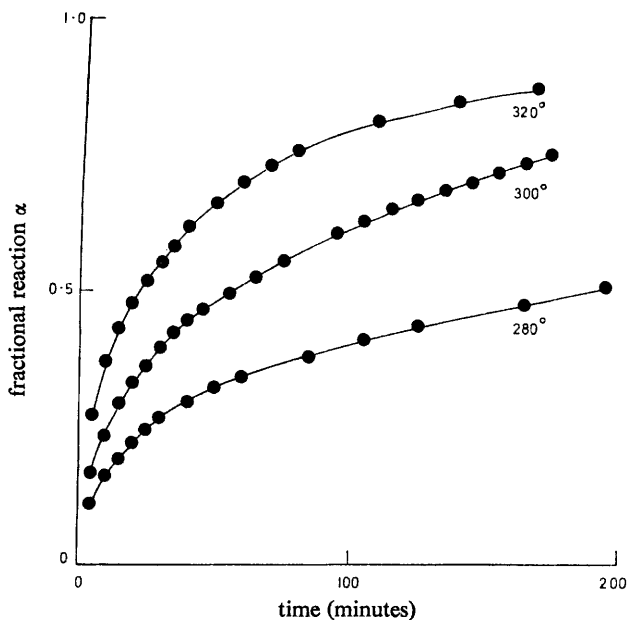


FIG. 1.—Plots of fractional reaction  $\alpha$  against time for carbon dioxide evolution during oxidation of preparation A.

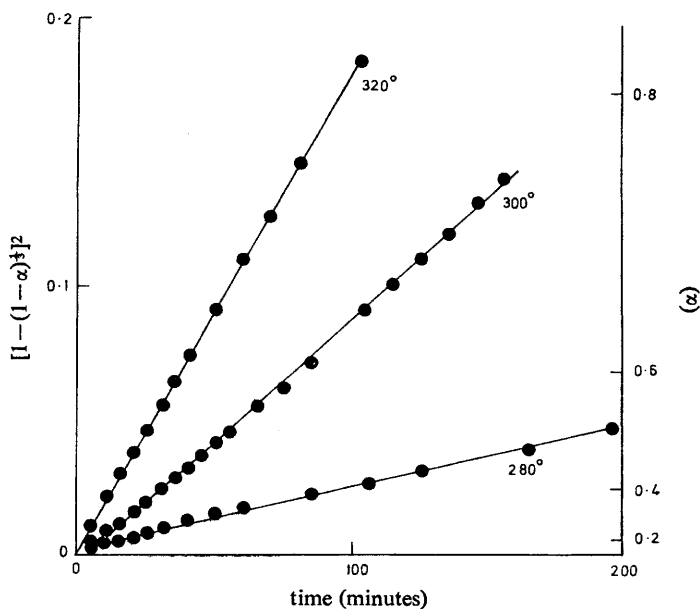


FIG. 2.—Jander plots ( $[1 - (1 - \alpha)^{1/2}]^2$  against time) for data shown in fig. 1.

by growth. The first-order and the contracting cube equations,<sup>9</sup> did not satisfactorily fit the data. Jander's equation was obeyed:<sup>10</sup>

$$[1 - (1 - \alpha)^{1/3}]^2 = kt, \quad [0.1 < \alpha < 0.85].$$

Typical plots are shown on fig. 2. In measuring values of  $\alpha$ , the total carbon dioxide yield for complete reaction of each particular specimen has been used in preference to an average value for the reactant sample, since they gave the more consistent kinetic analysis and the Jander plots were more accurately linear. Carbon contents for samples oxidized at 280° were measured after raising the reaction temperature to 300° in the latter stages.

The activation energy for carbon dioxide formation (280-330°) was  $30 \pm 3$  kcal mole<sup>-1</sup> from the linear Arrhenius plot obtained using Jander rate constants. The values found from tangential slopes of the  $\alpha$ -time plots at  $\alpha = 0.4$  and  $\alpha = 0.6$ , were also within the range  $30 \pm 3$  kcal mole<sup>-1</sup>.

The effect of variation in reactant oxygen pressure 15-100 mm on the reaction rate was small; the pressure dependency was within the limits  $P_{O_2}^{0.1} - P_{O_2}^{0.2}$ . The first reading in any experiment showed a greater sensitivity to oxygen pressure, probably due to gaseous reactant consumption.

#### OXIDATION OF REDUCED PREPARATION A

The carbidic carbon in each reactant sample was removed, after initial outgassing, by reaction<sup>3</sup> with hydrogen at 300°. On subsequent oxidation, samples yielded carbon dioxide by a rate process which was closely comparable to that described above for the unreduced reactant. Carbon dioxide evolution obeyed the Jander equation ( $0.1 < \alpha < 0.8$ ), the activation energy was *ca.* 30 kcal mole<sup>-1</sup> and reaction rate was slightly slower than that of the unreduced reactant (fig. 3, open circles).

#### OXIDATION OF DECOMPOSED PREPARATION A

A single sample of preparation A, (a sufficient quantity for several kinetic oxidation experiments) was heated in vacuum for 5 h at 450°, to effect thermal decomposition of the carbide phase.<sup>6</sup> The X-ray diffraction pattern of the resultant material showed nickel metal to be the main crystalline phase; diffraction patterns due to the oxide and carbide phases were not detected. Two diffraction maxima were observed at spacings  $d/n = 1.870$  and  $1.139$ ; these were absent from the controls used and remain unidentified, but may result from the presence of one of the phases mentioned by Hofer.<sup>5</sup>

The carbon dioxide formation reaction on oxidation gave kinetic characteristics different from that observed for preparation A. The Jander plot showed initial deviation (fig. 3, closed circles) but the later points were on a straight line; the activation energy in the latter stages was again *ca.* 30 kcal mole<sup>-1</sup>. The rate, however, was significantly lower than that of undecomposed reactant at the same temperature.

#### OXIDATION OF THE INTIMATE NICKEL-CARBON MIXTURE (PRODUCT FROM NICKEL PHTHALATE THERMAL DECOMPOSITION)

Two samples of nickel phthalate, each large enough to provide sufficient material for several measurements of the oxidation reaction, were thermally decomposed at 330° (preparation B) and 390° (preparation C) while evacuating by two-stage pumps during pyrolysis. The samples were from the same batch as that used previously<sup>11</sup> in a study of the kinetics of nickel phthalate thermal decomposition,

Preparations B and C contained 29.1 and 32.0 % carbon respectively. X-ray diffraction measurements showed nickel metal to be the main crystalline constituent in each, with the strongest line of the carbide pattern just discernible. Line broadening for both samples suggested small crystallite size, this effect being more pronounced for preparation B. No evidence for the presence of nickel oxide was found for either substance. The X-ray diffraction pattern for preparation C, but not that for preparation B, included both of the unidentified lines occurring in thermally decomposed preparation A.

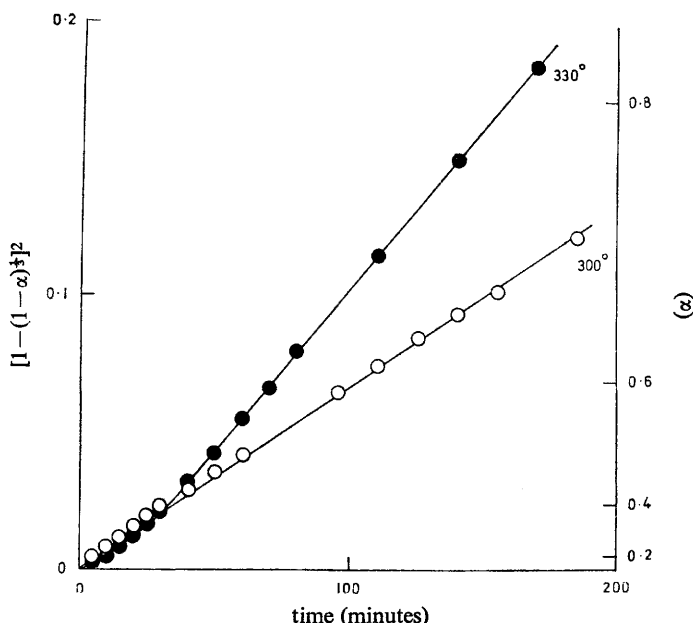


FIG. 3.—Jander plots for samples of preparation A after removal of carbidic carbon by (i) reaction with hydrogen (open circles) and (ii) thermal decomposition of carbide phase (closed circles).

#### OXIDATION OF PREPARATIONS B AND C

The products of oxidation of both samples were closely similar to those recorded for preparation A, but the carbon dioxide total yields showed greater reproducibility and corresponded to the total sample carbon content. From X-ray measurements, for both samples, significant amounts of nickel oxide were formed at low extent of carbon dioxide formation reaction. For example, after 5 min oxidation at 300° ( $\alpha = 0.1$ ) nickel oxide was the predominant crystalline phase, though metallic nickel was also present. Nickel metal could, however, only just be discerned in a sample after oxidation 35 min at 320° ( $\alpha = 0.4$ ).

The kinetic characteristics of the carbon dioxide formation reactions for both preparations were similar, though the reaction rates were somewhat different. The relative rates are given in table 1. Typical  $\alpha$ -time plots for the oxidation of preparation C are shown on fig. 4. They differ from those of fig. 1 in that in the early stages of reaction, product yields from preparation B and C show a relatively small temperature variation. Jander plots for both preparations were comparable to those for decomposed preparation A except that they showed a more pronounced slow initial period of

reaction. Rate constants from the slopes of the linear regions ( $\alpha > 0.3$ ) gave an activation energy of  $30 \pm 3$  kcal mole<sup>-1</sup> for both samples; comparative rates are shown in table 1. Measurements in 10-100 mm oxygen showed the dependence of rate on oxygen pressure to be close to  $P_{O_2}^{0.2}$ .

TABLE 1.—COMPARATIVE JANDER RATE CONSTANTS AT 300° FOR OXIDATION OF DIFFERENT REACTANT SAMPLES

reactant	$k \times 10^4 (\text{min}^{-1})$
A	8.7
reduced A	6.8
decomposed A	2.9
B	13.0
C	5.9

Activation energies for all samples were  $30 \pm 3$  kcal mole<sup>-1</sup>

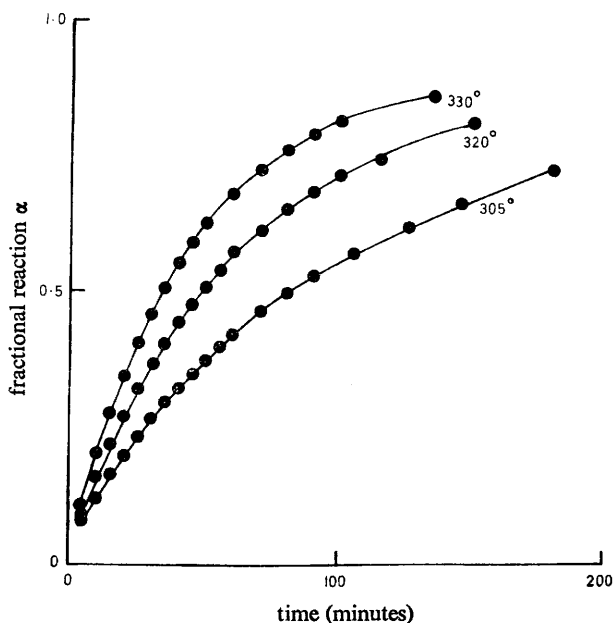


FIG. 4.—Plots of fractional reaction  $\alpha$  against time for carbon dioxide evolution during oxidation of preparation C.

#### REDUCTION OF PREPARATIONS B AND C

Both reactants yielded methane by a deceleratory rate process on heating in 50 mm hydrogen at 300°. This was followed by a persistent slow methane formation reaction in hydrogen which did not reach completion in any reasonable time interval. The yield of product carbon, as methane, from preparation B, at the time that reaction rate had decreased to 1/30th of the initial value, was 6 % of the reactant weight. The rate of preparation C reduction by hydrogen was too slow to enable measurements to be made in reasonable time intervals. Initial methane formation reaction rates on heating preparations A (from ref. (3)), B and C in hydrogen at 300° were in the ratio 1.0 : 0.3 : 0.1.

## OXIDATION OF REDUCED PREPARATION B

Jander rate constants and the activation energy for the carbon dioxide formation reaction for both the reduced and the unreduced reactants were identical within experimental error.

## ADDITIONAL EXPERIMENTS

(i) If the gaseous oxygen was removed by evacuation from the sample at a time corresponding to partial oxidation of preparation A, significant volumes of carbon dioxide continued to be evolved by a deceleratory reaction which persisted for a time in the absence of gaseous reactant.

(ii) Small volumes of carbon dioxide were evolved during normal outgassing and heating preparation A to reaction temperature, possibly due to reduction of small amounts of oxide, the presence of which was detected in X-ray studies of the original reactant.

(iii) A sample of preparation A was used to catalyze the cracking of propane to methane in the absence of gaseous hydrogen; carbon was deposited on the solid. On subsequent reaction with 50 mm oxygen at 300°, this sample gave a somewhat larger than normal volume of carbon dioxide in the first reading, but the reaction rate thereafter was significantly slower than normal and decreased more rapidly than the requirements of the Jander equation.

(iv) An intimate, mechanically ground, charcoal + nickel oxide mixture yielded carbon dioxide on heating under reaction conditions, but initial rates were <1 % of the values observed for any of the other systems studied.

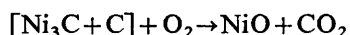
(v) The reaction of carbon monoxide with nickel carbide at 345° yielded insignificant amounts of carbon dioxide. Carbon monoxide, however, reacted readily with nickel oxide at 300° to form carbon dioxide.

## DISCUSSION

## STOICHIOMETRY OF REACTION

The data show that the oxidation reaction was not limited to reaction of carbidic carbon since (i) carbon dioxide yields were greater than would correspond to a reactant in which all the nickel was present as  $\text{Ni}_3\text{C}$  and (ii) significant carbon dioxide formation was observed for samples in which the carbidic carbon content had been reduced (or eliminated) by (a) reduction to methane<sup>3</sup> or (b) thermal decomposition.<sup>6</sup> Carbidic and non-carbidic carbon were oxidized with comparable ease, in contrast to the reduction reaction.<sup>3</sup>

The small yields of product carbon monoxide were consistent with the observation that once an appreciable amount of nickel oxide has been formed, carbon monoxide is readily oxidized. Furthermore, carbon monoxide is not formed in appreciable amounts by the reaction<sup>4</sup> of carbon dioxide with nickel carbide < ~300°. We therefore represent the oxidation by



where the square brackets imply an intimate reactant mixture. Quantitative measurements showed some inhomogeneity in preparation A and the graphite<sup>3</sup> in this reactant was not appreciably oxidized.

The relatively large methane yields obtained on hydrogenation of preparations B and C show that a part of the non-carbidic carbon was more reactive than that in preparation A, for which the methane yield probably corresponded more closely to the



carbide carbon content. This may result from (i) a greater active metal surface area of the decomposed salt residue which facilitated hydrogenation of the non-carbide carbon in preparations B and C, or (ii) the structure, or distribution of non-carbide carbon in preparations B and C differed from that in preparation A such that it could be hydrogenated relatively readily, since these observed differences cannot be quantitatively accounted for by surface area effects alone (45 and 160 m<sup>2</sup>/g).<sup>11</sup> Thus probably at least four different forms of carbon, possessing different reactivities, may be present in these samples: (i) carbide, (ii) non-carbide, reducible, (iii) non-carbide, irreducible and (iv) graphite (non oxidizable, in contrast to the other forms). Types (ii) and (iii) may, however, be more accurately represented as limiting degrees of dispersion of the nickel-carbon system, or degrees of aggregation of carbonaceous polymer at the surface of the metallic phase, rather than two distinct forms of carbon.

#### REACTION KINETICS

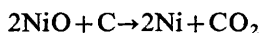
Since (i) both carbon and nickel oxidation occurred at comparable rates in preparation A and (ii) reaction was strongly deceleratory throughout, reaction probably occurred by a mechanism in which (i) oxidation of both elements occurred at a single interface and (ii) solid product formation over all reactant surfaces reduced the contact between combining species so that the diffusion of some entity through a nickel oxide layer controlled the reaction rate. The Jander equation is derived from a model of this type.<sup>10</sup> Such a mechanism is comparable to concurrent nickel oxidation and nickel oxide reduction by elemental carbon. Kinetic studies of the former reaction have been reported<sup>2, 12, 13</sup>; the latter reaction is also known.<sup>14</sup> Both reactions have been reported as occurring above 400°, but are expected to be detectable at lower temperatures for the finely divided reactants used in the present studies.

There was evidence that carbon oxidation proceeded through reaction of elemental or adsorbed carbon with oxide ions at the nickel oxide-gas interface since the value of *both* Arrhenius parameters for the early stages of preparation A oxidation were closely comparable with those for the nickel-oxide-catalyzed oxidation of propylene.<sup>15</sup> Approximately zero-order rate constants were estimated for the early stages, ( $0 < \alpha < 0.25$ ), of the present reaction, when it could be assumed that the reaction interface was approximately constant and equal to the original reactant surface area. The values of these Arrhenius parameters (*A* and *E*) were compared with values for oxidation of the propylene rich mixture (H series),<sup>15</sup> in which some carbon deposition on the surface may occur during reaction:

	$\log_{10} A$ (molecules cm <sup>-2</sup> sec <sup>-1</sup> )	<i>E</i> (kcal mole <sup>-1</sup> )
preparation A	24.1	30
propylene oxidation <sup>15</sup>	24.5	32.8

This agreement of both parameters suggests a common rate-determining step. Possible reactions may be the combination of an oxygen anion with carbon at the oxide surface or dissociation of a surface carbonate ion to yield product carbon dioxide. During oxidation of carbon in preparation A and in the H series of propylene oxidation experiments,<sup>15</sup> nickel ions may largely constitute the active reaction surface, whereas under more oxidizing conditions (i.e., the L series of propylene oxidation<sup>15</sup>) the active oxide surface may be largely comprised of anions; thus there is a marked difference in the Arrhenius parameters in the two series of experiments.

We propose, therefore, that in the present system carbon oxidation occurred at the nickel oxide/metallic phase interface which progresses through the reactant:





Metal thus reduced was subsequently re-oxidized and the carbon may be carbidic or non-carbidic.

The decrease in rate of nickel carbide oxidation with extent of reaction may be ascribed to the formation, and progressive increase in thickness of a barrier product layer, since the kinetic measurements obeyed the Jander equation. It is appropriate, therefore, to compare the present results with kinetic studies of nickel oxidation. Comparison of Arrhenius parameters for preparation A oxidation with those for metallic nickel oxidation may be made as follows. The Jander equation assumes<sup>13</sup> a parabolic reaction rate law,

$$dy/dt = k_1/y,$$

where  $y$  is the thickness of product at time  $t$ ; for nickel oxidation, we may write  $2k_1 = 2D$ , where  $D$  is the cation diffusion coefficient. Thus, Jander's equation may be rewritten<sup>13</sup>

$$[1 - (1 - \alpha)^{\frac{1}{2}}]^2 = 2k_1 t / r^2 = kt$$

where  $r$  is the reactant particle radius and  $k$  is the Jander rate constant.

The value of  $k_1$  for preparation A may be compared with that given by Moore and Lee<sup>2</sup> for nickel oxidation at 400° ( $1.58 \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$ ) by extrapolation of our Arrhenius plot to this temperature and assuming the reactant to be an assemblage of equi-sized spheres having a total area  $45 \text{ m}^2 \text{ g}^{-1}$ . The magnitude of  $k_1$  thus found for preparation A was  $1.8 \times 10^{-16} \text{ cm}^2 \text{ sec}^{-1}$  at 400°. Using these  $k_1$  values, the Arrhenius pre-exponential factors were  $10^{-5.5}$  and  $10^{-6.0} \text{ cm}^2 \text{ sec}^{-1}$  for the oxidation of nickel metal and nickel carbide respectively. Most of the small difference between these (pre-exponential) values must result from the presence of carbon, since, in preparation A, e.g., about 7 oxygen atoms were required to oxidize  $[\text{Ni}_3\text{C} + \text{C}]$ , only 3 of which oxidized the constituent nickel. After making this correction, the Arrhenius pre-exponential factors for both reactions agree within experimental error and the somewhat higher rate constant for the carbide oxidation reaction results from the slightly lower activation energy. Modification of the activation energy may result from the presence of bulky carbonate ions in the product lattice which may influence the ease of defect formation. It is concluded, therefore, that the model of oxidation proceeding by progression of the oxide-metal interface through the lattice provides a satisfactory interpretation of the kinetic data.

The close similarity between mechanisms of oxidation of nickel metal and of nickel carbide is also shown by the comparable values of the oxygen pressure dependency of reaction rate. The index for the latter reaction was close to 0.15 while that for nickel oxidation was  $p_{\text{O}_2}^{\frac{1}{2}}$  (ref. (16)).

This model for preparation A oxidation may show some differences in the detailed reaction mechanism from that occurring in the nickel-oxygen reaction, since the carbon distribution in the reactant is not necessarily homogeneous. The reactant particles are envisaged as a metallic lattice in which small agglomerates of carbon are randomly distributed within grain boundaries, faults and defects. Each carbon particle is oxidized after the reaction interface has reached it. There was no evidence, however, that carbidic carbon was oxidized in preference to free carbon (table 1).

The early stages of oxidation of (i) decomposed preparation A and (ii) preparations B and C (comparatively rich in carbon) showed deviations from the Jander equation. Also, the temperature dependence, and thus the activation energy, of this initial process was relatively small when  $\alpha < 0.2$ . This reaction may therefore be removal of excess carbon retained at the reactant surfaces in the initial stages during which adherent nickel-oxide product-phase-formation does not at first occur due to the adsorbed

carbon. The relatively slow reaction during this time implies some difficulty in establishing the normal reaction interface. X-ray evidence did, however, indicate that significant oxide formation occurred during these initial slow processes. This may derive from either inhomogeneity of samples, or recrystallization of oxide, which did not adhere to the original particle surfaces, to give a crystal which acted as a more efficient diffracting phase than the poorly crystalline preparations B and C. Following such initial deviations, the behaviour during subsequent oxidation was closely similar to that found for preparation A.

The value of  $k_1$  for preparation B oxidation at  $400^\circ$  was  $1.3 \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$ , assuming <sup>11</sup> the surface area to be  $160 \text{ m}^2 \text{ g}^{-1}$ , a value which is almost identical to that <sup>2</sup> for nickel oxidation at the same temperature. A direct comparison between these values is not possible since the greater carbon concentration in preparation B necessitates the passage of several oxygen atoms through the product phase for each metallic nickel atom oxidized. The effective carbon concentration in this sample is not known, due to the initial rate process indicated by a deviation from the Jander equation, but the rate constants are of comparable magnitude to those of preparation A.

The ratio (3.0) of rate constants at  $300^\circ$  (table 1) for oxidation of undecomposed and decomposed preparation A, was greater (2.2) than that for preparations B and C. Thus, these ratios, which presumably resulted from the sintering with recrystallization which accompanied thermal decomposition, was approximately equal for the two systems.

#### CONCLUSIONS

Nickel carbide oxidation is comparable with the nickel-oxygen reaction, in which cation vacancies are formed at the oxide/oxygen interface and these diffuse to the oxide/metal interface. Such a mechanism may be applied to nickel carbide oxidation but the bulky carbonate ions, probably temporarily retained at the outer oxide surfaces, may reduce the energy requirements for vacancy formation at the surfaces of the small carbide crystallites. These probably contain a greater concentration of superficial imperfections (step edges, high index planes, etc.) than are present at the surfaces of more massive metal particles used in other studies. Carbonate ions diffusing through the product in one direction might also influence the ease of diffusion of cation vacancies in the opposite direction, through the bulky ion exerting an "anchoring" effect. Thus, both effects suggest that values of both Arrhenius parameters,  $E$  and  $A$ , may be reduced below the values for reaction of pure metal, and this has been observed, though the values of  $A$  for both reactions are closely similar.

The authors thank Mr. P. D. Wilmot and the International Nickel Company for the gift of preparation A, I.C.I. Ltd. for a grant for the purchase of a recorder, and Miss I. Woodward for advice in the interpretation of X-ray data. J. F. thanks the Ministry of Education for Northern Ireland for a Scholarship held during the period that this work was carried out.

<sup>1</sup> B. Delmon, *Bull. Soc. Chim. France*, 1961, 590.

<sup>2</sup> W. J. Moore and J. K. Lee, *Trans. Faraday Soc.*, 1952, **48**, 916.

<sup>3</sup> A. K. Galwey, *J. Catalysis*, 1962, **1**, 227.

<sup>4</sup> A. K. Galwey, *J. Catalysis*, 1963, **2**, 176.

<sup>5</sup> L. J. E. Hofer, *Catalysis IV*, Ed. P. H. Emmett (Reinhold, New York, 1956) chap. 4.

<sup>6</sup> L. J. E. Hofer, E. M. Cohn and W. C. Peebles, *J. Physic. Chem.*, 1950, **54**, 1161.

<sup>7</sup> L. C. Browning and P. H. Emmett, *J. Amer. Chem. Soc.*, 1952, **74**, 1680.

- <sup>8</sup> W. W. Webb, J. T. Norton and C. Wagner, *J. Electrochem. Soc.*, 1956, **103**, 112.
- <sup>9</sup> P. W. M. Jacobs and F. C. Tompkins, *Chemistry of the Solid State*, ed. W. E. Garner (Butterworths, London, 1955) chap. 7.
- <sup>10</sup> W. Jander, *Z. anorg. u. allgem. Chem.*, 1927, **163**, 1.
- <sup>11</sup> A. K. Galwey, *J. Catalysis*, 1965, **4**, 697.
- <sup>12</sup> K. Fueki and J. B. Wagner, *J. Electrochem. Soc.*, 1965, **112**, 384.
- <sup>13</sup> R. E. Carter, *J. Chem. Phys.*, 1961, **34**, 2010.
- <sup>14</sup> J. W. Mellor, *Treatise on Inorganic and Theoretical Chemistry*, Vol. XV (Longmans, Green, London, 1936) p. 381.
- <sup>15</sup> Y. Morooka and A. Ozaki, *J. Catalysis*, 1966, **5**, 116.
- <sup>16</sup> T. B. Grimley, *Chemistry of the Solid State*, Ed. W. E. Garner (Butterworths, London, 1955) p. 336.