THE DECOMPOSITION OF FORMIC ACID
VAPOR ON EVAPORATED NICKEL FILMS

DISSERTATION

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I INTRODUCTION

The present research was undertaken to obtain further basic information about the mechanism of gaseous reactions on the surface of solids.

The vapor of formic acid, the simplest organic acid, was decomposed on reproducible evaporated nickel surfaces of known area in the temperature range from 125 to 190° C. The reaction rate was followed manometrically in a static system. Product samples were taken periodically and analyzed by a micro gas analysis apparatus and by mass spectrograph. The character of the nickel films was studied by X-ray and electron diffraction. The effect of varying the formic acid vapor pressure, the temperature, the nickel surface, and the effect of the addition of product gases were studied for the purpose of obtaining more information about catalytic mechanisms.

II LITERATURE REVIEW

The gas phase decomposition of formic acid vapor on nickel catalysts has been studied from 120 to 500° C. and from 10 mm. pressure to nearly a full atmosphere with varying results. Formation of a fresh, clean and reproducible surface in situ by vacuum evaporation of nickel or by evaporation in an inert atmosphere is an excellent method of catalyst preparation.

A. Properties of Formic Acid

Table I lists some properties of formic acid. These are listed mainly for reference purposes and to give a general picture of the acid. Formic acid forms a constant boiling mixture¹ with water (57 mole per cent formic acid) at 107.1° C. and is usually purified by vacuum distillation after the water has been removed by a drying agent. A method of purification is given in the Materials section. The formic acid monomer is a planar molecule and the hydrogen on the hydroxyl group is not trans.² The bond distances were found by electron diffraction² and microwave studies³. The dimerization of formic acid vapor at low temperatures is a complicating factor. At 125° C. and 21 mm. pressure, the formic acid is about two per cent dimer as calculated by the equation given in Table I. At 25° C. and 20 mm., it is 70 per cent dimer.

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1. International Critical Tables, vol. III, McGraw Hill Book Co., Inc., New York (1928), p. 215.
 2. I. L. Karle and J. Karle, J. Chem. Phys., 22, 43 (1954).
 3. R. Trambarulo and P. M. Morse, J. Chem. Phys., 22, 1622 (1954).

TABLE I
PROPERTIES OF 100 PER CENT FORMIC ACID

Reference*	Properties
4	Molecular Weight 46.03
	Boiling Point 100.8° C.
	Freezing Point 8.33° C.
	Dissociation Constant 2.14×10^{-4}
	Refractive Index $n_D/20^\circ \text{ C.} = 1.3714$
5	Density $d_4^{20} = 1.220$
2,3	Monomer Bond Distances
	C-O 1.23±0.01Å
	C-O 1.36±0.01Å
	O-O 2.27±0.005Å
	∠OCO 122.4±1°
	∠HC-O 121.7°
	O-H 0.97Å
	C-H 1.09Å
	∠COH 105.5°
6	Vapor Phase Dissociation of Dimer
	Dimer = 2 Monomer
	$\log_{10} K = -\frac{3085}{T} + 10.743$
	(0.1 atm. and 50-150° C.)
1	Vapor Pressure of Liquid
	P _{mm.} t° C.
	18.9 10
	33.1 20
	52.2 30
	82.6 40
	125.9 50
	189.7 60
	279.6 70
	398.1 80
	552.1 90
	753.4 100

* References listed in the tables of this section may be found in the text of this section.

4. "Formic Acid," Technical Bulletin FMT-2, Hayden Chemical Corporation, New York (1952).
5. "Handbook of Chemistry and Physics," 25th ed., Chemical Rubber Publishing Co., Cleveland (1941), p. 781.
6. M. D. Taylor and J. Bruton, J. Am. Chem. Soc., 74, 4151 (1952).

B. Formic Acid Vapor Decomposition on Nickel

In this section a review is given of the results of former investigations of the decomposition of formic acid vapor on nickel.

1. Decomposition Products

The main products of the decomposition of formic acid vapor on nickel are hydrogen and carbon dioxide. Varying amounts of carbon monoxide have been found, presumably coming from a second mode of decomposition into water vapor and carbon monoxide. The quantities of carbon monoxide are reported to be small and its presence is usually merely indicated^{7,8}. In the 200 to 450° C. temperature range, Ruka⁹, using a small quantity of catalyst in a glass vessel, attributed the 3 to 15 per cent carbon monoxide found in the product gases (hydrogen, carbon dioxide, and carbon monoxide) to the reaction occurring at the reaction vessel wall. At 200° C., Clark and Topley¹⁰ found about 2 per cent carbon monoxide coming from the vessel wall reaction. However, Wescott and Engelder¹¹ found the carbon dioxide to carbon monoxide ratio varied from about 10 to 1 at 200° C. to 1 to 1 at 500° C. and was greater than was expected from the glass surface alone.

Other products have been noted in this reaction. Some formaldehyde was detected by Platinov and Tomilov¹² while they were studying the

-
7. D. A. Dowden and P. W. Reynolds, *Disc. Faraday Soc.*, 8, 164 (1950).
 8. G.-M. Schwab and E. Schwab Agallidis, *Ber. deut. Chem. Ges.*, 76, 1228 (1943).
 9. R. Ruka, Doctoral Dissertation, U. of Mich. (1954).
 10. C.H.D. Clark and B. Topley, *J. Phys. Chem.*, 32, 121 (1928).
 11. B. B. Wescott and C. J. Engelder, *J. Phys. Chem.*, 30, 476 (1926).
 12. M. S. Platinov and V. I. Tomilov, *J. Gen. Chem. (U.S.S.R.)*, 8, 346 (1938); *C. A.*, 32, 5287 (1938).

effect of various poisons. Clark and Topley¹⁰ noted greenish liquid droplets on the catalyst after a reaction. These drops were assumed to be nickel formate. By electron diffraction, Ruka⁹ found nickel formate films on the surface of nickel exposed to formic acid vapor near its condensation pressure and at low temperatures (50° C.). At higher temperatures (185 to 450° C.) and at pressures lower than condensation, no nickel formate could be found even when the nickel was exposed for several days to 760 mm. of formic acid vapor.

No methane has been noted in the products of formic acid vapor decomposition on nickel catalysts although Cohn and Hedvall¹³ have found methane from the reaction of $3\text{H}_2 + \text{CO}$ on nickel at 300° C. Pichler¹⁴ also discusses the reaction of hydrogen and carbon monoxide to form methane. At low temperatures (below 300°C.) the methane and water of the equilibrium

are stable. Above 800° C., the hydrogen and carbon monoxide are stable. At 400° C. the equilibrium constant¹⁴ is 4.1×10^{15} .

2. Order of Reaction

Working at 12 to 25 mm. formic acid vapor pressure and in static systems, Schwab and Schwab-Agallidis⁸, and Rienaecker, Wittneben and Bade¹⁵ have reported the reaction to be zero order with respect to the formic acid vapor pressure. Clark and Topley¹⁰, who worked at formic acid vapor pressures near to an atmosphere, have reported the reaction

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13. G. Cohn and J. A. Hedvall, *J. Phys. Chem.*, 46, 841 (1942).
 14. H. Pichler, "Advances in Catalysis", vol. IV, Academic Press, Inc., New York (1952), pp. 327-337.
 15. G. Rienaecker, H. Wittneben and H. Bade, *Z. Electrochem.*, 46, 369 (1940).

as first order with respect to the formic acid vapor pressure.

3. Activation Energy

The activation energies reported vary from 11.6 to 30 kcal./mole. Dowden and Reynolds⁷ believe that their catalysts were poisoned and that their activation energy should have been lower than 30 kcal./mole. Rienaecker, Wittneben and Bade¹⁶ found that the activation energy varied with the treatment of the nickel. For sheet nickel annealed at 1000° C. the value was 11.6 kcal./mole, while that for cold worked nickel was 22.6 kcal./mole. Schwab and Schwab-Agallidis⁸ (static system) obtained a value of 17.7 kcal./mole for twice annealed nickel and 21.1 on cold worked nickel. Another value of 25.5 kcal./mole was obtained by Schwab and Schwab-Agallidis in the flow system⁸. Schwab¹⁶ says a recent and more reliable value of 15 kcal./mole has been obtained.

Both Ruka⁹ and Toyama and Kubokawa¹⁷, the most recent investigators of the decomposition reaction, got 20 kcal./mole for the activation energy. Ruka carried out his experiments in a flow system on electro-polished nickel. Toyama and Kubokawa, in a static system, used randomly oriented high vacuum evaporated nickel films and nitrogen evaporated films whose (110) plane was oriented parallel to the surface of the film backing.

4. Factors Affecting the Rate

Toyama and Kubokawa¹⁷ found that while the activation energies were the same, the nitrogen type films were about 2.5 times as active

16. G.-M. Schwab, Disc. Faraday Soc., 8, 208, (1950).

17. O. Toyama and Y. Kubokawa, J. Chem. Soc. Japan, Pure Chem. Section, 74, 289 (1953).

as the high vacuum films for the same weight of nickel, 1 mg. Unfortunately, no surface area measurements were made. Beeck, Smith and Wheeler¹⁸ measured the surface areas of both high vacuum and oriented nitrogen evaporated nickel films as a function of the weight of the nickel evaporated and found that the oriented nitrogen type films had a surface area about twice that of the high vacuum type films for the same weight of nickel. If Beeck's results can be applied to the observations of Toyama and Kubokawa it would seem that there is no difference between two types of films and an effect due to orientation of the nickel does not exist. Ruka⁹ noted no activity differences in the catalytic decomposition of formic acid vapor on any of three thin strips of nickel of different preferred orientation characteristics as found by electron microscope.

The effect, on the formic acid vapor decomposition reaction, of poisoning the nickel catalysts has been studied by Platinov and Tomilov¹², and Schwab and Pesmatjoglou¹⁹. Schwab and Pesmatjoglou found that NiS was an active catalyst but small traces of S added to pure nickel poisoned the reaction. Platinov and Tomilov found that small quantities of H_2O , H_2S , SO_2 , H_2SO_4 , As_2O_3 , and As_2O_5 activated the catalysts while still greater quantities poisoned the nickel.

Ruka⁹ found that the pretreatment of the formic acid affected the rate more than small changes in the impurities of nearly pure nickel (several tenths of a per cent total of Si, Al, Cu, Ca, and Fe).

18. O. Beeck, A. E. Smith and A. Wheeler, Proc. Roy. Soc., A177, 62, (1940).

19. G. M. Schwab and S. Pesmatjoglou, Festkr, Tillagvad. J. Arvid. Hedvall, 533 (1948); C. A., 42, 6218 (1948).

Formic acid, which was given a final purification by percolation through Amberlite IRA-410 anion exchange resin, decomposed fastest.

Cohn²⁰ observed an activation energy of 18 kcal./mole below and 26 kcal/mole above the Curie temperature for the decomposition of formic acid vapor on Co-Pd alloys. This shift in the activation energy was believed to be related to the change from the ferromagnetic to the paramagnetic state of the catalyst. Schwab²¹ has studied the reaction on nickel from 300 to 410° C. A slight anomaly was noted in activity at the Curie temperature of the nickel (360° C.), but no variation in the activation energy was observed. Ruka⁹ noted no peculiarities in this region.

5. Decomposition Rates

Surface areas were measured by Dowden and Reynolds⁷ by the Brunauer-Emmett-Teller method using argon. The zero order rate constant for the production of CO₂ and H₂ from formic acid vapor decomposition at 253° C. was 2×10^{-3} cm.³ cm.⁻² min.⁻¹ as taken from the graph given in their paper.

Geometric areas were measured by others. Ruka⁹ found the formic acid which was given a final purification by percolation through Amberlite IRA-410 decomposed fastest to give a rate of 0.3 ml. cm.⁻² min.⁻¹ at 360° C. Schwab and Schwab-Agallidis⁸ observed a rate of hydrogen evolution of 7.6 cm.³ cm.⁻² min.⁻¹ at 350° C. on cold worked nickel. This value was calculated from experiment number 108 in Table 2 of their paper by dividing the rate of hydrogen evolution,

20. G. Cohn, Svensk Kem. Ted., 52, 49 (1940).

21. G.-M. Schwab, Chimica e industria (Milan), 35, 810 (1953).

13 cm.³ min⁻¹, by the geometric surface, 1.67 cm². Clark and Topley¹⁰, presumably using nearly one atmosphere of formic acid vapor pressure, found the first order constant for the decomposition to be 1.0×10^{-4} min⁻¹ on one square cm. of surface at 200° C. The initial rate for an initial pressure of 760 mm. of formic acid vapor is then 0.076 mm. cm.⁻² min⁻¹. Clark and Topley used a glass reaction vessel similar to that described earlier by Hinshelwood and Tingey²² who gave the vessel volume as 15 cm.³. Using this value, an initial rate can be calculated in terms of cm³ (STP) evolved per square centimeter of surface per minute, i.e., rate = $\frac{15 \times 0.076}{473} \cdot \frac{273}{760} = 8.7 \times 10^{-4}$ cm.³ cm.⁻² min⁻¹.

A better way of tabulating the rate data is to give the number of molecules of formic acid vapor decomposed per square centimeter of surface per minute. The rate constants listed above in terms of cm.³ cm.⁻² min⁻¹ are converted by multiplying by the factor $\frac{6 \times 10^{23} \text{ molecules/mole}}{22,400 \text{ cm}^3/\text{mole}}$. These rate values are summarized below.

Reference	Method of Surface Measurement	Temperature °C.	Activation Energy kcal./mole	Rate molecules min. cm ²
7 (Dowden)	B.E.T. (argon)	253	30	5.3×10^{16}
9 (Ruka)	Geometric	360	20	8.0×10^{18}
8 (Schwab)	Geometric	350	25.5	2.0×10^{20}
10 (Clark)	Geometric	200	--	2.0×10^{15}

22. H. C. Tingey and C. N. Hinshelwood, J. Chem. Soc., 121, 1668 (1922).

TABLE II
SUMMARY OF KINETIC DATA FOR THE DECOMPOSITION
OF FORMIC ACID VAPOR ON NICKEL

Reference	Method	Temperature Range °C.	Pressure Range mm. Hg.	Products	Reaction Law with Respect to Formic Acid Vapor	Activation Energy kcal./mole
10	Static	183-210	760	Ni formate $H_2 + CO_2, CO,$	1st order	---
12	Flow	250-350	---	$H_2, CO_2, H_2O,$ $CO, HCOH$	Studied effect of $H_2S, SO_2, H_2SO_4, H_2O$ $As_2O_3,$ and As_2O_5 on reaction	
15	Static	120-220	12-25	$H_2 + CO_2$	0 order	11.6 to 22.5
23	Static	120-200	25	$H_2 + CO_2$		11.6
11	Flow	200-500	---	H_2, CO_2, CO	---	---
7	Flow	250-300	$\frac{90cm^3 sec^{-1}}{40-120cm^2 \text{ surface}}$	H_2, CO_2, CO	---	20
17	Static	143-160	10	H_2, CO_2	---	20
9	Flow	200-450	---	H_2, CO_2, CO	---	20
8	Static	135-200	25	H_2, CO_2, CO	0 order	17.7 to 21.1
8	Flow	260-380	---	H_2, CO_2, CO	---	25.5
19	Flow	Poisoned pure nickel with S				

23. G. Riemsacker and H. Bode, Z. anorg. u. allgem. Chem., 248, 45 (1941).

The variation in these rates is easily seen by comparing Schwab's value of 2.0×10^{20} molecules $\text{cm}^{-2} \text{min}^{-1}$ at 350°C . with Ruka's value of 8.0×10^{18} molecules $\text{cm}^{-2} \text{min}^{-1}$ at 360°C .

Table II gives a more complete summary of the kinetic data for the decomposition of formic acid vapor on nickel.

C. Evaporated Nickel Films

Evaporation techniques furnish an excellent means of forming fresh, clean, and reproducible surfaces for fundamental catalytic studies. Evaporated film techniques have been reviewed by Rhodin²⁴ and Trapnell²⁵. Kemball²⁶ gives details for vacuum evaporation of metal films used in catalytic studies. The most complete study of the characteristics of evaporated nickel films has been made by the late Otto Beeck and his associates over a period of ten years, extending from 1940 to 1950. A brief review of their results is given here.

Beeck²⁷ studied the hydrogenation of ethylene on nickel films which were evaporated on the surface of a vessel, presumably Pyrex, one cm. in diameter and 10 cm. in length from a U-shaped nickel filament. The geometric surface of the glass onto which the metal was deposited was about 30 cm^2 .

A disadvantage of using a cylindrical tube as a reaction chamber is that the nickel evaporated from the U-shaped filaments cannot be

24. T. N. Rhodin, Jr., "Advances in Catalysis", vol. V, Academic Press Inc., (1953), pp. 78-85.

25. B.M.W. Trapnell, "Chemisorption", Academic Press Inc., (1956), p. 21.

26. C. Kemball, Proc. Roy. Soc., A214, 413 (1952)

27. O. Beeck, A. Smith and A. Wheeler, loc. cit.

deposited uniformly on the walls of the glass tube, and the film thicknesses will vary along the length of the tube as well as around its circumference. Reactions are then taking place on a film of greatly varying thickness. Beeck²⁷ says that the metal films for electron diffraction work were produced under exactly the same conditions as the films used in the kinetic studies, but they were produced in a special glass apparatus on a 1 to 2 cm.² water-cooled glass surface which could be easily removed and placed in the electron microscope. It is supposed that the water-cooled glass surface was placed in the same position to the nickel filament for each evaporation so that the relative film thicknesses as a function of the weight of nickel evaporated were correct.

Electron diffraction studies of films, evaporated at 23° C. in a high vacuum, showed that they were randomly oriented when the films were thin (700-4000 atom layers), but showed an increasing tendency for (110) orientation parallel to the backing with increasing film thickness (12000 atom layers thickness and up). Electron diffraction studies of films evaporated under 0.5 - 2.0 mm. of nitrogen or argon at 23° C. were oriented with the (110) plane parallel to the surface of the backing. These films were highly oriented above a thickness of 3000 atom layers. The weight of nickel evaporated was less than 100 mg. in most cases. Later Beeck²⁸ evaporated up to 1 gram of nickel.

28. O. Beeck, "Advances in Catalysis", vol. II, Academic Press, Inc., New York (1950), p. 160.

Three main factors affected the catalyst activity²⁷; (1) the film thickness, (2) the pressure of the inert gas in which the film was evaporated, and (3) the temperature of the glass surface onto which the metal vapor was condensed.

The surface areas as measured by both carbon monoxide and hydrogen chemisorption were a linear function of the weight of nickel evaporated²⁷. The surface area of the oriented type films was twice that of the unoriented type films.

Surface area measurements of nickel films evaporated at 23° C. were made by the rapid chemisorption of carbon monoxide²⁷ at -183° C. and hydrogen at -183° C.²⁷ and 23° C.^{27, 29}. Measurements were also made by the Brunauer-Emmett-Teller method²⁹ using neon at -257° C., krypton and methane at -196° C., and n-butane at -78° C. Nitrogen and ethylene could not be used in the BET method because they are chemisorbed by nickel at -196° C. At this temperature nitrogen gave surface values which were 50 per cent too high, and ethylene gave values 100 per cent too high.

Because the rapid chemisorption of hydrogen is followed by a slower absorption into the bulk of the nickel³⁰, surface areas were measured by the amount of hydrogen rapidly chemisorbed. No difference was noted between the adsorption of hydrogen at 23° C. and at -196° C.³¹. Surface coverage was shown to be complete at pressures of 0.1 mm.

A comparison was made of the amounts of hydrogen at 23° C., carbon monoxide at -183° C., nitrogen at -182° C., ethylene at 23° C. and

29. O. Beeck and A. W. Ritchie, *Disc. Faraday Soc.*, 8, 159 (1950).

30. O. Beeck, "Advances of Catalysis", vol. II, loc. cit.

31. O. Beeck, ibid. p. 160.

oxygen at 23° C. adsorbed on the same type of nickel film²⁷. A pressure of 0.1 mm. of these gases was shown to be the pressure of complete surface coverage. The ratio of the amounts of these gases adsorbed relative to carbon monoxide are;

Gas	CO	H ₂	N ₂	C ₂ H ₄	O ₂
Ratio	1	1/2	1/2	1/4	2

No nitrogen is adsorbed at room temperature. Twice as much carbon monoxide was adsorbed as hydrogen, indicating that the hydrogen was adsorbed as atoms.

Surface areas measured by physical adsorption of neon, argon, methane and n-butane were nearly identical for the same weight of nickel on the high vacuum type films, but varied with the size of the adsorbate molecule on the oriented type films²⁹. The smaller pores of the oriented films blocked the larger adsorbate molecules. A linear relation was found between the size of the adsorbate molecule and the apparent surface area.

Heats of adsorption on nickel were measured for hydrogen³² at -182 and 23° C., ethylene³³ at 23° C., nitrogen³² at -196° C., and oxygen³⁴. No difference was noted in the heats of adsorption of hydrogen on oriented and unoriented type films. The heat of adsorption of hydrogen dropped from 30 kcal./mole on the bare surface to about 10 kcal./mole for the completely covered surface. The adsorption of ethylene drops rapidly from 60 kcal./mole on the bare nickel surface to about 15 kcal./mole for high vacuum type nickel films. The heat of adsorption

32. O. Beeck, W. A. Cole, and A. Wheeler, *Disc. Faraday Soc.*, 8, 314 (1950).

33. O. Beeck, *ibid.*, p. 118.

34. O. Beeck, "Advances in Catalysis", loc. cit., p. 181.

of nitrogen drops from about 10 kcal./mole on the bare surface to 5 kcal./mole on the fully covered surface. The value for oxygen adsorption was constant at 130 kcal./mole until the surface was completely covered.

Electrical conductivities of the two types of films were measured³⁵. Two very thin platinum rings were worked into the 1.2 cm. reaction tube 2.7 cm. apart, so as to form two conductive rings which were connected to a Leeds and Northrup Wheatstone bridge by sealed-in leads. Conductivities in reciprocal ohms were then plotted as a function of the weight of evaporated nickel. Except for slight variations at thicknesses below 700 atom layers, the conductivity varies linearly with the weight of the nickel film, and the conductivity of the vacuum evaporated nickel films is 4 times as great as the conductivity of the oriented type films. By calculation, the high vacuum films have 7 times the resistance of bulk nickel and the oriented films have 28 times the resistance of bulk nickel.

The gas pressure during evaporations affects the type of film deposited³⁶. In the 1 cm. diameter cell Beeck used, films evaporated in high vacuum were randomly oriented. If the inert gas pressure was from 0.5-2 mm., the films were oriented with the 110 plane parallel to the surface of the backing. At 5×10^{-2} mm. inert gas pressure, the evaporated nickel films were of markedly less orientation and about 30 per cent lower catalytic activity. The orientation gradually disappears if the pressure is increased above 2 mm. At 8 to 10 mm., the films are again randomly oriented but have an activity comparable to the oriented films.

35. O. Beeck, A. Smith and A. Wheeler, loc. cit., pp. 70-71.

36. O. Beeck, A. Smith, A. Wheeler, loc. cit., pp. 75-76.

Degassing of the surface before evaporation is important. The film thickness of a nitrogen evaporated film deposited on a poorly degassed surface has to be much thicker than 3000 atom layers to be well oriented.³⁷ Films evaporated on surfaces which were merely degassed by evacuation were of lower activity than in cases where the glass surface was evacuated and baked at 500° C. for 1 hour before evaporation of the nickel. Films treated in the latter manner had a constant high activity.

The temperature of the glass surface at the time of film deposition is another important factor in producing evaporated films. Strongly oriented films were still obtainable in a nitrogen atmosphere up to 80° C., but a film deposited at 165° C. was completely non-oriented³⁸. A film deposited at 23° C. and then raised to as high as 500° C. sintering temperature does not lose its orientation, but sintering of the films decreases the surface area³⁹. The surface areas, as found by the rapid chemisorption of carbon monoxide and hydrogen and by the physical adsorption of krypton, for both high vacuum and nitrogen evaporated films deposited at 23° C. and sintered at different temperatures are given below relative to the surface area of films sintered at 23° C.

Surface Area	1	0.4	0.2	very low
Sintering Temp. °C. 23	100	200	400	

37. O. Beeck, A. Smith, A. Wheeler, loc. cit., p. 76.

38. O. Beeck, A. Smith, A. Wheeler, loc. cit., p. 76.

39. O. Beeck, "Advances in Catalysis", loc. cit., p. 164.

The slow absorption of the hydrogen which takes place after the rapid chemisorption is a function of nickel weight alone⁴⁰ and is not affected by the temperature of sintering. The amount of the slow sorption of hydrogen is equal for equal weights of nickel whether sintering has taken place at 23 or 200° C.

Thus it is seen that in order to produce fresh, clean and reproducible films, certain requirements must be met. The system must be well degassed; care must be taken to sinter the films at the same temperature; and the inert gas pressure must be regulated in the production of oriented films.

An example of the extreme care which may be taken is given by Becker⁴¹ who says, with respect to the adsorption of hydrogen on tungsten, that only systems which have been evacuated to 2×10^{-10} mm. can be clean. In the comparison with Beeck's work, he says, Beeck's surfaces were probably free from serious contamination, although the system had stopcocks, mercury columns, and portions of glass which could not be completely baked out.

40. O. Beeck, "Advances in Catalysis", loc. cit., pp. 163-164.

41. J. A. Becker, "Advances in Catalysis", vol. VII, Academic Press, Inc., New York (1955), p. 208.

III APPARATUS AND EXPERIMENTAL PROCEDURE

Briefly, the inside of a well degassed flask is coated with a thin film of nickel prepared by evaporation in a vacuum or in a nitrogen atmosphere at about 1 mm. pressure. The flask is evacuated and heated in a controlled furnace to sinter the film. The temperature is lowered to that selected for the reaction and formic acid vapor is admitted. As the formic acid vapor decomposes, the pressure rise is followed as a function of time to give the decomposition rate data. During the reaction, samples are taken from the flask and the products are analyzed. The effect of the products formed during the reaction on the reaction rate is studied by admitting a pure product gas to the reaction flask before admitting the formic acid vapor. Surface areas are found by measuring the amount of hydrogen chemisorbed by the nickel films. The effective accomplishment of the above steps will now be taken up in detail.

A. Furnace

The basic furnace design is shown in Figures 1 and 2. The reaction vessel was heated by a pot type furnace with a range from room temperature to 800° C. An alundum furnace core (Norton Co., No. 8601) was wrapped with two layers of No. 20 (B. and S.) Nichrome wire. The inner winding, which also covered the core bottom, was used for continuous constant heating. The outer or control winding covered only the sides of the core and was insulated from the inner winding by Norton Alundum Cement, which was used to hold both windings in place. The maximum current drawn by the inner winding was 4.7 amperes at 135 volts when the furnace was at 800° C.

Figure 1. Front angle view of furnace without oven core, fan motor, or terminals

Figure 2. Rear angle view showing fan motor, oven core, and terminals

PLATE I - FURNACE DESIGN

The outer shell of the furnace, made from 1/4 inch thick Transite and sheet iron, was insulated from the core by three inches of Vermiculite (expanded mica). A fire brick was sawed into sections about 1 inch thick and was used to cover the open end of the pot.

At a furnace temperature of 180° C., a temperature gradient of nearly 10° C. along the 9 inch core length was noted. This gradient was reduced by mounting a 1/60 horsepower electric fan motor onto the bottom of the furnace. A hole was cut through the bottom of the core and furnace shell and then a tube was inserted to allow the fan shaft to pass. Glass wool, placed around the fan shaft in the space between the motor and the furnace shell, insulated the interior of the furnace from the exterior room air.

When used in conjunction with the rest of the equipment, the furnace and temperature controlling apparatus were mounted on a mobile rack which facilitated the removal of the furnace during evaporations. The furnace was raised and lowered with an automobile jack also mounted on the mobile rack.

B. Temperature Control

A continuous control circuit similar to the one described by Sturtevant¹ was connected to the outer furnace winding. However, there were a few major deviations from his design. Because no high quality low-impedance-to-grid transformer was available, a condenser coupling (0.1 mfd. condenser with a 1 megohm grid resistor) was used between the bridge and the amplifier. Stray and very troublesome 60 and 120 cycle pickup, which was carried along the phase control line, was sufficiently

1. J. M. Sturtevant, "Technique of Organic Chemistry," 2nd ed., edited by A. Weissberger, Vol. 1, Part 1, Academic Press, New York (1949), pp. 43-47.

reduced by using a 100 ohm resistor (R_{14} of Sturtevant) instead of a 2000 ohm resistor as the cathode bias resistor for the 6SJ7 tube in the first stage of signal amplification. This resistor is one-half of a voltage dividing circuit coming from the phase control circuit, and in order to maintain the same voltage drops across this circuit the other resistor (R_{15} of Sturtevant) had to be changed accordingly, i.e., decreased by a factor of 20 to 5000 ohms.

A 25 ohm platinum resistance thermometer was used as the temperature sensitive element in the bridge circuit. To avoid any confusion of this thermometer with another platinum resistance thermometer used to measure temperatures, the thermometer used in the bridge circuit will be referred to as the temperature sensitive element. The bridge balance point could be varied continuously with a 100 ohm Helipot.

The bridge balance point was not stable and changed with line voltage which was observed to vary irregularly from 90 to 117 volts. This trouble was eliminated by using a 3KVA "Sola" constant voltage transformer to furnish power to both the furnace and the controller.

The controlled furnace temperature with the fan was observed for nearly six hours at 191° C. without the reaction flask; the temperature variation was $\pm 0.1^{\circ}$ C. With the 500 ml. reaction flask in the oven, the temperature varied $\pm 0.2^{\circ}$ C. over a 10 hour period at 189° C.

Measurement of the temperature at different points in the furnace showed that, with the fan in operation and the furnace temperature at 95° C., the temperature was nearly the same at two check points 2.5 inches and 6.5 inches off the oven core bottom. The respective temperatures were 94.66° and 94.63° C.

However, even with the fan, a temperature difference was observed when the 500 ml. reaction flask was in the furnace. Temperatures were measured at the top, middle, and bottom of the flask. The temperature decreased from the bottom to the top of the flask. The temperature difference varied from 24 to 28° C. at 190° C., the highest temperature used in the decomposition experiments, and from 20 to 24° C. at 125° C., the lowest temperature. The temperature difference from the bottom to the middle of the flask was smaller and more nearly constant; it was 7.8 to 8.2° at 190°, and 6.8 to 7.4° at 125°. All temperature measurements for the kinetic data reported later were made with the temperature measuring elements (thermocouple, or thermocouple and platinum resistance thermometer) near the bottom of the flask and at the same depth for each experiment. The flask also was immersed as nearly as possible to the same depth in the furnace for each experiment. Temperature differences between experiments are thus correct as reported. The temperatures reported are those measured near the hottest part of the flask.

C. Temperature Measurements

During the preliminary work either one or two uncalibrated iron-constantan thermocouples was used to measure the temperature. After the nickel evaporation procedure was perfected, temperature measurements were made with a calibrated platinum resistance thermometer and an iron-constantan thermocouple which was calibrated near the end of the experimental work, or with the thermocouple alone. The average of the two temperatures was taken when both temperature measuring elements were used. The resistance thermometer was placed inside the oven against

one side of the flask with the sensitive section below the middle of the flask, and the thermocouple was placed on the opposite side of the flask from the resistance thermometer and near the bottom of the flask. The temperature sensitive element of the furnace control circuit was placed against the flask on the same side as the thermocouple and just below the middle of the flask.

1. Platinum Thermometer

When the platinum resistance thermometer was used, the thermometer and a standard known resistance were connected in series and a 2 ma current was passed through them. The voltage drop was measured with a potentiometer and galvanometer across the known resistance and then across the thermometer². This procedure was repeated rapidly for three times to make sure that any change in battery strength might be noticed. The thermometer resistance was then calculated by

$$R_t = \frac{E_{pt}}{E_{std.}} \times R_{std.},$$

where:

R_t = Resistance of the platinum thermometer at temperature $t^{\circ}\text{C}$.

E_{pt} = Potential drop across the platinum thermometer,

$E_{std.}$ = Potential drop across the standard resistance

$R_{std.}$ Standard resistance

= 25.1844 ohms at 25°C . as measured by a Mueller Bridge.

Data concerning thermometer constants were not available with the thermometer. A calibration was made using the ice point and the corrected

2. R. L. Weber, "Heat and Temperature Measurement", Prentice-Hall, Inc., New York (1950), p. 136.

boiling point of water. The value of α in the Callendar formula

$$t = \frac{R_t - R_0}{R_{100} - R_0} \times 100 + \alpha \left(\frac{t}{100} - 1 \right) \frac{t}{100}$$

was assumed to be 1.50. R_0 and R_{100} , the thermometer resistance at 0° and 100° C., were found to be 26.367 and 36.508 ohms respectively.

The resistance thermometer was checked against a regulated water bath set at 25.00° C. by means of a mercury thermometer calibrated by the National Bureau of Standards. The temperature measured with the resistance thermometer was 24.97° C.

2. Thermocouple

The iron-constantan thermocouple was calibrated to the nearest 0.1° C. with a platinum resistance thermometer. It was calibrated near the end of the experimental work from 120 to 205° C. to cover the range of temperatures at which data were taken. All thermocouple readings were then converted to temperatures in accord with this calibration.

D. Vacuum System

An overall view of the apparatus is shown in Figure 3. The evacuation system is at the right; it consisted of a trap, A, Figure 3, immersed in liquid nitrogen, followed by a National Research Corporation type H-2-P diffusion pump, B, filled with Dow-Corning type 703 silicone oil. The diffusion pump was backed by a type 1405 Welch Duo-Seal pump (not shown). The pressure was measured with a National Research Corporation type 507 ion gauge, C. A pressure of 2×10^{-7} mm. Hg could be obtained, with the pumps running, in the high vacuum portion of the system.

Figure 3. Overall view of apparatus

A	Trap
B	Diffusion Pump
C	Ion Gauge
D	Electrically Heated Trap Filled with Copper Turnings
E	Trap Filled with Glass Beads
F	Trap Filled with Activated Charcoal
G,H,I,J	Stopcocks Isolating Portion of Gas Expansion System
K	McLeod Gauge
L	Spoon-type Bourdon Gauge
M	Sloping Manometer
N	Drying Tube Filled with CaSO_4
O	Stopcock between Bourdon Gauge and Low Vacuum Line
P	Trap in Sampling System
Q	Manometer in Sampling System
R	Toepler Pump
S	Storage Bulb
T	Stopcock between Flask and Sampling System
U	Formic Acid Container
V	Stopcock for Degassing Formic Acid
W	Reaction Flask
X	Expansion Chamber used with Bourdon Gauge
Y	Stopcock connecting Formic Acid Container and Reaction Flask.
Z	Stopcock for Equalizing Pressure on Inside and Outside of Bourdon

LEGEND FOR FIGURE 3

Another Welch 1405 Duo-Seal (not shown) was used to evacuate the gas sampling system as well as the low vacuum side of the Bourdon gauge, L.

In early work the recommended Narcoil 20 was used with the diffusion pump, but because Narcoil oxidizes easily, a mercury diffusion pump was installed and the pressure was read with a McLeod gauge. Later, when it was feared that poisoning of the evaporated nickel films was being caused by a slow degassing of the mercury in the system, or by the mercury itself, all mercury was eliminated in the high vacuum system and the Dow-Corning silicone oil was used.

E. Gas Entry System

The electrically heated trap with copper turnings, D, Figure 3, the trap with glass beads, E, and the trap with activated charcoal, F, were used to remove impurities from gases entering the system through stopcock G. This is similar to the system described by Joyner³. Another entry was provided through stopcock H. The tubing connecting stopcocks G, H, I, and J served as part of the gas expansion system used to reduce the pressure of entering gases from nearly one atmosphere to a few millimeters or lower.

F. Bourdon Gauge

In preliminary work a mercury manometer was used to measure pressure increases. In all the later experiments in the mercury-free system, a spoon-type Bourdon gauge, L, Figure 3, with three spoons was used as a

3. W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques", Instruments Publishing Co., (1949), page 272.

null gauge. A Gaertner 33 power telemicroscope with a mechanical working distance of 120 mm. was used to detect deviations from the null point. The pressure was measured indirectly on a sloping manometer, M. The manometer was adjusted with dry air introduced through the calcium sulfate filled tube, N, and expansion chamber, X, and could be evacuated through stopcock, O.

Multiplying the sloping manometer readings by 0.432 converted the pressures to mm. Hg, correct to the nearest 0.2 mm. Hg. A levelled carpenter's square was used to measure the horizontal (21.25 inches) and vertical (9.72 inches) distances necessary to calculate the manometer correction factor. The factor is the sine of the angle made between the horizontal and the sloping sides of the manometer, i.e., factor = $9.72 / \sqrt{(21.25)^2 + (9.72)^2} = 0.432$.

A Zimmerli gauge, which could be read to the nearest 0.1 mm. Hg, later replaced the sloping manometer. A Zimmerli gauge looks like a piece of glass tubing bent into the shape of a tall "W". The bottom of the "W", including the middle point, is filled with mercury, care being taken to keep the height of the mercury in the two outside arms of the "W" lower than the middle point. This difference determines the range of the gauge. Both of the top ends of the "W" are attached to the system whose pressure is to be measured. At pressures lower than the difference of the mercury levels in the point and outside arms of the "W", the mercury column splits at the middle point forming a mercury vacuum. The pressure is then the difference of the mercury levels in two adjacent outside arms.

The spoon gauges were more sensitive than the manometers, which were the limiting factors in pressure measurements.

G. Formic Acid Vapor Entry System

The formic acid container, U, Figure 3, was either a 250 or 500 ml. round-bottomed flask attached through a standard-taper joint for easy removal. The acid was degassed just prior to the start of an experiment by evacuation with a vacuum pump through stopcock, V. The formic acid vapor from the container was introduced into the reaction flask through stopcock Y.

H. Reaction Flask

The reaction flask, W, Figure 3, is the most important part of the system. It houses the electrodes and the nickel which forms the evaporated film where the reaction occurs. Several designs were made, tested, and altered according to the requirements as the experimental work progressed. Five-hundred ml. round-bottomed Pyrex flasks were used in all the experimental work except for a few experiments which were done in a larger cylindrical flask 150 mm. in length and 100 mm. outside diameter. The latest design, Figure 4, will be discussed first. This will be followed by a discussion of earlier designs.

1. Latest Design

The reaction flask itself consisted of a 500 ml. flask carrying a 110 mm. length of the outside member of a $\overline{\text{T}}$ 34/45 joint in place of the original neck. A side arm on the neck of the flask near the standard taper joint served for evacuation. The inner member of a 12/5 ball-socket

Figure 4. Flask, electrode housing, and nickel couplings

joint was fastened to this side arm to allow for the easy removal of the flask from the rest of the system.

The electrodes for evaporation entered the flask through the inner member of the 34/45 joint. A test-tube like appendage was added at the narrow end of the inner member to eliminate most of the dead space in the neck of the flask. It had an outside diameter which was nearly equal to the inside diameter of the neck of the flask.

The electrodes were 1/8-inch diameter tungsten rods sealed with uranium glass to Pyrex tubing, which was inset in the appendage, so that only about 1/2 inch of the end of the bare tungsten stuck out into the flask. Heavy braided copper wire was welded to the tungsten electrodes to serve as flexible leads to the outside. Each end of the filament, from which the nickel was evaporated, was attached to the electrodes by means of a nickel coupling which could be tightened to the filament and electrode with set screws.

In all the experiments with this flask the nickel was evaporated from 25 gauge (B & S) nickel wire which was used as the filament. Most of the early work involved evaporation of nickel wire wrapped around a tungsten filament. The current requirement in the latter case was around 40 to 50 amperes while the direct evaporation from the nickel wire required 5 to 7 amperes. A ten-ampere Variac operated off the line voltage and used with a heavy-duty 115-volt to 12-volt step-down transformer, furnished the power for the system. The current was measured with a General Electric type 8AP9ACA14 ammeter, which reads to 0.05 amperes in the 0-10 ampere range used.

Although it was never needed with this flask, cooling water could be circulated around the glass to metal seals and electrodes by passing water in at the open end of the inner member of the joint and removing it through a side arm attached about two inches from the top of the open end.

2. Early Designs

The flask just described had the advantages of being easy to assemble and disassemble and it eliminated much of the dead space in the flask. The first design attempted to avoid any ground glass joints in the system. In these flasks the tungsten filament was spot welded to two 3/32 inch glass-beaded electrodes which were sealed into the reaction vessel. The reaction vessel was then sealed onto the rest of the system. Every time the reaction flask was cleaned, the line between the flask and the rest of the system had to be broken. Furthermore, the amount of nickel evaporated could not be determined by weighing the filament before and after the evaporation. Another disadvantage of this system was that the glass-to-metal seals were poor and cracked from the heavy current required during the evaporations.

A refinement of this system eliminated the difficulty of filament weighing and the weak glass-to-metal seals. Kovar seals were used to introduce 1/4 inch cold-rolled steel electrodes which were attached to the filament by set screws. Because the metal of the Kovar seal was soft-soldered to the steel and the joint had to be kept out of the oven, and because the electrodes, for easy removal, were set in a standard taper joint which also had to be kept out of the oven, the dead space in this flask was considerable.

Another electrode system was made from brass in the form of a cap which fastened over the end of the flask neck. One electrode passed through the center of the cap which formed the other electrode. They were separated by means of an O-ring on the inside and a Bakelite spacer on the outside. The electrodes were cooled by passing water through a glass cylinder fastened with rubber tubing around the outside of the cap. The vacuum-tight seal of the cap with the flask was made with another O-ring. The filament was attached to the electrode system with set screws. The neck of the flask had to stick out of the oven to keep the O-rings in the cap cool and thus increased the dead space in the flask.

To eliminate the dead space as much as possible, a piston-type electrode system was made. The general construction was similar to the cap, but the outer electrode was grooved for two or three O-rings, and was made to slide down the elongated neck of a flask. With this system the electrodes were slipped back after the evaporation and the neck of the flask was sealed off under vacuum. Nearly all dead space could be eliminated this way. One fatal difficulty was that in the sealing off process enough degassing of the glass occurred to poison the film and render it useless. Another disadvantage was that with the long brass electrodes a purple film was formed in the neck of the flask, indicating evaporation of zinc from the brass even though the outside electrodes were cooled with water. Copper electrodes eliminated this difficulty.

I. Preparation for Evaporation of the Nickel

The flask and electrode system described in Figure 4 were cleaned between experiments by rinsing with dilute nitric acid, tap water,

alcoholic sodium hydroxide, tap water, potassium dichromate in sulfuric acid (cleaning solution), tap water, dilute nitric acid, and finally with distilled water. The flask and electrodes were then dried in an oven at 110° C. A one-foot length of 25 gauge (B & S) nickel was shaped into a U-shaped filament with two loops about one-inch in diameter at the bend of the U. It was weighed and attached to the nickel couplings which were in turn connected to the electrode system. The electrodes and nickel were rinsed with acetone, distilled water, and finally with C. P. acetone. For X-ray examination of the evaporated film, pieces of glass about 3x3 mm. square were placed in the flask. The electrodes were set in the flask and the filament was aligned so that the loops would be in the center of the flask. The last traces of acetone were removed by sucking on the flask with an aspirator. The standard taper joint between the flask and the electrodes was then heated gently over a Fisher burner and Apiezon W hard wax was applied. Next, the ball-socket joint attaching the flask to the rest of the system was heated and waxed with Apiezon W. The flask was first evacuated with a mechanical pump, and later connected to the high vacuum system.

When the pressure reached 2×10^{-6} mm. Hg, the furnace was raised around the flask and set for approximately 500° C. The system was left to pump for several days until a pressure of 1×10^{-6} mm. Hg or lower was reached with the flask degassing at 500° C.

The filament was then degassed for about two hours by passing a 3.5 ampere current through it while the flask was at 500° C. If the pressure reached 1×10^{-6} mm. Hg or lower during the filament degassing process, the system was assumed to be degassed well enough for the evaporation of the nickel.

Two hours prior to the evaporation the nickel filament was again degassed at 3.5 amperes and 500° C. The filament current was then turned off; the furnace was removed and the flask was cooled and immersed in a Dewar flask full of ice water. At this point the pressure was 3×10^{-7} mm. or lower. If the pressure was higher the flask was degassed for another day at 500° C. and then another attempt to evaporate the nickel was made.

J. Evaporation of Nickel

The evaporation of nickel was carried out in a high vacuum or in a nitrogen atmosphere of 1 to 2 mm. with the flask at 0° C.

1. High Vacuum Evaporations

With the flask evacuated as above, the evaporation was started by raising the filament current to 5.05 amperes. The evaporation was usually continued for about 100 minutes. As the nickel evaporated and the wire became thinner its resistance increased and the current decreased. The filament current ammeter was checked approximately every half hour during the evaporation and the current maintained at 4.90 amperes. The pressure during the evaporations ranged from 1 to 3.0×10^{-7} mm. Hg. About 30 to 40 mg. of nickel could be evaporated in this way in the 100-minute period.

2. Nitrogen Evaporations

Pure nitrogen was introduced into the flask and the pressure was adjusted to 1 to 2 mm. Hg. The evaporation in this nitrogen atmosphere was started at a filament current of 6.60 amperes and 0° C. A higher current was needed in the nitrogen evaporations because the nitrogen

conducted the heat away from the filament. Every half hour the filament current was checked and was maintained at 6.50 amperes. Approximately 20 to 30 mg. of nickel could be evaporated during the 100-minute period.

Immediately after the evaporation was finished the nitrogen was withdrawn through the high vacuum system. From here on the procedure was the same for both the high vacuum and nitrogen evaporated films.

K. Decomposition Procedure

The films were always sintered under high vacuum two hours or more at 190° C. before a decomposition experiment was carried out. The furnace temperature control was next set for the desired temperature (190° C. or lower) and left until equilibrium was reached.

Pure and degassed formic acid vapor was introduced and the decomposition was followed by noting the pressure increase with time. In the preliminary work a wall clock with a sweep second hand was used, and in later work the time was measured to the nearest second with a Time-It timer, capable of being read to the nearest tenth of a second.

For experiments investigating the effect of products on the reaction, a pure product gas was introduced into the reaction flask 5 to 10 minutes prior to the introduction of formic acid vapor. The formic acid vapor was added to the product gas and the reaction was followed as usual.

L. Sampling System

The sampling system consisted of a trap, P, Figure 3, with a connected manometer, Q, for fractionating the sample and a Toepler pump, R, for removing the sample to a storage bulb, S. At a certain

point in the reaction, a sample was taken from the reaction flask through stopcock T into the trap and the pressure was measured. Dry ice was then placed around the trap and the non-condensable gases, hydrogen, carbon dioxide, carbon monoxide and methane were removed by the Toepler pump and stored over mercury in the sample bulb for later analysis with the gas analysis apparatus and mass spectrometer.

The dry ice bath was then removed and the trap was warmed to room temperature and the pressure of the condensable gases, water vapor and formic acid vapor, was measured. The small amount of water vapor and formic acid vapor were then pumped out through a mechanical pump. When combined with the percentage of gases found with the gas analysis apparatus, pressure measurements with the manometer permit the calculation of the percentage of formic acid decomposition.

The manometer was also used to show that there are equal amounts of water and carbon monoxide being given off in the reactions.

IV MATERIALS

A. Nickel

The nickel, Low Carbon and 99 Alloy 25 gauge (B & S) wires, was obtained from the Driver-Harris Company, and was used without any treatment other than rinsing with acetone and distilled water. In very early work, Driver-Harris Company A nickel was used.

Qualitative spectrographic analysis of the nickel was made with an Arl-Dietert 1.5 meter grating spectrograph using a D.C. arc between spectrographic carbon electrodes at 12 amperes and 50 volts. A rotating sector was used and each sample was burned for 2 minutes.

Identification and estimation of the amounts of impurities were made by E. D. Loughran.

The low carbon and 99 alloy nickel were prepared for the analysis as follows. A new piece of 0.0179 inch diameter wire was cut in approximately 3/16 inch lengths with blued-steel wire cutters. The cuttings fell onto a double-folded Kleenex where they were rinsed with about 10 to 20 ml. of dilute nitric acid made from one part concentrated nitric acid and five parts of distilled water. The nickel sections were then shaken onto another double-folded Kleenex and washed with distilled water. Two more transfers to fresh Kleenex and washings with distilled water were made. Finally the nickel pieces were shaken onto a dry Kleenex and then transferred to an envelope for storage until the analysis was made.

The results are tabulated in Table III.

B. Formic Acid

Reagent grade formic acid (88-90%) was saturated with C.P. calcium chloride and left standing for several days. It was then vacuum distilled at 31 to 38° C. and 52 to 59 mm. Hg. The distillate was again saturated with calcium chloride and vacuum distilled again. After the second distillation the water content decreased to less than 0.05% as checked with Karl Fisher reagent¹. The refractive index and density were $n_D^{20} = 1.3714 \pm .00015$ and $d_4^{20} = 1.2205 \pm .0005$ g/ml. (compare with Table I).

The acid was kept frozen in ice and was partially melted before use. The first few milliliters to melt were discarded. The next portion to melt was poured into the formic acid container which was then attached to the system and degassed. The acid, when kept in this manner, remained water-free indefinitely.

C. Hydrogen

Tank hydrogen was passed over hot copper (300° C.) and through a liquid nitrogen trap before use.

D. Carbon Monoxide

Tank carbon monoxide was let into an evacuated bulb which was immersed in liquid nitrogen before the carbon monoxide was removed for use. Mass spectrometer analysis showed the carbon monoxide prepared in this way contained oxygen.

1. H. L. Clever, Doctoral Dissertation, O.S.U. (1951).

TABLE III
IMPURITIES FOUND IN LOW CARBON AND 99 ALLOY NICKEL WIRE

IMPURITIES	ESTIMATED PERCENT IN LOW CARBON	ESTIMATED PERCENT IN 99 ALLOY
Copper	.01	.002
Chromium	.2	.002
Manganese	.2	.005
Silicon	.1	.02
Iron	.1	.01
Molybdenum	.1	.1
Magnesium	.03	.03
Cobalt	.5	.5
Calcium	.01	None

Carbon monoxide was also prepared by heating oxalic acid and concentrated sulfuric acid and then passing the gaseous products through a concentrated sodium hydroxide solution to remove the carbon dioxide and a liquid nitrogen trap to remove water vapor. This carbon monoxide also contained oxygen, which was removed by letting the impure carbon monoxide stand in a closed trap over yellow phosphorus. Just before using the carbon monoxide, the yellow phosphorus trap was immersed in liquid nitrogen to remove any condensable impurities which might be present.

E. Nitrogen

Tank nitrogen was passed through a tower containing amalgamated mossy zinc and vanadium pentoxide in sulfuric acid to remove oxygen². It was next bubbled through a water tower and two calcium sulfate towers and a liquid nitrogen trap before use.

F. Oxygen

Tank oxygen was passed through a liquid nitrogen trap before use.

G. Methane

Phillips 66 research grade methane was flushed thoroughly through a holder, which was then closed off with stopcocks and attached to the system and used. The glass tubing between the methane container and the main system was evacuated to approximately 2×10^{-7} mm. before the methane was introduced.

2. L. Meites and T. Meites, Anal. Chem., 20, 984 (1948).

H. Carbon Dioxide

Carbon dioxide was obtained from a tank of 99.5% stated purity. The gas was passed through a dry ice-acetone trap before flushing out the container used to introduce the gas into the system. The connecting tubing between the carbon dioxide container and the rest of the system was evacuated to approximately 2×10^{-7} mm.

I. Water

Double distilled water was used. The second distillation was made from a basic potassium permanganate solution. A small amount of the liquid was placed in a tube and attached to the vacuum system where it was degassed for about five minutes with a mechanical pump. The water vapor was then introduced into the system.

J. Other Materials Used in Flasks and Electrode Systems

Tests were made to observe any spurious reactions that might occur on the glass of the flask not covered with nickel and on the various materials used for the electrodes. The results are summarized in Table IV.

No reaction was noted in 20 minutes at 189° C. in the flask described in Figure 4 before a nickel film was evaporated. This means that the reaction on Pyrex glass, tungsten electrodes, nickel couplings, and the nickel filament is negligible. Experiments were also carried out with small pieces (as much or more than would normally be exposed as electrodes) of stainless steel at 32 and 172° C., copper at 28 and 155° C., and brass at 30° C. None of these showed any sign of reacting in 20 to 30 minute test periods.

TABLE IV
RESULTS OF TESTS FOR REACTION OF FORMIC ACID VAPOR ON
MATERIALS USED IN FLASKS AND ELECTRODE SYSTEMS

MATERIAL	TEMPERATURE (°C.)	REACTION
Pyrex flask before evaporation	189	None in 20 - 30 min.
Stainless Steel	32, 172	None in 20 - 30 min.
Copper	28, 155	None in 20 - 30 min.
Brass	30	None in 20 - 30 min.
Apiezon T Stopcock Grease	Room Temperature	None in 20 - 30 min.
Teflon	Room Temperature	None in 20 - 30 min.
Buna-N O-rings	Room Temperature	Rapid absorption of formic acid vapor
Silicone Rubber O-ring	Room Temperature	Rapid absorption of formic acid vapor

Apiezon "T" stopcock grease did not absorb the formic acid vapor nor did it cause any reaction at room temperature. However a disadvantage of all the electrode systems using O-rings made of Buna-N and of silicone rubber is that formic acid vapor is readily absorbed in these O-rings. The higher the formic acid vapor pressure is, the greater the absorption by the O-rings. Tests were not made to determine the absorption of products by the O-rings. No O-rings were used in the later designs of apparatus from which the data, reported later, were obtained. Teflon did not absorb the formic acid vapor but its vapor pressure was deemed to be too high, about 1×10^{-5} mm. at room temperature, to be usable.

V EXPERIMENTAL

A. Character of the Nickel Films

The high vacuum and nitrogen evaporated nickel films up to 7000 Å thickness and sintered at room temperature and 190° C. are randomly oriented on both soft and Pyrex glass backing. The average width of the crystallite is 270 Å for the high vacuum and 160 Å for the nitrogen films sintered at 190° C. After use, the high vacuum films appeared to have an amorphous substance on the surface but no carbon or nickel oxide lines were detectable. Samples which were not properly degassed before evaporation showed nickel oxide lines. Visual examination showed that the high vacuum evaporated nickel surfaces were bright, shiny and mirror-like in appearance, while the nitrogen evaporated films had a glossy, blue-black appearance.

1. Experimental Examination

The experimental examination of the films was carried out by X-ray and electron diffraction.

a. X-ray

X-ray diffraction photographs were taken with a Cr target tube operated at 30 KV. and 10 ma. filament current and a camera having a diameter of 57.3 mm. Kodak Type K Industrial X-ray film was used and was exposed from 2 to 4 hours. A vanadium filter removed all but the k_{α_1} and k_{α_2} lines. The k_{α_1} and k_{α_2} lines were unresolved on the photographs of both the evaporated and the bulk nickel. All of the

Figure 5. X-ray Photograph of High Vacuum
Evaporated Nickel Film

Figure 6. X-ray Photograph of Nitrogen
Evaporated Nickel Film

nickel samples were examined before exposure to the formic acid vapor and its decomposition products. The samples of nickel were evaporated on small sections (3x3 mm.) of Pyrex glass obtained by blowing bubbles and then choosing a flat section which was just strong enough to stand vertically under its own weight. The thin sections of glass were used to cut down the scattering of the X-rays by the glass. This scattering caused very dense backgrounds when heavier pieces of glass were used. The samples were oscillated $\pm 7.5^\circ$ from positions perpendicular to, parallel to, and at $67^\circ 12'$ ($\theta = 67^\circ 12'$ for the 220 reflection) to the X-ray beam. Plate II shows the results of 4 hour exposures of high vacuum and nitrogen type films oscillated $\pm 7.5^\circ$ from the perpendicular to the beam.

The photograph of the bulk nickel sample was made from an untreated piece of 1/32 inch thick sheet nickel which was about 3/8 inches square. It was oscillated $\pm 7.5^\circ$ perpendicular to the X-ray beam for an exposure time of one hour.

The crystallite sizes were determined by the relation¹

$$t = K \frac{\lambda}{\beta} \cos \theta, \quad (1)$$

where t is the crystallite size, β is the true line broadening in radians, θ is the Bragg angle, λ is the wave length of the X-radiation, and K is the shape factor (1.0 for cubic crystals).

Because of the finite width of the X-ray beam, the observed line widths could not be used directly. The true broadening, β , was found with the expression¹

1. G. G. Libowitz and S. H. Bauer, J. Phys. Chem., 59, 214 (1955).

$$R^2 = (\beta_E)^2 - \beta_B^2 \quad (2)$$

where β_B is the half-width of the lines of bulk nickel and β_E is the half-width of the evaporated nickel. The half-widths were measured from the photographs by means of a microdensitometer.

b. Electron Diffraction

The low-angle electron diffraction photographs were taken by Dr. A. Prebus and his assistant, Robert Hanson, with an RCA model EMU electron microscope. A piece of gold wire, which was hammered into a thin strip and then annealed, was used for calibration purposes. The nickel and nickel oxide lines were identified relative to the gold lines. The nickel films were evaporated on both Pyrex and soft glass backing. Some of the samples were taken from the reaction flask after a decomposition reaction and another group was examined before any reaction took place.

The films were mounted nearly parallel to the electron beam. The edges of the glass were painted with India ink to form a conducting surface from the nickel film to the brass sample mount. Only a large splotch was observed if the film became charged by the electron beam. Exposure times were of the order of seconds.

Plate III gives examples of these photographs.

2. Results

The X-ray and electron diffraction studies showed that both the high vacuum and nitrogen type films are randomly oriented up to 7000 Å film thickness. This is the film thickness calculated for the

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

LEGEND FOR PLATE III

- Figure 7. Electron diffraction photograph of nitrogen evaporated nickel film (16.7 mg.), sintered at room temperature, soft glass backing, no reaction performed on film.
- Figure 8. Electron diffraction photograph of nitrogen evaporated nickel film (16.7 mg.), sintered at room temperature, Pyrex glass backing, no reaction performed on film.
- Figure 9. Electron diffraction photograph of high vacuum evaporated nickel film (22.9 mg.), sintered at room temperature, soft glass backing, no reaction performed on film.
- Figure 10. Electron diffraction photograph of nitrogen evaporated nickel film (14.9 mg.), sintered at 190° C., soft glass backing. Photograph made after decomposition was performed.
- Figure 11. Electron diffraction photograph of high vacuum evaporated nickel film (71 mg.), sintered at 190° C., soft glass backing. Photograph made after decomposition was performed.

weight of the heaviest nickel film used for both decomposition work and electron diffraction, 100 mg., the area over which the film was deposited, 300 cm.² for a 500 ml. flask, and the specific gravity of nickel, $1/2 \times 8.9 = 4.5$ g/cc. appropriate for porous evaporated films²,

$$\frac{100}{300} \cdot \frac{1}{4.500} = 7000 \text{ \AA}.$$

a. Crystallite Size

The crystallite size was calculated from the (220) back reflection lines of the bulk nickel and evaporated nickel films by equation (1). The calculations were made from photographs of samples oscillated $\pm 7.5^\circ$ perpendicular to the X-ray beam for one hour and four hours respectively for bulk and evaporated nickel. These photographs were judged to be of nearly equal intensities by visual comparison of the entire film and by comparison of the line intensities by means of the microdensitometer. Both the high vacuum and nitrogen type films examined were sintered at 190° C. and no formic acid decomposition experiment was performed on them. The weight of the high vacuum and nitrogen films for these experiments was 46.7 and 57 mg. respectively or 3300 and 4000 $\text{\AA}$ thick. The crystallite size is 160 $\text{\AA}$ for the nitrogen type film and 270 $\text{\AA}$ for the high vacuum type film.

b. Effect of Sintering Temperature on Orientation

High vacuum and nitrogen type nickel films prepared at 0° C. and sintered at room temperature were compared by electron diffraction with similar films sintered at 190° C. All the films showed random orientation. See Plate III.

2. A. Wheeler, "Advances in Catalysis", vol. 3, Academic Press, Inc., New York (1951), p. 305.

c. Effect of Backing on Orientation

Both soft glass and Pyrex glass backing for the films were examined by the electron microscope. Random orientation was observed for these films. See Plate III, figures 7 and 8.

d. Effect of Improper Degassing

Some of the films prepared for examination were degassed for one day at 500° C. instead of the usual five days. The pressure during those evaporations was 10^{-6} mm. instead of 10^{-7} mm. These films showed strong nickel oxide lines. Reactions performed on films of this type were slow. See Plate III, figures 7, 8, and 9.

e. Effect of Use

Electron diffraction photographs of several films were made after use. The high vacuum type films (Plate III, figure 11) showed an amorphous type structure on the surface which nearly obscured the nickel lines. These samples were taken from the reaction vessel after reactions at 156 and 189° C., the range used for the high vacuum type films. No such disturbance was noted for the nitrogen type film sample (Plate III, figure 10) taken after reaction at 154° C., the highest temperature used for the nitrogen type films.

4. Discussion

a. Comparison with Others

The lack of any orientation of the nitrogen type films is the most interesting difference between the nickel films obtained in this dissertation and films formed by Beeck, Smith and Wheeler³, and

3. O. Beeck, A. E. Smith, and A. Wheeler, Proc. Roy. Soc. London, A177, 62 (1940).

Toyama and Kubokawa⁴.

Beeck studied evaporated nickel films in great detail and found that the catalytic activity of these films is affected by (1) the film thickness, (2) the pressure of the inert gas in which the metal vapor is condensed, and (3) the temperature of the glass surface on to which the metal vapor is condensed. With regards to orientation, films evaporated in 1 to 2 mm. of nitrogen at 23° C. were found to be oriented with the (110) plane parallel to the surface of the backing for all weights of nickel evaporated, and these films were strongly oriented beyond 10,000 Å thickness. However, at nitrogen pressures lower than 0.5 mm. and greater than 2 mm., some random orientation was observed. At 5×10^{-2} mm., the orientation caused by the presence of nitrogen was markedly less. As the inert gas pressure was increased above 2 mm., the orientation gradually disappeared until at 8 to 10 mm. no orientation was shown. The high vacuum type films evaporated at 23° C. were randomly oriented, but the heavy films (about 40,000 Å film thickness) showed some evidence of orientation.

In a review of Beeck's work, Wheeler⁵ says that electron diffraction pictures showed that the crystallite size of the high vacuum films, presumably evaporated and sintered at 23° C., was about 100 to 300 Å as compared to the 270 Å found in this dissertation by X-ray examination of the films evaporated at 0° C. and sintered at 190° C. No value of

4. O. Toyama and Y. Kubokawa, J. Chem. Soc. Japan, Pure Chem. Section, 74, 289 (1953).

5. A. Wheeler, "Structures and Properties of Solid Surfaces", The University of Chicago Press, Chicago (1952), p. 451.

the crystallite size was given by Wheeler for the oriented nitrogen type films.

Beeck found that sintering the films evaporated at 23° C. did not alter the orientation, even when the sintering temperature was 500° C.⁶ Toyama and Kubokawa also found by electron diffraction that the nickel films evaporated in 1 to 2 mm. of nitrogen at 23° C. were oriented with the (110) plane parallel to the backing, and the high vacuum films were randomly oriented. Sintering these films at 180° C. did not affect the orientation.

Although the exact treatment of the films is not given, the electron diffraction photographs shown by Beeck⁷ exhibit nickel oxide lines. These photographs are similar to Plate III, Figure 9 of this dissertation, where it is believed the nickel oxide lines came from improper degassing of the system before evaporation.

Table V compares the data of this dissertation with the data of Beeck et al. and Toyama and Kubokawa. Although the films of this dissertation were evaporated at 0° C. instead of 23° C., no great difference is noted except in the reaction vessel radius, which was ten times greater than the radius of the vessel used by Beeck. Other differences are that Beeck used a mercury diffusion pump, McLeod gauge, and used a mercury manometer to replace a Bourdon gauge for following pressure changes during the course of a reaction. An interesting correlation appears between the vessel radius and the inert gas pressure

6. O. Beeck, A. E. Smith, and A. Wheeler, loc. cit.

7. O. Beeck, A. Smith and A. Wheeler, loc. cit., facing p. 80.

TABLE V
COMPARISON OF EVAPORATION DATA OF BEECK ET AL.
TOYAMA AND KUBOKAWA, AND THE WRITER

OBSERVER	DEPOSITION TEMPERATURE °C.	REACTION VESSEL RADIUS CM.	PRESSURE DURING FILM DEPOSITION mm. Hg.	ORIENTATION OF FILM
Beeck	23	0.5	High Vacuum	Random
	23	0.5	5×10^{-2} N ₂ or A	Oriented & Random
	23	0.5	1 - 2 N ₂ or A	Oriented
	23	0.5	8 - 10 N ₂ or A	Random
Toyama and Kubokawa	23	---	High Vacuum	Random
	23	---	1 - 2 N ₂	Oriented
Walton	0	5	High Vacuum	Random
	0	5	1 - 2 N ₂	Random

used during the evaporation. The 0.5 cm. radius of Beeck's vessel multiplied by 10 mm. nitrogen gives the same product as the 5 cm. radius of this dissertation multiplied by 1 mm. nitrogen pressure, and both of these films were randomly oriented. The vessel dimensions as well as the inert gas pressure may be important in producing oriented films, i.e., there may be a relation between the energy lost by the nickel particles due to the total number of collisions with the inert gas atmosphere and the resulting orientation or lack of orientation of the deposited film.

Toyama and Kubokawa used the same films for repeated experiments in the decomposition of formic acid vapor from 143 to 160° C. The films used in the present work were good for only one decomposition experiment; the initial activity was never regained. The presence of an amorphous substance on the surface of the high vacuum films after a reaction at 156° and 189° C. may indicate the deposition of a reaction-poisoning material. However, this amorphous type deposit was not noted on the nitrogen evaporated type film examined after reaction at 154° C.

B. Surface Area of the Nickel Films

The surface area was determined by measuring the amount of hydrogen chemisorbed at 0° C. Hydrogen chemisorption was chosen in place of the more familiar BET method for the following reasons;

(1) Nitrogen cannot be used. At -195° C. nitrogen is chemisorbed and the calculated surface area is 50 per cent too large⁸. (2) If an inert gas such as argon is used, the ratio of the volume of dead space to the volume of gas adsorbed is too large for accurate surface measurement. At -195° C. the condensation pressure of argon is 220 mm.⁹. If adsorption measurements are made at a relative pressure of 0.01, i.e.,

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8. O. Beeck, "Advances in Catalysis," vol. 2, Academic Press, Inc., New York (1950), p. 151.
 9. International Critical Tables, vol. III, McGraw-Hill Book Co., Inc., New York (1928), p. 103.

at 2 mm. of argon, the STP volume of gas required to fill the 500 ml. reaction flask is 1.3 cm.³. The amount of argon required to cover 1000 cm.² of surface (the approximate experimental area) is calculated from the area an argon atom covers at -196° C., (1.5×10^{-15} cm²/atom)¹⁰ as $1000/1.5 \times 10^{-15} = 6.5 \times 10^{17}$ argon atoms. This is 10^{-6} moles, or 0.02 cm.³ of argon STP. The ratio of these two values is $1.3/0.02 = 60/1$, i.e., the amount of gas required to fill the dead space is 60 times as great as the amount adsorbed. An error of only 1 per cent in measuring the total amount of gas adsorbed and in the dead space could cause a 60 per cent error in the volume adsorbed. (3) The BET method is based on physical adsorption and will measure the amount of poisoned surface as well as the non-poisoned surface, and will give an inaccurate measure of active surface. (4) Beeck and Ritchie¹¹ found the surface area of the porous nitrogen type films, measured by the BET method, varied with the size of the adsorbate molecule. A gas such as butane at the temperature of -116° C. has a condensation pressure of 0.17 mm.¹² and the dead space to volume adsorbed ratio is lowered sufficiently to measure small surface areas. However, the larger molecules might not give an accurate surface measurement without some kind of calibration. (5) The ease of working at 0° C. with the hydrogen chemisorption makes it the best choice.

The adsorption was determined by introducing a measured number of hydrogen molecules from the bulb of a McLeod gauge and determining how many were left after adsorption had occurred. One hydrogen atom is adsorbed per nickel atom in the surface.¹³

10. H. K. Livingston, J. Colloid Sci., 4, 447 (1949).

11. O. Beeck and A. W. Ritchie, Disc. Faraday Soc., 8, 159 (1950).

12. L. A. Wooten and C. Brown, J. Am. Chem. Soc., 65, 113 (1943).

13. O. Beeck, A. Smith and A. Wheeler, loc. cit.

1. Apparatus

The McLeod gauge, K, Figure 3, was constructed to cover the range from 0.005 to 5.0 mm. Hg. It was calibrated with considerable care with both mercury and water, since accurate pressures and volumes of gases were needed for surface area experiments. A sloping ring seal was made at the base of the 54.7 ml. bulb (including the capillary tip) so that no gas other than that inside the bulb would be trapped above the cut off. After the gas was trapped in the bulb, that in the reference side of the gauge was pumped off; this practice made it unnecessary to apply any corrections in the high pressure region. The equation used to calculate pressures with the McLeod gauge is

$$P_1 = \frac{P_2 (hx0.08016 - 0.0017)}{54.7} \quad (1)$$

where

P_1 = pressure to be measured (cm.)

P_2 = distance between mercury menisci in the closed and open capillaries (cm.)

h = distance from the end of the capillary to the middle of the mercury meniscus in the closed capillary (cm.)

0.08016 = area of cross section of closed capillary (cm.²)

0.0017 = volume correction to allow for non-uniformity in the closed tip of the capillary (cm.³)

The capillary, made of Tru-Bore tubing, was calibrated by adding and weighing small amounts of mercury to the capillary and then measuring the length of the mercury column. Beyond 0.3 cm. from the sealed end of the capillary, the tubing remained uniform at a diameter of $3.19 \pm$

0.01 mm. (cross sectional area of 0.08016 cm.²). The 0.0017 cm.³ correction was needed when the tip was included in the McLeod gauge equation to account for contraction at the sealed end. It was because of this contraction that the lower limit of the McLeod gauge was set at 0.005 mm. Hg. Beyond this pressure it would be necessary to work in the last 0.3 cm. of the sealed capillary.

Raising and lowering the mercury in the two arms of the gauge changed the values of P_2 and h while the value of P_1 remained constant. The reproducibility of the gauge, when it was read with a cathetometer to the nearest 0.1 mm., was 0.5% of the pressure in the range mentioned.

2. Procedure and Calculations

Before any nickel was evaporated, the total volume of the system involved in the determination of surface areas was measured at room temperature by expanding hydrogen from the known volume of the McLeod gauge into the rest of the system to be measured. The pressure of the gas trapped in the 54.7 ml. of the McLeod gauge was measured and then the gas was expanded into the entire system and the pressure was remeasured. The pressures, both before and after expansion, were measured at three different values of P_2 and h , and the average pressures were used. The total volume of the system is then found by

$$\text{Total Volume} = \frac{(\text{Pressure before expansion}) \times 54.7}{(\text{Pressure after expansion})} \quad (2)$$

The volume of the flask was found by measuring the amount of water necessary to fill the flask. The volume outside the flask is found by

$$\text{Total Volume} - \text{Flask Volume} = \text{Volume Outside of Flask.} \quad (3)$$

During an adsorption measurement, the flask was kept at 0° C., while the rest of the apparatus was at room temperature. The number of hydrogen molecules adsorbed is given by

No. of hydrogen molecules adsorbed	=	Original no. of molecules in measured volume of McLeod gauge.	-	No. in flask at 0° C. after adsorption.	-	No. outside of flask at room temperature after adsorption.
------------------------------------	---	---	---	---	---	--

or,

$$\text{No. adsorbed} = \frac{P_1 \times 54.7}{R \times T_1} - \frac{P_2 \times \text{Flask Vol.}}{R \times 273.16} - \frac{P_2 \times \text{Vol. at room temp.}}{R \times T_2} \quad (5)$$

Where;

P_1 = Initial pressure in cm. Hg. of gas contained in 54.7 ml. volume of the McLeod gauge

P_2 = Pressure in cm. Hg. after expansion and adsorption.

T_1 = Room temperature before adsorption. (°K)

T_2 = Room temperature after adsorption. (°K)

R = 1.035×10^{-20} cm.-c.c./°K/molecule.

However, the initial pressure during an adsorption was about 2 mm. Hg. and the final pressure was in the range of 0.01 mm. Hg. and the lower pressure was in the range where thermomolecular flow must be taken into consideration. The McLeod gauge was connected to the reaction flask through 8 mm. tubing whose inside diameter was approximately 6 mm. The mean free path of a hydrogen molecule at 0.01 mm. Hg. and 25° C. is 0.931 cm. The ratio of the diameter of the connecting tubing to the mean free path was .6 cm./0.931 cm. = .64. The pressure correction necessary for thermomolecular flow when the mean free path

is of the same order of magnitude as the diameter of the connecting tube is given in the review by Dushman¹⁴. The equation for thermomolecular flow under these conditions is

$$\frac{dP}{dT} = \frac{3}{8} \cdot \frac{k_2}{(1 + 2a/L)} \cdot \frac{P}{T} \quad (6)$$

Where;

k_2 is nearly $4/3$

L is the mean free path

$2a$ is the diameter of the connecting tubing.

If we set $\frac{3}{8} \frac{k_2}{(1 + 2a/L)} = K$, integrate equation (6), and find the ratio of the pressures P_3 and P_4 at two temperatures T_3 and T_4 , we get

$$\frac{P_3}{P_4} = \left(\frac{T_3}{T_4}\right)^K = \left(\frac{T_3}{T_4}\right)^{\frac{3}{8} \frac{k_2}{(1+2a/L)}} \quad (7)$$

By substituting $k_2 = 4/3$, $2a = .6$ cm., and $L = 0.000931/P_{\text{cm.}}$, where $P_{\text{cm.}}$ is the pressure in cm. Hg equation (7) becomes

$$\frac{P_3}{P_4} = \left(\frac{T_3}{T_4}\right)^{\frac{1}{2+1300 P_{\text{cm.}}}}$$

When equation (7) is applied to equation (5), the number of hydrogen molecules adsorbed is

$$\frac{P_1 \times 54.7}{R \times T_1} - \frac{P_2 \times \text{Flask Vol.}}{R \times 273.16} \times \left(\frac{273.16}{T_2}\right)^{\frac{1}{2+1300 P_2}} - \frac{P_2 \times \text{Vol. at room temp.}}{R \times T_2}$$

(8)

14. S. Dushman, "Scientific Foundations of Vacuum Technique," Wiley, New York (1949), p. 66.

Equation (8) is the equation used to calculate the number of hydrogen molecules adsorbed by the nickel films. The number of hydrogen atoms adsorbed is twice the number of molecules.

3. Results

Surface areas of nitrogen and high vacuum evaporated nickel films were measured as a function of the weight of the film. The films were sintered for several hours at 190° C. before the surface area measurements were made at 0° C. by the chemisorption of hydrogen. The surface areas of the films were found to be reproducible and the areas do not increase linearly with the weight of the nickel film.

a. Surface area as a function of weight of nickel evaporated

Table VI gives the results of the surface area measurements. The weight of nickel evaporated, type of film (nitrogen or high vacuum), number of hydrogen atoms adsorbed, and the surface area are given. The average value of the area per H atom site for the random type films is $6.72 \text{ \AA}^2$. The surface area is the product of $6.72 \text{ \AA}^2$ times the number of H atoms adsorbed. Random type films are likely to have the low index planes (100), (110) and (111) exposed to roughly equal extents. The areas per site in these three planes for face centered cubic nickel with a lattice constant of $3.52 \text{ \AA}$ are respectively 6.16, 8.70 and $5.32 \text{ \AA}^2$, the mean is $6.72 \text{ \AA}^2$.

The values given in Table VI are plotted in Figure 12. The ordinate giving the number of hydrogen atoms adsorbed for the high vacuum films is on the left side of the graph. The nitrogen film ordinate is given on the right side of the graph. The abscissa gives the weight of nickel evaporated.

TABLE VI
SURFACE AREAS OF EVAPORATED 99 ALLOY NICKEL FILMS
SINTERED AT 190° C.

EXPERIMENT NUMBER	WEIGHT OF NICKEL EVAPORATED mg.	TYPE OF FILM	H ATOMS $\times 10^{-18}$ ADSORBED	SURFACE AREA cm ²
7-24	15.7	H.V.	0.598	402
7-17	29.1	H.V.	0.836	562
6-111	31.3	H.V.	0.894	601
7-20	40.5	H.V.	0.894	601
7-8	71	H.V.	1.04	699
7-14	100.8	H.V.	1.32	887
7-27	14.9	N ₂	2.58	1732
7-30	41.6	N ₂	3.94	2649
7-2	45.9	N ₂	3.86	2594

The areas do not vary linearly with the weight of nickel. They have been fitted into an equation of the type $y = Ax^n$ where y is the number of hydrogen atoms adsorbed and x is the weight of the nickel evaporated. A and n are 0.227×10^{18} and 0.377 respectively for the high vacuum films and 0.920×10^{18} and 0.377 for the nitrogen type films. The curves in Figure 12 were drawn from these equations. The nitrogen type films have four times as much surface area as the high vacuum type for the same weight of nickel.

b. Reproducibility of the surfaces

The reproducibility of the surfaces is demonstrated by the agreement of experiments 6-11¹ and 7-17 performed more than one month apart in which respectively 31.3 and 29.1 mg. of nickel were evaporated to give 0.89 and 0.84×10^{18} H atoms adsorbed. Experiments 7-30 and 7-2, which also showed the surface reproducibility, were performed on the nitrogen type films. There were 3.94×10^{18} hydrogen atoms adsorbed on 41.6 mg. of nickel in experiment 7-30 and 3.86×10^{18} hydrogen atoms adsorbed on 45.9 mg. of nickel in experiment 7-2.

4. Discussion

Beeck¹⁵ found that at pressures of 0.1 mm. the rapid chemisorption of hydrogen on evaporated nickel films at -183° C. and room temperature covered the surface completely. Because of this, the surface measurements at 0° C. of this work have been carried out at pressures $>10^{-2}$ mm. and as near to 0.1 mm. as possible.

a. Comparison with others

For the same weight of nickel, the nitrogen evaporated films

15. O. Beeck, loc. cit.

Figure 12. Surface area of high vacuum $\circ$ and nitrogen $\diamond$ evaporated 99 Alloy nickel films sintered at 190°C . against the weight of nickel evaporated. The areas were measured at 0°C . by hydrogen chemisorption.

adsorbed four times as much hydrogen as the high vacuum type films. Beeck¹⁶ found the oriented nitrogen evaporated type films had an area about twice as great as the high vacuum films. He also says that the randomly oriented films, obtained by evaporation in 10 mm. nitrogen, were of a high activity, comparable to that of the oriented films.

Beeck also found that increasing the temperature of sintering decreased the surface area of the nickel films^{15,16}; the surface area was also found, in his work to increase linearly with the weight of nickel evaporated for films sintered at room temperature¹⁶. Figure 12 of this work shows that the surface areas of films sintered at 190° C. do not increase linearly with the weight of evaporated nickel, but show a decreasing increment with increasing amounts of nickel. In the experiments of Toyama and Kubokawa¹⁷, the decreasing activity with increasing weight of high vacuum evaporated nickel indicates a similar effect for their films, sintered at 180° C. This may mean that at higher temperatures sintering is occurring to such an extent as to make the surface areas tend towards the geometric surface for all weights of nickel, and at 180 to 190° C. this process is taking place to some extent.

According to Beeck the surface area for a film sintered at 190° C. is about 20 per cent of the value corresponding to 23° sintering^{15,16}. High vacuum and nitrogen films adsorbed respectively 14 and 28 x 10¹⁸ hydrogen atoms per 100 mg. of evaporated nickel on 23° sintered films¹⁸, or 3.5 and 7.0 x 10¹⁸ hydrogen atoms per 25 mg. of nickel as calculated by the linear relationship indicated in Beeck's work. For films

16. O. Beeck, A. E. Smith, and A. Wheeler, loc. cit.

17. O. Toyama and Y. Kubokawa, loc. cit.

18. O. Beeck and A. W. Ritchie, loc. cit.

sintered at 190° C. the values then become 0.7 and 1.4×10^{18} hydrogen atoms per 25 mg. of nickel. These values compare to 0.76 and 3.2×10^{18} hydrogen atoms per 25 mg. of nickel as taken from Figure 12 of this dissertation.

C. Products of Decomposition

The products of decomposition, hydrogen, carbon dioxide, carbon monoxide, water vapor, and methane, were identified by mass spectrographic analysis; no other gases were detected. Hydrogen, carbon dioxide, and carbon monoxide were measured by gas analysis and the small amount of methane were determined from mass spectrograms. Water vapor was determined indirectly in the products of reactions which went to completion and was found to be present in equal amounts to the carbon monoxide formed.

1. Gas Analysis

Figure 13 shows the semi-micro apparatus for analysis of product samples of volumes up to 2 c.c. STP. The apparatus is a modification of that described by Blacet et al.,¹⁹ that of Sutton²⁰, and that of Taylor²¹.

a. Blacet-Leighton Apparatus

The samples were kept in holders, H, fastened by a rubber band to a wooden spool, F, which rotated freely about the 1/4 inch iron rod, I.

-
19. a. F.E. Blacet and P.A. Leighton, *Ind. Eng. Chem. Anal. Ed.*, 3, 266 (1931); b. F.E. Blacet, G.D. MacDonald, and P.A. Leighton, *ibid.*, 5, 272 (1933); c. F.E. Blacet and G.D. MacDonald, *ibid.*, 6, 334 (1934); d. F.E. Blacet and D.F. Volman, *ibid.*, 9, 44 (1937); e. F.E. Blacet, A.G. Sellers, and W.J. Blaedel, *ibid.*, 12, 356 (1940); f. P.A. Leighton and R.N. Smith, *Anal. Chem.*, 14, 758 (1942)
20. C. T. Sutton, *J. Sci. Inst.*, 15, 133 (1938)
21. J. E. Taylor, unpublished.

Figure 13. Gas analysis apparatus

LEGEND FOR FIGURE 13

- B. Buret.
- C. Sample Transfer Tube.
- F. Wooden Spool.
- H. Sample Holder.
- I. Iron Rod.
- L. Lever used to raise the reagent holder into the sample holder.
- R. Reagent Holder.
- S. 5 c.c. syringe for drawing sample into buret.
- T. Set screw arrangement for fastening reagent holder to lever.
- W. Hot wire mechanism.

Levers, L, were used to raise the reagents attached to platinum wires at the end of glass rods, R, into the sample holders. These reagent holders were held to the levers by the set screw arrangement, T. The sample holders were rotated over the reagents which were immersed in the mercury and then the lever was raised until the reagent was seen to appear in the gas space in the sample holder. Care was taken not to touch the walls or top of the sample holder with the reagent. While the absorption was taking place, the lever was propped up with a small piece of rubber.

Volume measurements were made by drawing the sample into the calibrated buret, B, surrounded with a water jacket, by means of a 5 c.c. syringe, S.

The pressure equalization arm, E, connected the syringe end of the buret directly back to the pot of mercury holding the samples. When the stopcock on this arm was opened, the pressure was immediately equalized on both sides of the gas column in the buret and a reading could be made. Leveling of the buret was facilitated when arm E was open, as the gas column moved when the buret was not level.

The transfer tube, C, consisting of a medicine dropper bulb on a capillary with one end drawn out to a fine tip, was used to transfer samples from storage bulbs into position for analysis. Air was first expelled from the transfer tube under mercury and then some mercury was drawn into the tube. Without removing the tip from the mercury, the tip was moved under the storage bulb full of gas and some gas was drawn in. Next, the tip was again immersed in the mercury and more mercury was drawn into the transfer tube to sandwich the gas between

two columns of mercury. The sample was released by forcing some of the mercury from the tip of the transfer tube while it was under the mercury surface in order to get rid of any air trapped during the transfer. The tip of the transfer tube was then placed under an empty sample holder and the gas was expelled.

The sample holders were made from 20 mm. Pyrex tubing and were about 25 mm. deep; the handles to the holders were of 4 mm. Pyrex rod. The reagent holders were made by imbedding short pieces of 0.020 inch diameter platinum wire in 3 mm. soft glass rod bent as shown at R in Figure 4. The hot wire mechanism, used for combustions, was made by pulling out a piece of 6 mm. soft glass tubing until a 6 inch length of 0.020 inch diameter platinum would just slip through. The glass was sealed close to one end of the platinum and the end of the glass tube was bent into the shape of a hook. A piece of 0.010 inch diameter platinum wire was spot welded to the short stub of the heavier wire protruding beyond the glass-to-metal seal. The free end of the small wire dangled into the mercury to form one contact and the other end was attached to the heavy wire which passed through the glass to form the other contact. A piece of wire bent in the shape of a reagent holder was taped onto the glass and used to raise and lower the hot-wire device into the sample holders. A 6-ampere Variac set at 80 volts furnished the power to heat the wire for combustions.

The gas buret was made by fastening the barrel of a 50 ml. buret (with rubber stoppers and DeKhotinsky cement) around a fairly uniform piece of 2 mm. capillary tubing, and then calibrating the capillary.

The capillary was calibrated by running a section of mercury at constant temperature through the capillary and taking readings at random but overlapping buret markings. The meniscus of the mercury was read at a point about $1/2$ to $2/3$ of the way from the base of the meniscus to the top of the meniscus. The mercury was weighed and the volume between the marks was thus computed. The buret had 500 divisions and four sections of mercury ranging from 10 units in length to 250 units were used in the calibration. A conversion table was then made to convert from buret readings to ml. The average total volume of the capillary was 1.9510 ± 0.0008 ml.

b. Procedure

The procedure was as follows; the total dry volume of the sample of non-condensables containing hydrogen, carbon dioxide, carbon monoxide, and methane was measured; the carbon dioxide was removed with potassium hydroxide and the dry sample volume was again measured; an excess of oxygen was added and the remainder of the sample was oxidized with the hot wire; the sample was again dried with phosphorus pentoxide and the volume measured; carbon dioxide resulting from the combustion of carbon monoxide was removed by potassium hydroxide; hydrogen was found by difference. When large amounts of carbon monoxide and hydrogen were present, the oxygen had to be added slowly (in small doses) during the oxidation. Otherwise an explosion occurred and the sample was lost.

c. Calculations

The calculations are made as follows;

$$\%CO_2 = 100 - \frac{\text{Dry volume after removal of } CO_2 \times 100}{\text{Total dry volume of sample}}$$

$$\%CO = \frac{\text{Dry volume after combustion} - \text{Dry vol. after removal of oxidized CO}}{\text{Total dry volume of sample}}$$

$$\times 100 - \%CH_4$$

$$\%H_2 = 100 - \%CO_2 - \%CO - \%CH_4$$

Usually the methane was neglected because it amounted to only a few tenths of a per cent at the most.

d. Reagents

Water vapor was removed by phosphorus pentoxide powder which had been fused onto the platinum tip of a reagent holder with an electrically heated coil of Nichrome wire.

Carbon dioxide was removed by a small pellet of potassium hydroxide which had been fused to the reagent holder by heating with an electrically heated coil of Nichrome wire.

Hydrogen and carbon monoxide were oxidized by adding sufficient tank oxygen to react with the reducing gases and the gases were oxidized by a platinum wire heated electrically.

e. Sources of Error

Incomplete reaction with the reagents may be detected by exposure to a fresh absorbent sample before proceeding to the next determination.

Contamination by the reagents put into the gas may be avoided by careful preparation and use of them.

Inaccurate measurement of the gas volume may be prevented by having the buret very clean and by using care in reading the gas

volume. Several readings in different parts of the buret should be taken.

Pressure and temperature variations may be corrected by observing the barometric pressure and the temperature with every volume measurement. These variations were usually slight and were neglected.

The greatest error is to be expected in the determination of carbon monoxide. The error in reading the buret was constant and was relatively large for small volumes. The reproducibility obtained with the buret was ± 0.0010 ml., and often the volume of carbon monoxide was of the order 0.0400 to 0.0800 ml. A rough check was given by comparing the per cent of carbon dioxide with the per cent of hydrogen. These values should have been very nearly equal, and if they were not within a few per cent, another analysis was made to check the results. All of the samples contained a small amount of methane which was determined along with the carbon monoxide as carbon dioxide after the combustion. After the amount of methane was determined by the mass spectrometer, a correction, less than one per cent, could be made to the carbon monoxide determination.

f. Analysis of Knowns

Table VII gives the results of the analysis of knowns. The known mixtures were made up of carbon dioxide, hydrogen, and carbon monoxide. The hydrogen was prepared from mossy zinc and dilute sulfuric acid. The carbon monoxide was prepared from formic acid and concentrated sulfuric acid. The carbon dioxide was prepared from sodium carbonate and dilute sulfuric acid. All of these gases were passed through traps

TABLE VII
ANALYSIS OF KNOWN SAMPLES

SAMPLE NUMBER	% KNOWN			% ANALYZED		
	CO ₂	H ₂	CO	CO ₂	H ₂	CO
2-50-1	48.4	48.7	2.7	47.4	50.3	2.3
2-50-2	48.4	48.7	2.7	48.0	49.7	2.3
2-60-1	48.4	48.7	2.8	48.8	49.0	2.2
2-60-2	48.4	48.7	2.8	48.8	48.8	2.4
2-68-1	49.1	48.6	2.3	49.1	48.7	2.2
2-68-2	49.1	48.6	2.3	49.0	48.6	2.4

of potassium hydroxide and calcium sulfate before storing for use. The mixtures were then prepared by mixing known amounts of the three gases. These are listed as percentages in columns 2, 3, and 4 in Table VII. The sample size was about 0.6 ml. in all cases. The analyzed per cents are given in columns 5, 6, and 7. Altogether, three mixtures were analyzed in duplicate, 2-50, 2-60, and 2-68. A comparison of the known percentages with the analyzed percentages indicates that the carbon dioxide varied about ± 0.4 per cent from the approximate 49 per cent in the samples. The carbon monoxide analyzed a few tenths of a per cent low. Since hydrogen is obtained by difference, it analyzed high. In sample number 2-50, where both carbon dioxide and carbon monoxide analyzed low, the hydrogen differed by more than a full per cent from its known value. The consistently low carbon monoxide values may be caused by incomplete combustion. Impure carbon monoxide could also be the cause.

The time required for an analysis generally was about 2 to 2-1/2 hours including the calculation of the data, but not including the time required for cleaning and drying the buret.

2. Mass-spectrographic Analysis

Methane was determined with a 120° G.E. analytical mass spectrometer with 75 volts ionizing potential and 2000 volts acceleration potential. The percentage of methane found in the formic acid decomposition products was less than one per cent in all cases, and was too small to be measured by the gas analysis apparatus.

Methane was the sole contributor to the peak at mass 16 and was easily detected by merely watching for the appearance of this peak. The amount of methane in the total sample volumes of 150 to 200 microliters, μ .l., was usually small; the methane peak heights were correspondingly small, generally about 0.5 to 3 units high and an error of ± 2 of a unit was easily made in estimating the peak height.

Quantitative measurements can be made if the sensitivity for methane at mass 16 is known. A method of approximating the sensitivity was used to estimate the amount of methane present in the samples.

Carbon dioxide was the sole contributor to the peak at mass 44. The percentage of carbon dioxide in every sample was found by analysis with the gas analysis apparatus. With that information the sensitivity of carbon dioxide, S_{CO_2} , at mass 44 was calculated by

$$S_{CO_2} = \frac{\text{Peak height at mass 44}}{\%CO_2 \times \text{Sample volume } (\mu\text{.l.})} \times 100$$

Although the sensitivity varied rather widely from day to day, the variation during any one day was found to be about $\pm 5\%$. On three occasions a product sample was analyzed on the same day that Robert M. Smith checked a pure methane sample to obtain the methane sensitivity, S_{CH_4} . The ratio of the carbon dioxide sensitivity to the methane sensitivity on the three occasions was 1.33, 1.37, and 1.45 (average 1.45).

The methane sensitivity in other analyses was then found from the carbon dioxide sensitivity by the equation

$$\frac{S_{CO_2}}{1.45} = S_{CH_4} \quad (1)$$

The percentage of methane was then calculated by

$$\%CH_4 = \frac{\text{Peak height at mass 15}}{S_{CH_4} \times \text{Sample volume } (\mu.l.)} \times 100 \quad (2)$$

Substituting equation (1) in equation (2), we get

$$\%CH_4 = \frac{\text{Peak height at mass 15}}{\frac{S_{CD_2}}{1.45} \times \text{Sample volume } (\mu.l.)} \times 100 \quad (3)$$

or,

$$\%CH_4 = \frac{\text{Peak height at mass 15}}{0.69 S_{CO_2} \times \text{Sample volume } (\mu.l.)} \times 100 \quad (4)$$

The percentage of methane in the product sample containing the non-condensables, hydrogen, carbon dioxide, carbon monoxide, and methane, was calculated by equation (4).

3. Results

The product analysis did not include water vapor which was shown to be present in amounts equal to the amount of carbon monoxide. This equality is first demonstrated and is followed by the gas analysis and mass spectrographic analysis data.

a. Water Vapor

Water vapor and formic acid vapor condensed while the sample was being transferred by means of a Toepler pump from the reaction flask to the sample holders for analysis and could not be directly analyzed. The amount of water vapor is equal to the amount of carbon monoxide found. Proof of this equality is easily demonstrated. The only gases detected were hydrogen, carbon dioxide, carbon monoxide, water vapor, and methane, and hydrogen and carbon dioxide were found in equal amounts.

When the hydrogen and carbon monoxide were removed, the remaining pressure was half the total sample pressure. Hence we have, if methane is neglected,

$$P_{H_2} + P_{CO_2} + P_{H_2O} + P_{CO} = P \quad (1)$$

$$P_{H_2} = P_{CO_2} \quad (2)$$

and $P_{CO_2} + P_{H_2O} = 1/2 P.$ (3)

From equations (1) and (2)

$$2P_{CO_2} + P_{H_2O} + P_{CO} = P. \quad (4)$$

Multiply equation (3) by 2,

$$2P_{CO_2} + 2P_{H_2O} = P, \quad (5)$$

and set equation (4) equal to (5)

$$2P_{CO_2} + P_{H_2O} + P_{CO} = P = 2P_{CO_2} + 2P_{H_2O}$$

so that

$$P_{H_2O} = P_{CO}. \quad (6)$$

This equality was proved experimentally as follows. A product sample was taken at the end of a reaction, i.e., 100 per cent decomposition, and the pressure measured in the sampling system described in section III - L. The sampling system consisted of a manometer attached to a trap used as a gas reservoir and placed between the reaction flask and Toepler pump. The water vapor and carbon dioxide were frozen out at liquid nitrogen temperature, and the hydrogen and carbon monoxide were pumped off with a mechanical pump for about five minutes. The liquid

nitrogen was then removed and the remainder of the sample was warmed to room temperature where the pressure was again measured.

In experiment 5-42, two samples were analyzed and the final sample pressures after the removal of hydrogen and carbon monoxide were both 53 per cent of the initial pressure. One sample from experiment 6-36 gave 49 per cent. These values are close to the 50 per cent expected and the amount of carbon monoxide equals the amount of water vapor.

b. Hydrogen, Carbon Dioxide, Carbon Monoxide, and Methane

The results of the gas and mass spectrographic analyses are given in Table VIII. The complete data are found in the Appendix tables by the experiment number. Although gas samples were taken during experiment 6-36, the data are not in the Appendix because a sticking manometer ruined the data. The calculations were made according to section V-C-1-c for the gas analysis and section V-C-2 for the mass spectrographic analysis. The mixture of hydrogen, carbon dioxide, carbon monoxide, and methane are referred to as the non-condensable portion of the sample in Table VIII. Column 1 gives the experiment number, column 2 the temperature of the experiment, column 3 the per cent decomposition, and the remaining columns give the percentages of hydrogen, carbon dioxide, carbon monoxide and methane.

The per cent of formic acid vapor decomposition was calculated from the pressure increase of the reaction at the time of sampling as compared to the total pressure increase expected. For example, if the pressure increase were 5 mm. at the time of sampling and the total increase expected was 20 mm., the per cent decomposition was $5 \times 100/20$ or 25 per cent.

Another method of calculating the per cent of formic acid vapor decomposition was used in cases where samples were taken at different times during the course of a single experiment. Experiments 6-36, 6-45, 6-53, 6-59, and 6-95 are of this type. In such cases it is necessary to determine the initial pressure of formic acid, appropriate to the amount of material present in the flask when the later samples are taken, from the contents of the flask, their composition as obtained by analysis, and the stoichiometry of the reaction, without recourse to the initial pressure, which is unknown after the first sample is taken. The determination of these initial pressures, corrected for sample withdrawal, is complicated by dimerization of formic acid at low temperatures.

The sample was let into the sampling system (section III-L.) and the pressure, P_T , was measured. The sample was cooled to dry ice temperature and the carbon monoxide, hydrogen, carbon dioxide, and methane were pumped off. The remaining formic acid vapor and water vapor were then rewarmed to room temperature and the pressure, $P_{F_2 + H_2O}$, was measured. The formic acid vapor was assumed to exist as dimer, F_2 , at room temperature although the pressures were in the 25 mm. range. The pressure, $P_{N.C.}$, of the carbon monoxide, hydrogen, carbon dioxide, and methane is then found by

$$P_{N.C.} = P_T - P_{F_2 + H_2O}$$

The percent of carbon monoxide in the carbon monoxide, hydrogen, carbon dioxide, and methane mixture is found by gas analysis and is equal to the per cent of water vapor. The water vapor pressure, P_{H_2O} , is then

$$P_{H_2O} = \%CO \times P_{N.C.}/100$$

Now, the pressure of the formic acid dimer is

$$P_{F_2} = P_{F_2+H_2O} - P_{H_2O}$$

And the pressure of the formic acid^{as}/monomer, P_{F_1} , is

$$P_{F_1} = 2 \times P_{F_2}$$

The total pressure of the sample in terms of formic acid vapor monomer, P'_T , is

$$P'_T = P_T - P_{F_2} + P_{F_1}$$

The initial formic acid vapor monomer pressure, P_{1F_1} present at the beginning of the experiment is

$$P_{1F_1} = 1/2 (P'_T - P_{F_1}) + P_{F_1}$$

And the per cent of formic acid vapor decomposition is then

$$\% \text{ Decomposition} = \frac{P_{1F_1} - P_{F_1}}{P_{1F_1}} \times 100,$$

or, in terms of the experimentally measured quantities

$$\% \text{ Decomposition} = \frac{100}{1 + 4 \left[\frac{P_{F_2} + H_2O - \%CO(P_T - P_{F_2} + H_2O)}{100} \right] \left[\frac{P_T - P_{F_2} + H_2O + \%CO(P_T - P_{F_2} + H_2O)}{100} \right]}$$

The results obtained by this equation give decomposition percentages within about six per cent of the first method. The big error in this calculation is the assumption that formic acid vapor is all dimer at room temperature and low sample pressures. The amount of dimer at 20 mm. formic acid vapor pressure and 25° C. is 70 per cent as calculated from the equation given in Table I of the Literature Review section, i.e., 14 mm. of the total pressure can be attributed to the dimer.

4. Discussion

The results of the gas analyses show that the formic acid vapor is decomposing simultaneously into carbon dioxide and hydrogen, and carbon monoxide and water vapor. The temperature coefficients of the two reactions are nearly the same over the 125 to 190° C. temperature range studied. Corresponding to a shift towards equilibrium in the water gas reaction, $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$, there is relatively more carbon dioxide at the end of the reaction than at the beginning. The methane is believed to be formed by a secondary reaction involving the products.

It has been previously reported^{22, 23, 24, 25} that the decomposition of formic acid on metal surfaces produces mainly carbon dioxide and hydrogen. The formation of carbon monoxide and water has been reported on glass surfaces at 183° C.²⁴ The appearance of both sets of products in this research is therefore unexpected. It is evident from Table VIII, however, that both sets of products appear at the earliest stages of the reaction, and that the ratio of dehydrogenation to dehydration remains constant throughout the main course of the reaction. The conclusion is that the two reactions are occurring simultaneously on the nickel surface. No reaction whatsoever was observed in the flask in the absence of a nickel film, even at the highest temperature, showing that any possible reaction on a glass surface is negligible. (See Appendix, Experiment 5-86).

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TABLE VIII
PRODUCT ANALYSIS FOR VARIOUS EXTENTS OF REACTION
ON 99 ALLOY NICKEL

A. HIGH VACUUM TYPE FILMS

Experiment Number	Temperature °C.	% HCOOH Decomposed	%CO ₂ , H ₂ , CO, and CH ₄ in Non- Condensable Portion of Sample				Ratio CO ₂ :CO
			CO ₂	H ₂	CO	CH ₄	
5-55	189	17	44.0	44.3	11.1	0	4:1
5-65	187.9	37	40.6	43.9	15.6	0.05	2.6:1
5-58	188	45	40.3	43.9	16.2	0	2.5:1
5-60	188	51	40.0	40.9	18.9	0.05	2.1:1
5-52	188	51	41.8	43.5	14.7	0	2.8:1
5-81	188.2	55	39.2	43.0	17.8	0.44	2.2:1
5-92	188.7	56	40.8	43.0	16.2	0.31	2.5:1
5-72	188.5	65	42.1	42.2	15.7	0.27	2.7:1
5-77	188.5	68	40.0	42.4	17.5	0.42	2.3:1
6-111	189.2	70	41.2	44.6	15.2	0.10	2.7:1
5-42	187	100	45.6	45.7	8.5	0.96	5.4:1
6-59	167.4	27	39.8	44.2	15.9	0.092	2.5:1
6-53	168.3	45	41.0	40.2	18.6	0.03	2.2:1
6-59	167.4	81	43.6	43.1	14.4	0.14	3.0:1
6-53	168.3	100	42.4	43.4	14.1	0	3.0:1
6-59	167.4	100	42.4	44.6	13.3	0.17	3.2:1
6-36	147.6	16	39.6	42.6	17.4	0.0077	2.3:1
6-45	146.4	35	41.3	42.3	16.4	0.028	2.5:1
6-45	146.4	45	41.7	41.9	16.4	0.017	2.5:1
6-31	150.5	66	42.1	43.3	14.7	0.029	2.9:1
6-45	146.4	84	43.5	42.3	14.3	0	3.0:1
6-36	147.6	85	42.9	43.7	13.5	0.014	3.2:1
6-36	147.6	100	44.3	44.3	11.4	0.014	3.9:1

TABLE VIII
PRODUCT ANALYSIS FOR VARIOUS EXTENTS OF REACTION
ON 99 ALLOY NICKEL

B. NITROGEN TYPE FILMS

Experiment Number	Temperature °C.	%HCOOH Decomposed	%CO ₂ , H ₂ , CO, and CH ₄ in Non- Condensable Portion of Sample				Ratio CO ₂ :CO
			CO ₂	H ₂	CO	CH ₄	
6-78	189	82	40.8	40.6	18.5	0.08	2.2:1
6-81	169	78	43.8	44.5	11.8	0.07	3.7:1
6-87	146.0	57	41.6	43.8	14.6	0	2.9:1
7-3	146.0	44	43.4	42.9	13.7	0.08	3.2:1
6-97	147.2	33	41.7	45.8	12.5	0.28	3.3:1
6-106	153.5	65	41.8	44.9	13.3	0.05	3.1:1
6-97	147.2	95	45.2	46.8	9.0	0.11	5.0:1
6-101	124.7	16	41.8	42.0	16.2	---	2.6:1
6-91	125.3	>20	42.5	43.5	14.0	0	3.0:1

The temperature coefficients of both reactions appear to be very nearly the same. The data in Table VIII show no definite change in the ratio of the products $\text{CO}_2:\text{CO}$ except after long periods of reaction. If ratios for decompositions greater than 90 per cent are omitted, the ratio of $\text{CO}_2:\text{CO}$ is nearly constant for all temperatures, indicating similar temperature coefficients for both reactions. Average $\text{CO}_2:\text{CO}$ values are given as a function of temperature in Table IX. The average ratio of $\text{CO}_2:\text{CO}$ is 2.6:1 for the high temperature samples (high vacuum type films) and 3.0:1 for the low temperature samples (nitrogen type films). This represents less than 1 kcal./mole difference in the activation energies for the two reactions, the carbon monoxide reaction having the higher activation energy of the two. However, this difference is slight and the temperature coefficients for both of the reactions are very nearly the same over the 125 to 190° C. temperature range studied.

The amount of hydrogen was determined by difference after combustion of hydrogen and carbon monoxide. The hydrogen values are usually higher than the carbon dioxide values, even in the analysis of known samples. (See Table VII.) This may be caused by incomplete combustion of the carbon monoxide to carbon dioxide, which was the form measured by absorption by potassium hydroxide. The difference between the percentage of carbon dioxide and hydrogen is then the amount of carbon monoxide not oxidized. If the difference is added to the amount of carbon monoxide already found, the ratio of $\text{CO}_2:\text{CO}$ will be decreased to about 2.4:1 for the high temperature samples and 2.8:1 for the low temperature samples. This is essentially the same result found without any correction.

TABLE IX
AVERAGE CARBON DIOXIDE TO CARBON MONOXIDE RATIOS
TAKEN ACCORDING TO TEMPERATURE GROUPS AND EXCLUDING
RATIOS AT DECOMPOSITIONS GREATER THAN 90 PER CENT

A. HIGH VACUUM TYPE FILMS

Temperature °C.	Average Ratio CO ₂ :CO	Number of Values Averaged
187-189	2.6	10
167-168	2.6	3
146-150	2.7	6

B. NITROGEN TYPE FILMS

Temperature °C.	Average Ratio CO ₂ :CO	Number of Values Averaged
189	2.2	1
169	3.7	1
146	3.0	2
147-153	3.2	2
125	2.8	2

At 100 per cent decomposition, or after long periods of reaction, the percentage of carbon monoxide is relatively low and the percentage of carbon dioxide is relatively high, due to a shift toward equilibrium in the water gas reaction, $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$. At 190°C . the equilibrium ratio of $\text{CO}_2:\text{CO}$ is 165:1²⁶. At 125°C . it is 38.6:1. The carbon dioxide enrichment and carbon monoxide decrease found experimentally are in line with the shift towards these equilibrium values. The slowness of the shift at these temperatures on nickel is demonstrated at 189°C . by experiment 5-42 which was studied over a nine hour period. This is more than twice the time required for apparently complete decomposition at this temperature. The ratio of $\text{CO}_2:\text{CO}$ changed from the usual value of about 2.5:1 to 5.4:1, still far from equilibrium.

The amount of methane found in the products increases with the length of the reaction, and more methane is found at higher temperatures than at the lower temperatures. The methane is probably formed through the secondary reaction of hydrogen and carbon monoxide, or perhaps hydrogen and carbon dioxide. Pichler²⁷ has discussed the synthesis of hydrocarbons and the water gas equilibrium on iron, cobalt, and nickel catalysts.

D. Rate of Decomposition

The initial rate of decomposition of formic acid vapor on evaporated nickel films has been found to be zero order with respect to formic acid vapor pressure from 10 to 50 mm. and over the temperature range studied from 125 to 190°C .

26. H. Pichler, "Advances in Catalysis", vol. 4, Academic Press, Inc., New York (1952), p. 328.

27. H. Pichler, ibid., p. 327 ff.

Variation of the temperature indicates that there is no difference between temperature coefficients of reactions on the high vacuum and nitrogen type nickel films, and the activation energy for the combined data is 16.5 ± 1.3 kcal./mole.

The addition of a product gas causes the initial rate to decrease. The general shape of all the curves, giving pressure increase with time, is similar for all the experiments in which product gases are added, except carbon dioxide, which acts as a strong poison after the first few minutes of the reaction. Oxygen is a strong poison for the reaction.

The degree of degassing, before and during the evaporation of nickel, affects the initial activity of the films. Films evaporated at 10^{-7} mm. are about 2 to 3 times as active as those evaporated at 10^{-6} mm.

The first decomposition experiment on a nickel film has the highest initial rate. The initial rates of the slower subsequent decompositions on the same film depend upon the evacuation pressure between experiments. The initial rate is slower when the flask is evacuated to 10^{-6} mm. between experiments than when evacuated to 10^{-5} mm.

There is no significant difference between the Low Carbon and 99 Alloy nickel used as catalysts.

1. Preliminary Work with High Vacuum Evaporated Nickel Films

Much of the early work was devoted to developing a suitable technique and to finding the conditions necessary for carrying out the experiments. A maximum reaction temperature of 190° C. was chosen and all the films were sintered, for several hours before use,

at this temperature so that no corrections would be necessary for variations of surface area with sintering temperature.

At this time the amount of nickel to be evaporated was not controllable and the nickel surfaces were not reproducible. The nickel was evaporated from tungsten filaments which weakened and broke with alloy formation during the evaporation. Usually only 10 to 20 mg. of nickel could be easily evaporated.

A summary of these early data is found in Table X. The complete data for these experiments are found in the Appendix by the experiment numbers. The formic acid used in all the experiments was greater than 99.98% water-free. The experiment number is given in column 1. (The numbers refer to the data book and page of the data book, e.g. experiment 3-1 would come chronologically before 3-2 just as 3-1 would come before 4-1.) The weight of nickel evaporated is in column 2; the type of nickel used is found in column 3; the initial pressure in mm. Hg is in column 4; the maximum rate in terms of the pressure increase in mm. Hg per minute is given in column 5; and the reaction temperature is given in column 6. The term maximum rate denotes that part of the reaction where the rate of decomposition of formic acid vapor is at a maximum, e.g., point A in Figure 14. It was measured by a straight edge placed along the part of the curve judged to have the steepest slope.

Some information can be obtained from consecutive experiments on one film even though there can be no comparison made of the different films. The series of experiments performed on one film were carried out in two ways. (1) After each experiment the flask was evacuated and

Figure 14. Comparison of experiment with absorption (4-79-1, 187°C.) with experiment without absorption (5-37, 190°C.)

TABLE X

SUMMARY OF DATA OBTAINED IN PRELIMINARY DECOMPOSITION EXPERIMENTS ON
HIGH VACUUM FILMS EVAPORATED FROM TUNGSTEN FILAMENTS

EXPERIMENT NUMBER	WEIGHT OF NICKEL EVAPORATED mg.	TYPE OF NICKEL	INITIAL PRESSURE mm. Hg.	MAXIMUM RATE mm. Hg./min.	TEMPERATURE °C.
4-79-1	9.7	A Nickel	10.0	0.13	187
4-79-2	9.7	A Nickel	8.8	0.060	177
4-79-3	9.7	A Nickel	8.4	0.027	187
4-79-4	9.7	A Nickel	7.6	0.024	189
4-87-1	6.8	99 Alloy	5.0	0.22	190
4-87-2	6.8	99 Alloy	3 mm. added near end of first part of reaction	0.15	190
4-87-3	6.8	99 Alloy	10.7	0.22	189
4-87-4	6.8	99 Alloy	12.0 mm. added after about 30% of first part reacted	0.20	189
4-93-1	24.6	99 Alloy	5.0	0.091	189
4-93-2	24.6	99 Alloy	10.0	0.057	190
5-15-1	16.2	99 Alloy	25.0	0.032	188
5-15-2	16.2	99 Alloy	19.4	0.011	189

more formic acid vapor was added to start the next experiment. (2) Instead of evacuating the flask between experiments more formic acid vapor was added directly to the reactant and products already in the flask. Examples of the first method are given in experiments 4-79-1, -2, -3, -4; 4-87-1, -3; 4-93-1, -2; and 5-15-1, -2. Examples of the second method are 4-87-1, -2; and 4-87-3, -4. The data from the first of these methods show that when the initial formic acid vapor pressure was varied randomly from 5 to 25 mm. the very first experiment on the film gave the highest maximum rate with subsequent decompositions always being slower. This activity decline masked the temperature dependence sought in the series 4-79-1 to 4-79-4. The second of these methods shows a slight decrease in maximum rate after more formic acid vapor was added.

These data were further complicated by absorption effects due to O-rings used in the system, by poor time measurement, and by poisoning of the films due to poor degassing of the system. Absorption effects often caused a pressure decrease or a slow pressure increase resembling an induction period during the first part of the reaction. Figure 14 gives a comparison of an experiment with absorption by O-rings (expt. 4-79-1) with one without absorption (expt. 5-37). A wall clock with a sweep second hand was used to measure the time. Time measurement was less important where absorption was involved but it was of great importance in the mercury-free system where the first four or five minutes were the most valuable part of the reaction. The seriousness of the poisoning is exemplified by the fact that the number of hydrogen

atoms chemisorbed at 0° C. on nickel films of approximately 20 mg. varied from 10^{16} to 10^{18} . The sum of these effects nullifies any attempt at quantitative comparison of these data.

2. Summary of Rate Data

Tables XI, XII, XIII, and XIV summarize the rate data obtained in the system with a spoon-type Bourdon gauge and no O-rings, and in which nickel was evaporated directly from a nickel filament. The complete data for these experiments are given in the Appendix Tables which are listed in order according to experiment numbers. In these experiments, where no absorption effects are present, the initial part of the reaction is the most rapid. The plotted rate data give curves similar in shape to experiment 5-37 shown in Figure 14.

Table XI summarizes the first results obtained in the system. These data are placed in a separate table because the time was measured with a wall clock to the nearest half minute and because the data during the initial part of the reaction are scant. The initial rate is listed in column 5 in units of mm. of pressure increase per second per H atom adsorbed $\times 10^{-18}$. The first point was measured about one-half a minute after the formic acid vapor was let into the reaction flask. The initial rate was found by drawing a smooth curve through the experimental points and extrapolating back to zero time. The initial slope was then drawn in with a straight edge and measured. This slope was then divided by the surface area calculated from the weight of nickel evaporated as found in Figure 12. The initial pressure was estimated from the point of intersection of the initial slope with the ordinate.

In the later experiments, Tables XII, XIII and XIV, a Time-it was used to measure the time to the nearest second and more points were taken during the first part of the reaction. The initial rate was found by fitting the first 4 or 5 minutes of the decomposition data to a cubic equation by the method of least squares. The derivative of the equation at zero time is the initial rate. The initial pressure is also an extrapolated value obtained from the constant found in the cubic equation. In these experiments the initial rate has been divided by the surface area corresponding to the weight of nickel from Figure 12, and it is given in terms of mm. pressure increase per second per H atom adsorbed $\times 10^{-18}$.

A few decompositions could not be reliably fitted to a cubic equation. In these experiments there were not enough points taken in the initial part of the reaction. These experiments are 5-85, 6-101, 7-15; their initial rates were estimated in the same manner as for the data in Table XI.

The least squares value of the initial rate for experiment 7-30 was disregarded for the reason given below. Curves A and B of Figure 15 demonstrate the two general shapes of cubic curves obtained in the least squares treatment of the pressure-time data taken during the decomposition reactions. The rate data that these curves were forced to fit usually fell in the region between $t=0$ and $t=a$. Most of the rate data were fitted by the type A curve characterized by a positive coefficient for the t^3 term. Only experiments 5-81, 6-87, and 6-91, and 7-30 were fitted by curves of type B characterized by a negative coefficient for the t^3 term. The inflection points of curves A and B

are marked by x's. The inflection point of the curves of type A always appeared near $t=a$ and well onto the positive side of the t -axis. The inflection point of the type B curves usually appeared near b , in the negative portion of the t -axis. However, the inflection point of the curve fitted to experiment 7-30, a type B curve, appeared on the positive side of the t -axis at 1.5 minutes. A plot of the least squares curve showed the initial rate, the slope of the curve at $t=0$, was definitely going to be low, and the least square value of the initial rate for experiment 7-30 was rejected. If curve B of Figure 15 is shifted to the right so that the inflection point is on the positive side of the t -axis, this effect is readily noted. There were, however, enough points in the initial part of the experiment 7-30 to estimate the slope reasonably well by drawing it in. This is the value given in Table XI.

Table XII summarizes the data obtained on high vacuum evaporated films; Table XIII the data from nitrogen evaporated films; and Table XVI the data obtained by introducing a gas into the reaction flask before the formic acid vapor.

3. Variation of Rate with Initial Formic Acid Vapor Pressure

The data in Tables XII and XI I are grouped according to temperature. Within these temperature groups the arrangement is in order of increasing initial pressure.

Table XII gives the data on high vacuum films. By comparing rates with the same initial pressures and temperatures, the variations from experiment to experiment may be noted. The poorest agreement is in the 156 to 159° group where the rates differ by a factor of two. In the

Figure 15. General shape of the two types of cubic least squares curves (A and B) which were fitted to the decomposition rate data

TABLE XI
SUMMARY OF FORMIC ACID VAPOR DECOMPOSITIONS ON
HIGH VACUUM EVAPORATED NICKEL FILMS

EXPERIMENT NUMBER	WEIGHT OF NICKEL EVAPORATED mg.	TYPE OF NICKEL	INITIAL PRESSURE mm.Hg.	INITIAL RATE	TEMPERA- TURE °C.
				$\frac{\text{mm. Hg.}}{\text{Sec.}-\text{H atom} \times 10^{-18}}$	
5-26-1	39.4	Low Carbon	14.2	0.027	192
5-26-2	39.4	Low Carbon	24.0	0.0057	192
5-26-3	39.4	Low Carbon	20.1	0.00095	192
5-33	50.7	Low Carbon	19.9	0.037	190
5-37	28.3	Low Carbon	26.4	0.040	190
5-42	64.0	99 Alloy	31.6	0.025	187
5-52	50.5	99 Alloy	14.5	0.042	188
5-55	26.6	99 Alloy	50.2	0.042	189
5-58	37.4	99 Alloy	14.0	0.043	188
5-60	24.0	99 Alloy	10.1	0.055	188

TABLE XII

SUMMARY OF FORMIC ACID VAPOR DECOMPOSITIONS ON
HIGH VACUUM EVAPORATED NICKEL FILMS.
ALL EXPERIMENTS PERFORMED ON 99 ALLOY NICKEL.

EXPERIMENT NUMBER	WEIGHT OF NICKEL EVAPORATED mg.	INITIAL PRESSURE mm. Hg.	INITIAL RATE	TEMPERATURE °C.
			$\frac{\text{mm. Hg.}}{\text{Sec.-H atom} \times 10^{-18}}$	
5-86	None	17.3	0.000	187.5
6-111	31.3	14.9	0.0750	189.2
5-77	30.3	17.4	0.0773	188.6
5-65	33.8	20.3	0.0522	187.9
5-72	27.6	23.2	0.0437	188.5
6-71	38.3	25.4	0.0669	188.8
7-18	29.1	25.8	0.0764	188.5
5-81	27.4	27.9	0.0464	188.2
6-53	44.5	12.1	0.0350	168.3
7-24	13.7	12.2	0.0340	173.3
7-15	100.8	24.7	0.0221	171.1
6-59	28.9	25.3	0.0359	167.4
6-69	38.0	51.1	0.0347	168.6
7-21	40.5	19.3	0.0213	169.0
7-9	71.0	21.0	0.00945	156.3
6-31	39.8	13.2	0.0178	150.5
6-45	30.2	28.9	0.0138	146.4

TABLE XIII
SUMMARY OF FORMIC ACID VAPOR DECOMPOSITIONS ON
NITROGEN EVAPORATED NICKEL FILMS.
ALL EXPERIMENTS PERFORMED ON 99 ALLOY NICKEL

EXPERIMENT NUMBER	WEIGHT OF NICKEL EVAPORATED mg.	INITIAL PRESSURE mm. Hg.	INITIAL RATE	TEMPERATURE °C.
			$\frac{\text{mm. Hg.}}{\text{Sec.-H atom} \times 10^{-18}}$	
6-106	15.1	13.1	0.0178	153.3
7-27	14.9	16.2	0.0126	153.5
6-97	13.4	27.1	0.0189	155.2
6-87	20.4	11.8	0.00493	146.0
6-95	19.8	22.4	0.0156	147.2
7-3	45.9	26.2	0.00880	146.0
7-30	41.6	19.3	0.00440	132.1
6-101	21.0	24.7	0.00178	124.7
6-91	34.9	32.0	0.00389	125.3

168 to 175° group, the initial formic acid vapor pressure varies from 12.1 to 51.1 mm. and the initial rate remains nearly constant at 0.035 $\frac{\text{mm.}}{\text{Sec.-H atom} \times 10^{-18}}$. In this range the initial rate is independent of formic acid vapor pressure. Inspection of the other groups in Table XII shows no trend in the initial rates with initial pressures.

Likewise, inspection of the groups in Table XIII, which gives the data for the nitrogen evaporated films, shows no trend of initial rate with pressure, although agreement of the initial rates in individual experiments is not so good as with high vacuum films. The poorest agreement is in the 146 to 147° group where the rates vary by a factor of three. The poorer agreement here may arise from poisoning of the nickel film in experiment 6-87 by slight impurities in the nitrogen.

Thus the initial rates are independent of formic acid vapor pressure and the reaction is zero order with respect to formic acid vapor pressure. This means the initial rates are zero order rate constants, k_1 .

4. Variation of Rate with Pressure During Evaporation of High Vacuum Films

The preliminary results listed in Table XI show a tendency for the initial rates to become higher with each experiment. This trend continues into Table XII with experiments 5-65, 5-72, 5-77, and 5-81 until the fairly constant value of 0.075 $\frac{\text{mm.}}{\text{Sec.-H atom} \times 10^{-18}}$ is reached.

The lack of data in the first part of the reactions makes accurate estimates of the initial rates impossible in Table XI. However, another comparison can be made by taking the first part (approximately first 20 per cent) of the reaction in question and adjusting it to coincide with the data of a typical later experiment with an initial rate of

0.075 $\frac{\text{mm.}}{\text{Sec.}-\text{H atom} \times 10^{-18}}$. The multiplication of the pressure increase (ΔP) by a constant factor should bring all the points onto one line. The pressure increases were found by subtracting the initial pressures listed in Tables XI and XII from the corresponding rate data given in the Appendix tables. Experiment 6-111 was chosen as the standard and the experiments of Table XI and the early experiments of Table XII were adjusted to coincide with it. The results are shown in Figure 16. It is evident that the time course of the reaction is the same in all experiments, in spite of the differences in initial rate. The factors listed in the legend to Figure 16 show no relationship to the initial pressure, though there is an inverse trend with initial rate, as is to be expected.

a. Effect of Evaporation Pressure on Rate

Since the initial rates are independent of formic acid vapor pressure, any large variations of these rates might be due to variations of the surface area beyond the changes expected and already taken into consideration from Figure 12. Poisoning of the film is possible by improper degassing of the system and this is indicated by the evacuation pressure before, and the pressure during the evaporation. The multiplication factors used to make the sets of data coincide are then directly proportional to the amount of poisoning. A plot of the factors used in Figure 16 against the average pressure during the evaporation is given in Figure 17. The average pressure was estimated as $1/2$ (pressure at the start of the evaporation + pressure at the end of the evaporation). The factors increase with the average pressure during the evaporation and show that consistent results cannot be obtained unless the evaporation

Figure 16. Plot of pressure increase against time. All data adjusted to coincide with experiment 6-III. Temperature range from 188 to 192°C.

Figure 17. Plot of factor from Figure 16 against average evaporation pressure. Temperature range of experiments from 188 to 192 °C.

pressure remains constant. The lowest pressure attainable with the diffusion pump was 2×10^{-7} mm. After experiment 5-72 evaporations were not attempted until the pressure of the system was 3×10^{-7} mm. or lower. Where nitrogen evaporations were made, the pressure before the introduction of the nitrogen was always below 3×10^{-7} mm.

Initial rates can be calculated by dividing the initial rate of the standard experiment 6-111 by the factors used in Figure 16. Table XIV compares these calculated rates with Table XI rates which were found by drawing in the slope. The results compare favorably since both of these methods have inherent weaknesses. There is an error in drawing in the slope in the one method, and the choice of the proper initial pressure to be used as a base for the pressure differences affects the other method.

Comparison of the least squares initial rates of experiments 5-65, 5-72, and 5-81 with the rates calculated by dividing $0.075 \frac{\text{mm.}}{\text{Sec.-H atom} \times 10^{-18}}$ by the factors of Figure 16 gives these results: The least squares values are respectively 0.052, 0.044, and 0.046; the values calculated from the factors are respectively, 0.042, 0.059, and $0.065 \frac{\text{mm.}}{\text{Sec.-H atoms} \times 10^{-18}}$. These values are compared in Table XV.

5. Variation of Rate with Kind of Nickel

Figure 17 compares the Low Carbon nickel of experiments 5-33 and 5-37 with the 99 Alloy used in all the later experiments. The experiments using Low Carbon Nickel appear to fall on the same curve with the 99 Alloy experiments and indicate that the change in the type of nickel does not have a pronounced effect on the reaction.

TABLE XIV

COMPARISON OF INITIAL RATES FOUND BY DRAWING IN THE SLOPE WITH THOSE
 CALCULATED BY DIVIDING $0.075 \frac{\text{mm.}}{\text{Sec.-H atoms} \times 10^{-18}}$
 BY THE FACTORS OF FIGURE 16

EXPERIMENT NUMBER	DRAWN	CALCULATED
	$\frac{\text{mm.Hg.}}{\text{Sec.-H atom} \times 10^{-18}}$	$\frac{\text{mm.Hg.}}{\text{Sec.-H atom} \times 10^{-18}}$
5-33	0.037	0.032
5-37	0.040	0.031
5-42	0.025	0.026
5-52	0.042	0.033
5-55	0.042	0.036
5-58	0.043	0.037
5-60	0.055	0.056

TABLE XV
COMPARISON OF INITIAL RATES FOUND BY LEAST SQUARES WITH
THOSE CALCULATED BY DIVIDING $0.075 \frac{\text{mm.}}{\text{Sec.-H atom} \times 10^{-18}}$
BY THE FACTORS OF FIGURE 16

EXPERIMENT NUMBER	LEAST SQUARES	CALCULATED
	mm.Hg.	mm.Hg.
	Sec.-H atom $\times 10^{-18}$	Sec.-H atom $\times 10^{-18}$
5-66	0.052	0.042
5-72	0.044	0.059
5-81	0.046	0.065

6. Variation of Rate with Temperature

The activation energy, A. E., of the reaction is found by plotting the logarithm of the rate constants against the reciprocal of the absolute temperature, i.e., $\log_{10} k_1$ against $1/T$. For a zero order reaction the initial rate and the initial rate constant k_1 are the same. The slope of the plot is related to the activation energy by the integrated Arrhenius equation,

$$\log_{10} k_1 = -A. E./2303 RT + \text{Constant},$$

by

$$-4.58 (\text{slope}) = A. E.$$

Some selection of data for the activation energy plot was made. Only the k_1 's calculated by the least squares method were used from Tables XII and XIII, i.e., experiments 5-65, 6-101 and 7-15 were omitted.

The results are shown in Figure 18. The least squares value of the activation energy for the high vacuum evaporated nickel films is 15.0 kcal./mole with a standard deviation of the mean of 1.9 kcal./mole. The value for nitrogen evaporated films is 18.0 ± 4.4 kcal./mole.

The difference in activation energy between the two groups is not significant according to Student's t test²⁸.

Student's $t = \frac{\text{Difference in Means}}{\text{Weighted Standard Error of Difference}}$, or

$$t = (18.0 - 15.0)/\sigma_W$$

where

$$\sigma_W = \frac{n_{H.V.} s_{H.V.}^2 + n_{N_2} s_{N_2}^2}{n_{H.V.} + n_{N_2} - 2} \sqrt{\frac{1}{n_{H.V.}} + \frac{1}{n_{N_2}}}$$

and $n_{H.V.}$ = number of high vacuum evaporated points = 14

$s_{H.V.}$ = standard deviation of mean of high vacuum points = 1.93

28. M. J. Moroney, "Facts from Figures", 2nd Edition, Penguin Books Ltd., Harmondsworth, Middlesex (1958), pp. 232-233.

Figure 18

n_{N_2} = number of nitrogen evaporated points = 8

s_{N_2} = standard deviation of mean of nitrogen points = 4.36

The calculated value $t = 1.9$ places the difference between the two sets of data beyond the 5 per cent limit of probable significance, and a difference cannot be established. The data were then combined and a least squares calculation made. The activation energy of the combined data is $16.5 \pm 1.3 \text{ kcal./mole}$. The equation for variation of initial rate with temperature is

$$k = 4.037 \times 10^6 e^{-16,500/1.987 T}$$

or

$$\log_{10} k_1 = -3,599/T + 6.606$$

where k_1 is in units of mm. pressure increase per second per H atoms adsorbed $\times 10^{-18}$.

7. Variation of Rate with Addition of a Gas

The effect on the initial rate of adding a gas before the addition of formic acid vapor is summarized in Table XVI. The complete rate data are given in the Appendix and may be located by the experiment number. High vacuum evaporated nickel films were used at a temperature of 188 to 189° C. The third and fourth columns of Table XVI give the added gas and its pressure in mm. Hg. The fifth column gives the pressure of the formic acid vapor added at the start of the reaction.

The procedure in these experiments was to let some of the gas into the reaction flask a few minutes before the start of the reaction and measure its pressure. Formic acid vapor was then introduced and the

TABLE XVI

SUMMARY OF FORMIC ACID VAPOR DECOMPOSITIONS ON HIGH VACUUM
EVAPORATED FILMS. REACTIONS TAKE PLACE IN PRESENCE OF GAS
ADDED BEFORE FORMIC ACID VAPOR.

ALL EXPERIMENTS PERFORMED ON 99 ALLOY NICKEL

EXPERIMENT NUMBER	WEIGHT OF NICKEL EVAPORATED mg.	ADDED GAS	PRESSURE OF ADDED GAS mm. Hg.	INITIAL PRESSURE OF HCOOH mm. Hg.	INITIAL RATE mm.Hg. Sec.-H atom $\times 10^{-18}$	TEMP- ERATURE °C.
5-92	35.2	CO	0.05	23.2	0.0763	188.7
6-74	31.7	CO	8.2	19.8	0.0823	188.5
6-25	41.2	CO	17.7	8.4	0.0550	189.0
5-96	44.9	CH ₄	0.09	19.2	0.0829	187.8
5-111	42.7	CO ₂	5.8	12.7	0.0728	189.0
6-2	39.5	CO ₂	17.3	5.0	0.0339	189.0
6-6	45.6	H ₂	14.7	17.1	0.0479	189.0
6-10	36.5	H ₂ O	11.6	24.2	0.0451	189.0
6-14-1	33.5	O ₂	4.3	21.2	0.0000	188.8
6-14-2	33.5	---	---	21.6	0.0000	188.8
6-65	37.4	CO(+O ₂)	9.0	24.6	0.0000	189.0

initial rate of decomposition in the presence of the gas was found as usual by the pressure increase with time.

a. Addition of Oxygen

All of the gases listed except oxygen were observed in the products. Oxygen was added to see what might be the effect of possible degassing of oxygen from stopcock grease and the walls of the system. Experiment 6-14-1 shows that the effect of adding oxygen is to stop the reaction and to give an initial rate of zero. The oxygen and the formic acid vapor were evacuated from the flask after experiment 6-14-1 and only formic acid vapor was introduced into the reaction vessel in experiment 6-14-2 performed on the same film. Again no reaction occurred over a ten minute period. Oxygen is therefore a very good poison in this reaction.

By mass spectrographic examination, oxygen was found in the carbon monoxide used in experiment 6-65 in which 9.0 mm. of carbon monoxide (plus oxygen) was added before 24.6 mm. of formic acid vapor. The oxygen poisoned the reaction and no initial pressure increase was noted. However, after 5.5 hours, a pressure increase of 22.4 mm. was observed. Analysis of the three products carbon dioxide, hydrogen, and carbon monoxide showed 43.3% carbon dioxide, 36.5% hydrogen, and 20.2% carbon monoxide. Normally $\%CO_2 = \%H_2 = 3\%CO$, but because of the addition of carbon monoxide at the beginning of the experiment, the product ratio expected was $\%CO_2 = \%H_2 \approx \%CO$. The high amount of carbon dioxide relative to hydrogen and the low amount of carbon monoxide indicates the carbon monoxide was oxidized to carbon dioxide by the oxygen. This may explain why the reaction took place after a period of no activity. When the oxygen was

removed, the formic acid vapor decomposition took place.

b. Addition of Product Gases

The addition of a product gas causes the initial rate to decrease.

The rate of a zero order reaction may be expressed by

$$\text{Rate} = k_0 S \quad (1)$$

where k_0 is the rate constant per unit surface area and S is the total surface area available for the reaction. If poisoning occurs S will decrease. The rate is now expressed by

$$\text{Rate} = k_0 S \left(1 - \frac{C_p}{C_s + C_F + C_p} \right), \quad (2)$$

where

$$\frac{C_p}{C_s + C_F + C_p} = \text{fraction of surface covered by adsorbed poison}$$

$$C_p = \text{concentration of sites where the poison is adsorbed}$$

$$C_s = \text{concentration of free surface sites}$$

$$C_F = \text{concentration of sites where formic acid is adsorbed.}$$

Equation (2) is now rearranged to give

$$\begin{aligned} \text{Rate} &= k_0 S \left(\frac{C_s + C_F}{C_s + C_F + C_p} \right) \\ &= k_0 S \left(\frac{1}{1 + C_p / (C_s + C_F)} \right). \end{aligned} \quad (3)$$

For a zero order reaction $C_F \gg C_s$ and C_s may be neglected.

$$\text{Rate} = k_0 S \left(\frac{1}{1 + C_p / C_F} \right) \quad (4)$$

The following equilibria exist between the gaseous and adsorbed molecules:

$$C_{F_g} + C_s \rightleftharpoons C_F; \quad K_F = \frac{C_F}{C_{F_g} C_s} \quad (5)$$

$$C_{pg} + C_s = C_p ; K_p = \frac{C_p}{C_{pg} C_s} \quad (6)$$

where

C_{Fg} = concentration of formic acid vapor

C_{pg} = concentration of gaseous products

K_F = formic acid vapor adsorption equilibrium constant

K_p = product adsorption equilibrium constant.

Equations (5) and (6) are solved for C_F and C_p and these values are substituted in equation (4).

$$\text{Rate} = k_o S \left(\frac{1}{1 + K_p C_{pg} / K_F C_{Fg}} \right) \quad (7)$$

or

$$\frac{\text{Rate}}{S} = k_o \left(\frac{1}{1 + K_p P_{pg} / P_{Fg}} \right) \quad (8)$$

K is the ratio of the adsorption constants and concentrations have been changed to pressures. Equation (8) shows that the reaction rate per unit surface area varies inversely with the ratio of the pressure of the poisoning gas to the pressure of the reacting gas.

This treatment assumes that the heat of adsorption remains constant for the various degrees of surface coverage. Examination of the plots of the heat of adsorption against the fraction of the surface covered for hydrogen on evaporated nickel surfaces²⁹ show that the heat of adsorption declines with greater surface coverage. The constant K_p will then represent an average constant.

29. O. Beeck, W. A. Cole and A. Wheeler, Disc. Faraday Soc., 8, 314 (1950).

Equation (8) may be plotted linearly if the reciprocal of both sides of the equation is taken. Figure 19 shows a plot of the reciprocal of the initial rates against the ratio of the pressure of the added gas to the initial formic acid vapor pressure. The straight line was calculated from

$$\frac{10^{18} \text{ H atoms}}{\text{Rate}} = \frac{1}{0.075} \left(1 + 0.3 \frac{P_{PG}}{P_{FG}} \right) \quad (9)$$

where k_0 is $0.075 \frac{\text{mm. Hg.}}{\text{Sec.-H atoms} \times 10^{-18}}$ and K is 0.3. The curve has been drawn as a single line, as if K_p had the same value for all product gases. In view of the small number of experiments, no separation into the effects of individual gases is really warranted. The data as they stand, however, would indicate that the retarding action changes in the order $\text{CO} < \text{CO}_2 < \text{H}_2 < \text{H}_2\text{O}$, with water giving the slowest reaction.

Figure 19 shows there is a definite decline in the initial rates of decomposition in the presence of an added product gas. The films are poisoned by the addition of product gases, and, within the limits of error in these experiments, no preferential adsorption of one product over the other can be claimed.

The shape of the curves giving the pressure increase data against time was similar for all the product gases added except carbon dioxide.

1) Effect of Carbon Dioxide

Examination of the complete rate data found in the appendix tables for experiments 5-111 and 6-2, in which carbon dioxide was added, shows that the reaction rate drops off very rapidly a few minutes after the addition of the formic acid vapor, when the reaction is still far from completion.

The effect of the addition of carbon dioxide is shown in Figure 20 which is a graph of the data from experiments 5-111 and 6-2. The initial activity of experiment 6-2 declines rapidly at about 100 seconds. The addition of more formic acid vapor at 620 seconds initiates a

Figure 19. Effect of added gas on rate

catalyst activity which is longer lived than after the first addition of formic acid vapor. The activity in experiment 5-111 declines rapidly after about 300 seconds.

The addition of carbon dioxide is similar to the other product gases in its effect on the initial reaction rate, but it is different from the other product gases in that the rate declines sharply a few minutes after the addition of the formic acid vapor, when the reaction is still far from completion. Since the addition of more formic acid vapor again initiates the catalyst activity, the sudden decline in reaction rate may arise from the formation of an intermediate compound, which poisons the surface by reaction of the carbon dioxide with one of the decomposition products of the formic acid vapor.

8. Variation of Rate with Film Use

After a fresh nickel film is once used, the original activity never returns. Experiments performed by evacuating the flask between experiments (5-26-1, 5-26-2 and 5-26-3 of Table XI) show a large decline in the initial rates. The third experiment is nearly thirty times slower than the first.

A more extensive series of experiments was performed to see if the films ever reached a constant activity. This series of experiments was performed on the film on which a small amount of methane was initially added, experiment 5-96. All of the subsequent experiments were forced to fit the initial experiment by the same method used in Section V-D-4. The pressure increases of an experiment were multiplied by a constant factor to make the data agree with experiment 5-96.

Figure 20. Plot of pressure increase against time from 189°C. experiments 5-III, $\bigcirc$, and 6-2 $\bigcirc$, in which CO_2 was added before the addition of formic acid vapor pressure

The original experiment has a factor of one and following experiments have larger factors showing an activity decline. The activity of a subsequent experiment is given by the reciprocal of the factor needed to make the rate data agree with experiment 5-96. The complete rate data for these experiments may be found in the Appendix tables under the experiment number.

An interesting result of this work indicates that the rate of decomposition is dependent upon the evacuation pressure before the start of the experiment. Table XVII lists the experiment numbers, activities ($1/\text{factor}$) and the evacuation pressure before evaporation.

Comparison of adjacent experiments, i.e., 5-100 with 5-101, 5-103 with 5-104 and 5-105 with 5-106 shows that when the flask was evacuated to 2×10^{-6} mm. between experiments the activity was always lower than when the evacuation pressure was 2×10^{-5} mm. A comparison of the activity of successive experiments when the evacuation pressure was 2×10^{-5} mm. shows the activity to be slowly leveling off at about 0.45. The activities of the experiments where the evacuation pressure was 2×10^{-6} mm. are tending to level off at about 0.3. Thus the activity reaches a constant value only if the pressure of evacuation is constant between experiments.

TABLE XVII

SUMMARY OF DATA AT 189° C. ON HIGH VACUUM EVAPORATED FILM
SHOWING ACTIVITY DECREASE OF FILM WITH USE AND WITH DECREASING
EVACUATION PRESSURE BEFORE THE START OF THE EXPERIMENT

EXPERIMENT NUMBER	ACTIVITY	EVACUATION PRESSURE BEFORE EXPERIMENT mm. Hg.
5-96-1	1.00	2×10^{-7}
5-96-2	0.55	-----
5-96-3	0.44	2×10^{-6}
5-96-4	0.71	2×10^{-5}
5-96-5	0.48	1×10^{-5}
5-96-6	0.58	2×10^{-5}
5-96-7	0.28	2×10^{-5}
5-96-8	0.32	2×10^{-5}
5-96-9	0.43	2×10^{-5}
5-96-10	0.48	2×10^{-5}

VI DISCUSSION OF RESULTS

In the following sections the results of this dissertation are compared with the results of others and with the results expected from the absolute reaction rate theory. Some theoretical and experimental aspects of formic acid vapor decomposition on nickel are considered, as well as a discussion of the reaction mechanism.

A. Comparison of Results

The experimental results of this paper are first compared with the experimental results which others have obtained from the decomposition of formic acid vapor on nickel. The results calculated from the absolute reaction rate theory are then compared to the experimental results. In order to avoid duplication, only a summary of the pertinent discussions previously given are mentioned below, and references to the sections giving the complete details are noted.

1. Comparison with Results of Others

a. Decomposition Products

The appearance of carbon monoxide and water as well as the expected hydrogen and carbon dioxide from the decomposition of formic acid vapor on nickel is unusual. (See Sections II-B-1 and V-C-4). The constant 3:1 ratio of dehydrogenation to dehydration throughout the main course of the reaction at all temperatures in the 125 to 190° C. range is entirely new and indicates that the two reactions are occurring

simultaneously. The discovery of methane in the products of formic acid decomposition on nickel is again something new, but not unexpected. (See sections II-B-1 and V-C-4.)

At 190° C. experiments 5-26-1 and 5-42 were followed to completion. The initial pressures in these experiments were 20.1 and 31.5 mm. respectively; the final pressures were 44.3 and 73.8 mm. There is no way by which formic acid vapor can decompose into hydrogen, carbon dioxide, water, carbon monoxide, and methane, and more than double the initial pressure. Dimerization of the formic acid in the section of the system beyond the heated reaction flask will account for a final pressure which is greater than twice the initial pressure. Depending upon the size of the Boudron gauge, of which several were used, the cool section of the system was estimated to vary from about 110 to 130 ml. The volume of the flask in the furnace was estimated to be about 530 ml. Formic acid is about 70 per cent dimer at 27° C. and 20 mm. pressure (calculated from data in Table I) i.e., 6 mm. are monomer and 14 mm. are dimer. The pressure increase expected in the formic acid vapor decomposition can now be calculated.

If the dimer is considered as an entity the total number of molecules, n , of gas present in the system at the two temperatures 463 and 300° K, corresponding to the hot and cool temperatures, is

$$n = \frac{P \times 530}{R \times 463} + \frac{P \times 120}{R \times 300} ,$$

where P is the pressure of the system, R is the gas constant, and 120 is the average cool space of the system. If the number of dimer

molecules are converted to monomer molecules and added to the number of monomer molecules already present, the total calculated number of monomer molecules, n_{monomer}^0 , present is

$$n_{\text{monomer}}^0 = \frac{P \times 530}{R \times 463} + \frac{1.7 \times P \times 120}{R \times 300}.$$

If we now take the fraction

$$\frac{n_{\text{monomer}}^0 - n}{n_{\text{monomer}}^0} = \frac{\frac{0.7 \times 120}{300}}{\frac{530}{463} + \frac{1.7 \times 120}{300}} = 0.15$$

and solve for n_{monomer}^0 , we find

$$n_{\text{monomer}}^0 = \frac{n}{1 - 0.15} = \frac{n}{0.85}.$$

This result means that if the initial formic acid vapor pressure is 20.1 mm. (experiment 5-26-1), a final pressure of $\frac{2 \times 20.1}{0.85} = 47$ mm. would be expected. For an initial pressure of 31.5 mm. (experiment 5-42), a final pressure of $\frac{2 \times 31.5}{0.85} = 74$ mm. is expected. These results agree with the 44.3 and 73.8 mm. actually observed.

The initial rates and initial portion of the reaction will not be greatly affected by the dimerization, since the dimer will have to diffuse into the reaction vessel against a flow of product molecules coming into the cooler portion of the system.

b. Order of the Reaction

The initial rates are independent of the formic acid vapor pressure and the reaction is zero order with respect to formic acid vapor pressure. These results agree with those of Rienaecker and Schwab who also worked at low pressures (approximately 25 mm.) and in the same temperature range.

(See Section II-B-2.) However they disagree with the results of Clark and Topley who found the reaction was first order with respect to formic acid vapor at 200° C. and nearly one atmosphere formic acid vapor pressure. (See Section II-B-2.)

c. Activation Energy

Section II-B-3 indicates that values of the activation energy ranging from 11.6 to 30 kcal./mole have been reported. If only the most recent values are considered, disregarding the value of Dowden and Reynolds supposedly obtained on poisoned surfaces, the values range from 15 kcal./mole as reported by Schwab to 20 kcal./mole as reported by both Ruka, and Toyama and Kubokawa (Section II-B-3). The value found in this research is 16.5 kcal./mole.

d. Factors Affecting the Rate

Several factors were studied with respect to their effect on the reaction rate.

The degree of degassing, before and during the evaporation of nickel, affects the initial activity of the films (see Section V-D-4). Films evaporated at 10^{-7} mm. are about two to three times as active as those evaporated at 10^{-6} mm.

The addition of product gases causes the initial rate to decrease. In general, the shape of all the curves giving pressure increase with time was similar for all the experiments in which product gases were added, except carbon dioxide, which acted as a strong poison after the first few minutes of the reaction. (See Section V-D-7.) a nickel oxide
Oxygen is a strong poison (V-D-7). Ruka¹ found that oxygen had

1. R. Ruka, Doctoral Dissertation, U. of Mich. (1954).

an activating effect on the reaction. However, during the course of the reaction the oxide disappeared and the surface roughness increased. Since Ruka worked in a flow system and did not measure initial rates, the activating effect of oxygen probably came from an increase in the surface area of the nickel catalyst caused by the removal of the oxide.

There was no significant difference in activity between the Low Carbon Alloy and the 99 Alloy nickel used as catalysts (see Section V-D-5). Ruka also found that small changes in the impurities in the nickel catalysts had no effect on the reaction rate (see Section II-B-4).

The first decomposition experiment on a nickel film had the highest initial rate. The initial rates of the slower subsequent decompositions on the same film depend upon the evacuation pressure between experiments. The initial rate is slower when the flask is evacuated to 10^{-6} mm. between experiments than when it is evacuated to 10^{-5} mm. (see Section V-D-8). Toyama and Kubokawa used their films for repeated experiments and presumably did not encounter this difficulty (see Section V-B-4).

Ruka noted that the pretreatment of the formic acid vapor often affected the rate by a factor of 4 or 5. Final purification of the acid by percolation through Amberlite IRA-410 produced an acid which gave the fastest rate (see Section II-B-4). In the present research, no great difference was noted in the reaction rates when small amounts of the usual product gases were added to the reaction vessel previous to the addition of the formic acid vapor (see Section V-D-7).

e. Decomposition Rates

The decomposition rates of this research are compared with the rates of others which were listed in Section II-B-5 in terms of molecules

increase $\text{cm.}^{-2} \text{ min.}^{-1}$. In order to compare rates at equal temperatures, the rates of this dissertation at 190° C. are changed by means of the Arrhenius equation to rates at the temperatures of comparison. First, it is necessary to convert the initial rate taken from Figure 18 at 190° C. , $0.068 \text{ mm. sec.}^{-1} (\text{H atoms adsorbed} \times 10^{-18})^{-1}$, into terms of molecules $\text{cm.}^{-2} \text{ min.}^{-1}$. For a randomly oriented nickel film the average crystallographic site size is ^{about} $6.75 \times 10^{-16} \text{ cm.}^2$, and 10^{18} H atoms adsorbed correspond to 675 cm.^2 . The pressure increase per second per H atoms adsorbed $\times 10^{-18}$ is converted to the increase in molecules per minute per cm.^2 by

$$\Delta n = \frac{\Delta P}{R} \left(\frac{V_1}{T_1} + \frac{V_2}{T_2} \right) \frac{\times 60}{6.75 \times 10^2} = \frac{3.94 \times 10^{20} \Delta P}{6.75 \times 10^2} = 1.325 \times 10^{18} \Delta P$$

where

$$\Delta P = \text{pressure increase in mm. sec.}^{-1} (\text{H atoms} \times 10^{-18})^{-1}$$

$$R = 1.035 \times 10^{-19} \text{ ml.-mm./}^\circ\text{K/molecule}$$

$$V_1 = 530 \text{ ml.} = \text{volume inside furnace}$$

$$V_2 = 120 \text{ ml.} = \text{volume outside furnace}$$

$$T_1 = 463^\circ \text{ K}$$

$$T_2 = 300^\circ \text{ K}$$

$$6.75 \times 10^2 = \text{surface area corresponding to } 10^{18} \text{ adsorbed H atoms}$$

$$60 \text{ sec.} = 1 \text{ minute}$$

The initial rate at 190° C. in $\frac{\text{molecules}}{\text{min.}^{-1} \text{ cm.}^{-2}}$ is then (cf. Fig. 18)

$$1.325 \times 10^{18} \times 0.068 = 9.01 \times 10^{16} \text{ molecules cm.}^{-2} \text{ min.}^{-1}$$

The results of this research are calculated for various temperatures by

$$\log \frac{k_2}{9.01 \times 10^{16}} = \frac{16,500 (T_2 - 463)}{4.58 \times 4.63 T_2}$$

where k_2 is the rate constant in molecules $\text{cm.}^{-2} \text{ min.}^{-1}$ at T_2 . A comparison is made in Table XVIII with the results given in Section II-B-5.

The rates of this dissertation are initial rates. Excepting the rate of Clark and Topley, which is an initial rate calculated from a first order rate constant, the other rates were obtained in flow systems and are not initial rates.

The rates of this research are 15 times as fast as that of Dowden and Reynolds, who believed their surfaces to be poisoned, about the same order of magnitude as the rate of Ruka, about 1/20 those of Schwab, and 65 times faster than those of Clark and Topley. The geometric surface areas of Ruka, Schwab, and Clark and Topley may be in considerable error, and their rates probably should be lower than listed. Dowden and Reynolds measured their surfaces by the BET method using argon and their surface values are probably reliable. Their low rate is in agreement with their belief that they had poisoned surfaces.

Another point to be noted is that the rates of this dissertation have been calculated using an activation energy of 16,500 cal./mole, to compare with the rates of other workers. If the other investigators' data were calculated, using the appropriate activation energies, to compare with the data of this research, the comparison would be different. For example, the rate of Schwab at 190° C. is calculated to be 1.6×10^{17} molecules $\text{min.}^{-1} \text{ cm.}^{-2}$ (activation energy 25.5 kcal./mole), as compared to the 9×10^{16} molecules $\text{min.}^{-1} \text{ cm.}^{-2}$ observed in the present

TABLE XVIII

TEMPERATURE °C.	RATES $\frac{\text{molecules}}{\text{min. cm.}^2}$	INVESTIGATOR	CALCULATED INITIAL RATE-THIS RESEARCH $\frac{\text{molecules}}{\text{min. cm.}^2}$
253	5.3×10^{16}	Dowden and Reynolds	7.7×10^{17}
360	8.0×10^{18}	Ruka	1.1×10^{19}
350	2.0×10^{20}	Schwab	9.1×10^{18}
200	2.0×10^{15}	Clark & Topley	1.3×10^{17}

research. Unless the activation energies are the same, a comparison of rates at widely different temperatures does not mean much.

The rates of this dissertation are low. A temperature difference was noted across the flask (see Section III-B) and the reaction temperature was taken near the hottest part of the flask. This means the reaction was taking place at an average temperature lower than the recorded temperature. The rates may be about 30 per cent too low.

2. Comparison with Rate Expected by Absolute Reaction Rate Theory

The zero-order absolute reaction rate law is²

$$\text{Rate (molecules sec.}^{-1} \text{ cm.}^{-2}) = C_a \frac{kT}{h} e^{-E_0/RT} \quad (1)$$

where

C_a = concentration of adsorbed reactant molecules cm.^{-2}

k = Boltzmann constant = 1.38×10^{-16} ergs/ $^{\circ}\text{K}$

h = Plank's constant = 6.624×10^{-27} erg. - sec.

T = absolute temperature

E_0 = activation energy at absolute zero per mole

The activation energy at absolute zero may be found by differentiating the logarithm of equation (1) and setting it equal to the Arrhenius expression

$$\frac{d \ln k}{dT} = \frac{E_{\text{experimental}}}{RT^2} \quad (2)$$

The results are that $E_0 = E_{\text{experimental}} - RT$. At 463°K , E_0 is 15,574 cal. mole^{-1} , where $E_{\text{experimental}}$ is 16,500 cal. mole.

2. K. Laidler, "Catalysis", vol. I, Reinhold Publishing Corp., New York (1954), p. 213.

The surface is completely covered with reactant for a zero-order reaction and C_a is then the number of surface sites per square centimeter. The average crystallographic area of one site for nickel is about $6.75 \times 10^{-16} \text{ cm.}^2$. Therefore there are $\frac{1}{6.75} \times 10^{16}$ sites cm.^{-2} or 1.5×10^{15} sites cm.^{-2} .

The calculated rate, using $T = 463^\circ \text{ C.}$, $E_0 = 15.6 \text{ kcal. mole}^{-1}$, and $C_a = 1.5 \times 10^{15}$ sites cm.^{-2} is 2.4×10^{20} molecules $\text{sec.}^{-1} \text{ cm.}^{-2}$. This compares to 1.5×10^{15} molecules $\text{sec.}^{-1} \text{ cm.}^{-2}$ of this research. The agreement is not very good. In order to get agreement C_a would have to be reduced by a factor of 10^5 , or E_0 increased to about 29 kcal./mole.

B. Applicability of Langmuir Treatment of Data

The theoretical treatment given the addition of product gases in Section V-D-7 follows the Langmuir type treatment³. The rate equation (see Section V-D-7) is

$$\text{rate} = k_o S \frac{1}{1 + K \frac{P_P P_{PG}}{K_F P_{FG}}} = k_o S \frac{1}{1 + K \frac{P_{PG}}{P_{FG}}}$$

where

k_o = the rate constant per unit surface area

S = total surface area available for the reaction

P_{pg} = pressure of product gases

P_{fg} = pressure of formic acid vapor

K_p = equilibrium constant for gaseous and adsorbed product gases

K_F = equilibrium constant for gaseous and adsorbed formic acid vapor

$K = K_p / K_F$

3. P. H. Emmett, "Catalysis", vol. I, Reinhold Publishing Corp., New York (1954) Chapters 3 and 4.

The data are treated as if K_p had the same value for all product gases.

The rate equation may be expressed as $\frac{dx}{dt} = k_o S \left(\frac{1}{1 + \frac{K' 2x}{a-x}} \right) = k_o S \frac{1}{1 + K' \frac{x}{a-x}}$

where x is the pressure of formic acid vapor decomposed at time t , a is the initial formic acid vapor pressure, and K' is $2K$. Since one formic acid vapor molecule decomposes to give two product molecules, the pressure of the product gases is twice the pressure of the decomposed acid.

The integrated equation has the form,

$$k_o S t = x (1-K') + K' a \ln \frac{a}{a-x}$$

or

$$\frac{K' a \ln \left(\frac{a}{a-x} \right)}{t} = k_o S - \frac{(1-K') x}{t}$$

A plot of $1/t \log_{10} \left[\frac{a}{a-x} \right]$ against x/t should be a straight line with a slope of $-\frac{(1-K')}{2.3K'a}$ and an intercept equal $\frac{k_o S}{2.3K'a}$. Figures 21, 22 and 23 give plots of $1/t \log_{10} \left[\frac{a}{a-x} \right]$ against x/t for experiments 6-71 and 5-72, both performed at 189°C .

The effective initial pressure is smaller at the beginning of the reaction than at the end because of dimerization of the formic acid vapor in the cool portion of the system outside of the reaction vessel (see Section VI-A-1-a). For this reason all of the points are not expected to lie on a straight line. The points nearest to the origin are the points corresponding to longest reaction times and are expected to differ from the points taken early in the reaction.

The data of experiments 6-71 and 5-72 were plotted for three values of initial pressure. In Figure 22 the value of the initial

pressure obtained from the least squares treatment of the data was used, i.e., 25.4 mm. for experiment 6-71 and $53.4(\text{mm.} \times 2.32) = 23.1$ mm. for experiment 5-72. Figures 21 and 23 show the effect of varying the initial pressure about ± 1 per cent from the value used for Figure 22. The results of these graphs are compared with the initial rates, calculated by the cubic least squares treatment in Table XIX.

The shape of the curves in Figures 21, 22, and 23 depends upon the choice of an initial pressure. Since this is an extrapolated value, some time may be lost selecting the correct initial pressure. Figure 22 gives the most nearly linear relationships in the early part of the reaction and Figures 21 and 23, while also roughly approximating straight lines, become less definite in shape. In curves where the points are scattered, there is considerable latitude in the choice of the best straight line. An error of 10 per cent in the intercept will affect the value of the rate by the same amount. However, an error of 10 per cent in the slope can affect the resulting value K' , and therefore the rate, by as much as 50 per cent. Thus, it is seen that if the points do not lie on a straight line, a considerable error can be incurred in the resulting rate.

In general, it is seen that the rates derived from the Langmuir treatment agree roughly with the rates obtained by the least squares treatment, i.e., the rates found for experiment 5-72 range from 0.04 to 0.06 mm. min.⁻¹ (H atoms adsorbed $\times 10^{-18}$)⁻¹ and those of 6-71 vary from 0.07 to 0.10 mm. min.⁻¹ (H atoms adsorbed $\times 10^{-18}$)⁻¹.

The value of K' ranges from about 3 to 7. This is twice the value of K , the ratio of adsorption constants of the products and formic acid

Figure 21 Plot of $\frac{1}{t} \log \frac{a}{a-x}$ against $\frac{x}{t}$ for experiment 6-71 ($a = 25.1 \text{ mm}$) and experiment 5-72 ($b = 53.0 \text{ mm.} \times 2.32 = 22.9 \text{ mm.}$) The units of $\frac{x}{t}$ are $\frac{\text{mm.}}{\text{sec.}}$ for experiment 6-71 and $\frac{\text{mm.} \times 232}{\text{sec.}}$ for experiment 5-72.

Figure 22. Plot of $\frac{1}{t} \log \frac{a}{a-x}$ against $\frac{x}{t}$ for experiment 6-71 ($a = 25.4 \text{ mm.}$) and experiment 5-72 [$a = 53.4 (\text{mm.} \times 2.32) = 23.1 \text{ mm.}$]. The units of $\frac{x}{t}$ are $\frac{\text{mm.}}{\text{sec.}}$ for experiment 6-71 and $\frac{\text{mm.} \times 2.32}{\text{sec.}}$ for experiment 5-72.

Figure 23. Plot of $\frac{1}{t} \log \frac{a}{a-x}$ against $\frac{x}{t}$ for experiment 6-71 ($a = 25.7 \text{ mm}$) and experiment 5-72 ($b = 540(\text{mm.} \times 2.32) = 23.3 \text{ mm}$). The units of $\frac{x}{t}$ are $\frac{\text{mm}}{\text{sec}}$ for experiment 6-71 and $\frac{\text{mm} \times 2.32}{\text{sec}}$ for experiment 5-72.

TABLE XIX

Experiment Number	5-72			6-71		
Initial Pressure	53.0	(mm. $\times$ 2.32) 53.4	54.0	25.1	(mm.) 25.4	25.7
K'	4.54	3.19	2.55	5.21	7.35	4.93
k_0 [mm. sec. ⁻¹ (H atoms adsorbed $\times 10^{-18}$) ⁻¹]	0.0558	0.0487	0.0381	0.0768	0.0953	0.0742
Initial Rate by Least Squares Treatment	---	0.0437	---	---	0.0669	---

vapor. This means the products are being adsorbed about 1.5 to 3.5 times as strongly as the formic acid vapor. Just the opposite result was obtained in Section V-D-7 ($K = 0.3$) when the effect of adding product gases before the formic acid vapor was studied.

It should also be noted that for positive slopes in the graphs, K' must be greater than one. Otherwise a meaningless negative adsorption constant will be obtained. Since K' is equal to $2K$, the value of K must be larger than 0.5. This means the value of K used in section V-D-7 should have been greater than 0.5.

In summary, the Langmuir treatment gives results consistent with those obtained by the least squares treatment. However, the choice of an initial pressure affects the shape of the curve. Small variations, to either side of the correct initial pressure, cause greater scattering of the points and increase the error in drawing in the line. Small deviations in the slope of this line can cause large deviations in the rate. The Langmuir treatment in this case is further complicated by an effectively changing initial pressure due to dimerization of the formic acid vapor in the cool part of the system. As mentioned in Section V-D-7, there is no valid reason for assuming that the adsorption constants for the various product gases are equal. The true Langmuir type expression should involve six equilibrium constants including one for methane.

C. Applicability of the Roginskii Treatment of Rate Data

The kinetics of a number of heterogeneous processes have been expressed by an equation of the form

$$\frac{dx}{dt} = k_0 S e^{-\frac{x}{ak_0 S}} \quad (1)$$

where x is the pressure increase corresponding to the amount of formic acid vapor decomposed, k_0 is the rate constant per unit surface area, S is the total surface area available for the reaction and a is a constant. Parravano⁴ attributes this equation to Roginskii. Others⁵ refer to it as the Ellovich equation.

Integration of equation (1) gives

$$x = 2.3 ak_0 S \log_{10} (1 + t/a). \quad (2)$$

The slope of a plot of x against $\log_{10} (1 + t/a)$ is $2.3 ak_0 S$, and k_0 is found by

$$k_0 = \text{slope}/2.3aS. \quad (3)$$

A difficulty with this method is that the constant a must be found by trial and error and the slope is not very sensitive to changes in a .

Figures 24 and 25 show respectively the data of experiments 5-77 and 5-42 as plotted according to equation (2) for various values of a , t being in seconds and ΔP in (mm. $\times 2.32$).

A value of 50 for a in experiment 5-77, Figure 24, gives a fairly linear plot. The slope of the line is $22(\text{mm.} \times 2.32) = 9.50 \text{ mm.}$ S , as found from Figure 12 for 30.3 mg. of evaporated nickel, is 0.85×10^{-18} H atoms adsorbed. The rate constant is then

$$k_0 = \frac{9.50}{50 \times 2.3 \times 0.85} = 0.0973 \frac{\text{mm.}}{\text{sec.} - \text{H atoms ads.} \times 10^{-18}}.$$

This is to be compared with $0.0773 \frac{\text{mm.}}{\text{sec.} - \text{H atoms ads.} \times 10^{-18}}$ found by the least squares treatment.

4. G. Parravano, J. Am. Chem. Soc., 75, 1448, (1953).

5. P. I. Emmet, loc. cit., p. 189.

A value of a equal to 1000 in experiment 5-42, Figure 25, gives a nearly linear plot. The slope of the line is $67.5(\text{mm.} \times 2.32) = 29.2 \text{ mm.}$ S is found from Figure 12 to be 1.09×10^{-13} H atoms adsorbed for 64.0 mg. of nickel. The rate constant is

$$k_0 = \frac{29.2}{1000 \times 2.3 \times 1.09} = 0.012 \frac{\text{mm.}}{\text{sec.} - \text{H atoms} \times 10^{-13}}$$

while the value $0.025 \frac{\text{mm.}}{\text{sec.} - \text{H atoms} \times 10^{-13}}$ is found by drawing a free-hand initial slope for the pressure-time data (see Section V-D-2).

The Roginskii treatment of the data will give rate constants which are in rough agreement with the least squares treatment. The disadvantages of this method arise in the time necessary to find the proper value of the constant a and in the insensitivity of the plot to small variations of a . These variations, as can be seen from equation (3), will accordingly affect the value of k_0 .

In conclusion, it may be stated that although the Langmuir and the Roginskii treatments of the present rate data give reasonable values of the rate constants, neither of these methods has any advantage over the least squares treatment of the data. They are more difficult than the least squares method inasmuch as there is considerable trial-and-error work involved in obtaining the best values of the rate constants.

Figure 24. Plot of ΔP against $\log_{10}(1 + \frac{1}{a})$ for experiment 5-77 for $a = 100$ seconds, ●; $a = 50$ seconds, ○; and $a = 10$ seconds, ◇.

Figure 25. Plot of ΔP against $\log_{10}(1 + \frac{1}{a})$ for experiment 5-42 for $a = 1000$ seconds, ○; $a = 600$ seconds, ●; and $a = 100$ seconds, ◇.

D. Mechanism

Schwab⁶ has correlated the degree of electron saturation of the first Brillouin zone of various alloys with the activation energy obtained for the decomposition of formic acid on those alloys. According to Schwab the two protons of the formic acid molecule occupy extra lattice sites in the catalyst surface and their electrons are dissolved in the electron gas of the metal. As the Brillouin zone becomes saturated more thermal energy is required for the dissolution of the electrons.

Lowden⁷ and Lowden and Reynolds⁸ arrive at essentially the same conclusion via the Pauling valence bond theory and the band theory of metals. In this case, more thermal energy is required to add electrons as the d-band holes become filled. Copper can fill the d-band holes of nickel, and a copper-nickel alloy of 60 atom per cent copper has a completely filled d-band. The rate of decomposition of formic acid vapor at 253° C. decreases by a factor of 3 in going from pure nickel to the alloy containing 60 atom per cent copper, because of the filling of the d-band holes. Dowden and Reynolds⁸ give the following mechanism, adopting the electron donation theory of Schwab;

However, there seems to be a certain amount of the reaction taking place by means of a mechanism other than electron donation to the metal since the decomposition rate on pure copper is still about 1/3 its value on

6. G.-M Schwab, Disc. Faraday Soc., 8, 166 (1950).

7. D. A. Lowden, Ind. Eng. Chem., 44, 977 (1952).

8. D. A. Lowden and P. W. Reynolds, Disc. Faraday Soc., 8, 184 (1950).

pure nickel (Figure 2, p. 188 of Dowden and Reynolds paper⁸). Dowden and Reynolds also say that the free radical counterpart of the above reaction might occur. There is no evidence for the formation of H-atoms even in the photolytic decomposition of formic acid.^{10a}

If the dissolution of electrons in the electron gas or the filling of d-band holes is the only prerequisite for the decomposition of formic acid vapor, then the activity observed by Dowden and Reynolds on pure copper cannot be explained. Pauling⁹ gives the resonating structures of an acid as

A given molecule possesses single structure at all times, and all such molecules have the same structure. The structure possessed by all of these molecules at all times is intermediate between A, B, and C. If an electron from the formic acid vapor molecule is given up, it seems reasonable that it might come from the carbonyl oxygen. It also appears that formic acid might take up an electron. This would explain the activity of the copper. In nickel, the effect due to filling the d-band seems to predominate⁸. Dowden⁷ has related the ionization potential and electronic work function of the catalyst to its catalytic activity.

It has been hypothesized that formic acid vapor decomposes on metals to give predominantly hydrogen and carbon dioxide, while on oxide

9. L. Pauling, "Nature of the Chemical Bond," Cornell University Press, New York (1940) p. 202 and p. 208.

10.a E. W. R. Steacie, "Atomic and Free Radical Reactions," vol. II, Rheinhold Publishing Corp., New York (1954), p. 595.

surfaces the decomposition to carbon monoxide and water predominates¹⁰. In this research, no formic acid vapor decomposition took place at the highest temperature, 189° C., on the Pyrex reaction vessel wall. The electron diffraction photographs taken after decomposition reactions on the evaporated nickel films (Plate III) showed that no nickel oxide was present. The production of carbon monoxide (constant 3CO₂:1CO at all temperatures) is then due to the nickel itself and not to an oxide surface. The hypothesis is not correct.

The carbon monoxide reaction has often been attributed to decomposition of the formic acid vapor on the reaction vessel wall. For example, Ruka¹¹ attributed 3 to 15 per cent carbon monoxide in the product gases-carbon monoxide, carbon dioxide, and hydrogen-in the 200 to 450° C. temperature range to the wall reaction. However, Sosnovsky¹² found that small amounts of hydrogen and carbon dioxide only were produced at the walls of a Pyrex vessel in the 155 to 200° C. range. At 187° C., Sosnovsky says that the rate of formic acid vapor decomposition on silver is of the order of 10^{12} to 10^{13} molecules sec.⁻¹ cm.⁻² geometrical area. The decomposition rate on glass (activation energy 23 kcal./mole) was found to be zero order and about 5 per cent of the rate on silver, i.e., 5×10^9 to 5×10^{10} molecules sec.⁻¹ cm.⁻², if an estimated 10:1 ratio in surface areas exists between the Pyrex reaction vessel and the silver crystals used by Sosnovsky. The rate of formic acid vapor decomposition on nickel surfaces in this research were of the order of 10^{15} molecules sec.⁻¹ cm.⁻² at 189° C. The fact that no reaction was observed

10. P. H. Emmett, "Catalysis", vol. I, Reinhold Publishing Corp., New York (1954), p. 149.

11. R. Ruka, Doctoral Dissertation, U. of Mich. (1951).

12. H. M. C. Sosnovsky, J. Chem. Phys., 23, 1486 (1955).

to take place on the Pyrex reaction vessel wall at this temperature is in agreement with Sosnovsky, because a rate of 10^{10} molecules sec.^{-1} cm.^{-2} was not easily observable with the apparatus used in the present research. Therefore, the presence of relatively high percentages of carbon monoxide reported by others may be attributed to the decomposition of formic acid vapor on the catalyst rather than the reaction vessel wall.

Since Clark and Topley¹³ reported a greenish liquid on their nickel catalyst after the decomposition of formic acid vapor, it is possible that a formate intermediate may exist.

Under special conditions of low temperature (55°C.) and formic acid vapor pressures near condensation, Ruka¹¹ produced a nickel formate film which was identified by electron diffraction. However, no traces of nickel formate were found on the nickel after the formic acid vapor decompositions which were carried out in the 200 to 450°C. range.

Bircumshaw and Edwards¹⁴ report that nickel formate decomposes in the 165 to 180°C. temperature range as

They report that the accumulation of gaseous products hindered the reaction, that there was an induction period in the reaction, and that the presence of the nickel residue accelerated the reaction. The fact that the nickel residue accelerates the reaction and that the reaction starts slowly and then proceeds more rapidly may indicate that the nickel formate is not decomposing as such but is passing through an intermediate stage involving the presence of nickel. The slow formation of nickel at the beginning of the reaction will then account for the induction period.

13. C. H. D. Clark and B. Topley, *J. Phys. Chem.*, **32**, 121 (1928).

14. L. Bircumshaw and J. Edwards, *J. Chem. Soc.*, 1800 (1950).

The product ratio $3\text{CO}_2:\text{lCO}$ of Biroumshaw and Edwards agrees very well with the results obtained in the same temperature range in this dissertation. Thus it might seem that nickel formate itself is not formed, although a nickel formate type intermediate may be formed.

The postulate of a step involving a formate type intermediate is not out of line with the Langmuir type mechanism already discussed in Section VI-B. However, the treatment of the reaction as an inhibited bimolecular surface reaction is of interest. The rate may be expressed by

$$\text{Rate} = k_0 S \theta^2$$

where k_0 is the rate constant per unit surface area

S is the total available surface area

θ is the fraction of the surface covered by formic acid vapor

$$\theta = \frac{K_F P_{Fg}}{1 + K_F P_{Fg} + K_p P_{pg}} \quad \text{as defined in Section VI-B.}$$

Where $K_F P_F$ and $K_p P_p$ are much greater than one, $\theta = \frac{K_F P_{Fg}}{K_F P_{Fg} + K_p P_{pg}}$.

If we set $P_{Fg} = (a-x)$ where a is the initial formic acid vapor pressure and x is the amount decomposed at time t , then P_{pg} , the product pressure, is $2x$ and the rate may be expressed as

$$\frac{dx}{dt} = k_0 S \frac{K_F^2 (a-x)^2}{K_F^2 (a-x)^2 + 4K_p K_F (a-x)x + 4K_p^2 x^2} \quad (1)$$

Integration of equation (1) gives

$$x \left[1 - 4 \frac{K_p}{K_F} + 4 \left(\frac{K_p}{K_F} \right)^2 \right] + 4a \left[\frac{K_p}{K_F} - 2 \left(\frac{K_p}{K_F} \right)^2 \right] \ln \frac{a}{a-x} + \frac{4a^2 \left(\frac{K_p}{K_F} \right)^2}{a-x} - 4a \left(\frac{K_p}{K_F} \right)^2 = k_0 S t \quad (2)$$

It is to be noted that if $\frac{K_p}{K_F} = 0.5$, the equation simplifies considerably,

$$\frac{a^2}{a-x} - a = k_0 S t. \quad (3)$$

The value of 0.5 for $\frac{K_p}{K_F}$ seems reasonable (see Section V-D-7) for trial calculations. Table IX lists the values of $k_0 S$ calculated from equation (3). The data from experiment 5-72 (189° C.) were used in the calculations. The initial pressure used was $53.4(\text{mm.} \times 2.32) = 23.2 \text{ mm.}$

It is seen that the rate remains fairly constant up to about 50 per cent decomposition. This is probably as good as can be expected if the value of a is considered to be effectively changing because of the dimerization of the formic acid in the cold part of the system. The average value of $k_0 S$, excluding the values for 1235 and 1626 seconds, is $0.0820(\text{mm.} \times 2.32)\text{sec.}^{-1}$. The surface area of the nickel for experiment 5-72 is $0.79 \times 10^{18} \text{ H atoms}$. The rate in $\text{mm. sec.}^{-1} (\text{H atoms adsorbed} \times 10^{-18})^{-1}$ is then

$$\frac{0.0820}{2.32 \times 0.79} = 0.045 \text{ mm. sec.}^{-1} (\text{H atoms adsorbed} \times 10^{-18})^{-1}.$$

This is in excellent agreement with the $0.044 \text{ mm. sec.}^{-1} (\text{H atoms adsorbed} \times 10^{-18})^{-1}$ obtained from the least squares treatment of the data.

Slight changes in the ratio of $\frac{K_p}{K_F}$ affect the value of $k_0 S$ considerably. For example, if $\frac{K_p}{K_F}$ is taken to be 0.6 and if $k_0 S$ is calculated by equation (1) for $t = 44$ and $t = 488$, the result is $k_0 S = 0.0889$ and $0.105(\text{mm.} \times 2.32)\text{sec.}^{-1}$ respectively. If the calculation is made for $\frac{K_p}{K_F} = 1$ for the same times, the result is $k_0 S = 0.0954(\text{mm.} \times 2.32)\text{sec.}^{-1}$ for $t = 44$ and $0.127(\text{mm.} \times 2.32)\text{sec.}^{-1}$ for $t = 488$ seconds. It is seen that the rate constants vary considerably when the ratio of $\frac{K_p}{K_F}$ is changed.

A similar calculation was made for experiment 6-71 (189° C.). The initial pressure used was 25.4 mm. For this experiment, equation (3)

TABLE XX

RATE CONSTANTS, k_0S , CALCULATED FROM $\frac{2851.5}{a - x} - 53.40 = k_0St$

FOR EXPERIMENT 5-72 WHERE $a = 53.4$ (mm. $\times$ 2.32).

EXPERIMENT PERFORMED AT 189° C.

t Seconds	x mm. $\times$ 2.32	k_0S mm. $\times$ 2.32/sec.
44	3.6	0.0875
79	5.1	0.0714
111	8.1	0.0859
147	9.8	0.0816
196	12.6	0.0841
239	14.3	0.0817
293	16.4	0.0808
352	18.6	0.0811
411	20.6	0.0817
488	22.6	0.0803
600	26.5	0.0877
804	29.2	0.0801
1235	33.8	0.0745
1626	36.8	0.0727

did not give constant values for k_0S . However, a value of $K_p/K_F = 0.7$ did give fairly constant values of k_0S when used in equation (2). The values of k_0S as calculated in equation (2) are listed in Table XXI. The average value of all the k_0S values is $0.0586 \text{ mm. sec.}^{-1}$. The surface area of the nickel film used in experiment 6-71 is 0.90×10^{18} H atoms adsorbed. The rate per unit surface area is then

$$\frac{0.0586}{0.90} = 0.065 \text{ mm. sec.}^{-1} \text{ (H atoms adsorbed } \times 10^{-18}\text{)}.$$

This is to be compared with the $0.067 \text{ mm. sec.}^{-1}$ (H atoms adsorbed $\times 10^{-18}$) obtained by the least squares treatment and again the agreement is very good between the two values.

As was to be expected if K_p and K_F are equilibrium constants, the values of K_p/K_F in both of these experiments performed at the same temperature do not differ widely, 0.5 for experiment 5-72 and 0.7 for experiment 6-71.

The ratio of $\frac{K_p}{K_F} = 0.5$ indicates that formic acid vapor is adsorbed about twice as strongly as the products. This is in agreement with experiment. In the poisoning experiments using carbon dioxide (see Figure 20), the rate increased upon addition of more formic acid vapor, thus showing displacement of the products adsorbed on the surface by the more strongly adsorbed formic acid vapor.

As stated before in Section V-D-7, there is no valid reason for assuming K_p is a collective constant in these equations. Since there is considerable trial-and-error work involved in solving equation (2), the least squares treatment still seems to be the easiest approach. However, if equation (3) is applicable, it would be the best method.

TABLE XXI

RATE CONSTANT, k_0S , CALCULATED FROM

$$0.16 \times -65.43 \log \frac{a}{a-x} + \frac{1264.5}{a-x} - 49.78 = k_0St \text{ FOR}$$

EXPERIMENT 6-71 WHERE $a = 25.4$ mm.EXPERIMENT PERFORMED AT 199°C .

t Seconds	x mm.	k_0S min. sec. ⁻¹
42	2.2	0.0593
81	4.2	0.0663
114	5.2	0.0625
156	6.5	0.0623
200	7.4	0.0561
239	8.3	0.0595
276	9.1	0.0603
324	9.6	0.0564
366	10.2	0.0559
443	11.1	0.0544
499	11.9	0.0558
566	12.6	0.0557
598	13.1	0.0577

The postulate of a bimolecular mechanism, involving a formate type intermediate for the decomposition of formic acid vapor, seems very reasonable.

Various side reactions among the product gases can take place on a nickel surface. These may explain some of the observations during the course of this research. Carbon dioxide is adsorbed on nickel at low pressures (10^{-4} to 0.1 mm.) and 150 to 200° C. with a heat of adsorption of 22 kcal./mole and may become completely dissociated on the surface¹⁵. The rate of adsorption is slow¹⁶, the longer the contact time, the greater the amount of carbon dioxide adsorbed. The adsorption of carbon monoxide on nickel to form adsorbed carbon and carbon dioxide takes place at 180 to 185° C. with the evolution of 34 kcal./mole¹⁷. Other reactions involving hydrogen, carbon monoxide, water, and carbon dioxide are discussed by Pichler¹⁸. Carbon deposits formed by adsorbed carbon monoxide and carbon dioxide can be removed by hydrogen or water¹⁸.

The variation of activity with the degree of evacuation between experiments (see Section V-D-8), the reaction vessel temperature remaining constant for reaction and evacuation, can be explained with the above information. During the evacuation the adsorbed carbon dioxide, carbon monoxide, and water decompose to form adsorbed carbon and oxygen on the surface of the nickel. These are removed by the reaction products during the next reaction. Since it takes longer to obtain a high vacuum than

15. T. Kwan, J. Chem. Phys., 18, 1309 (1950).

16. J. A. Dillon and H. E. Farnsworth, J. Chem. Phys., 22, 1601 (1954).

17. I. A. Zaidenman and K. G. Khomoyokov, Doklady Akad. Nauk. S. S. S. R., 78, 901 (1951); C. A. 46, 9398c, (1952).

18. H. Pichler, "Advances in Catalysis", vol. IV, Academic Press Inc., New York (1952), p. 321 ff.

it takes to obtain a low vacuum, the important factor in this effect may be the time between experiments rather than in the evacuation pressure attained, i.e., if there is only a short evacuation period between experiments (low vacuum), the adsorbed products have relatively little time to decompose and the surface is not as effectively poisoned as when longer periods of evacuation are used.

Thus it seems that a thorough study of many factors other than just the decomposition of formic acid vapor needs to be made before the kinetics of the decomposition of formic acid vapor on a nickel catalyst can be completely and satisfactorily explained.

E. Future Work

During the course of the present research, it became evident that many improvements must be made in the system if further work is to be done on evaporated metal films. Probably the most important of these needs is an improvement in the vacuum system. The present work was done near the ultimate vacuum expected with the equipment at hand (10^{-7} mm.) and the time required to degass the system was nearly one week. This seems very wasteful when it is considered that the most important part of the reaction is over in less than five minutes. The elimination of all stopcock grease by the use of metal valves might further decrease the degassing time. In the moderately high temperature range involved in these experiments (100 to 200° C.), a better method of temperature maintenance should be tried. A bath of molten Wood's metal would greatly decrease the temperature gradients. Dead space in the system can be eliminated by use of a Daniels type pressure gauge¹⁹ which may be placed directly in the reaction vessel.

19. F. Daniels and E. H. Johnston, J. Am. Chem. Soc., 43, 53 (1921).

An attempt to produce oriented nickel films should be made. As indicated earlier (Section V-B-4-a), there may be a relation between the energy lost by the nickel particles due to collisions with the inert gas atmosphere and the resulting orientation or lack of orientation of the film. Variation of the nitrogen pressure from 0.01 to 1 mm. should show if this effect is present. A corroboration might then be made with the work of Ruka and Toyama and Kubokawa on the effect of different crystal orientations of the nickel on the decomposition of formic acid vapor.

The effect of the product gases on the reaction should be studied further and more conclusive results obtained. Only preliminary work along this line was reported in Section V-D-7. In line with this approach, the reaction should be studied during the initial stages, before appreciable amounts of the products are evolved.

The surfaces should be studied more thoroughly. Electron diffraction^{of} photographs and electron microscope pictures offer rapid means/obtaining information along this line. Variations of the surfaces before and during the reaction can be actually observed with the electron microscope.

Since the d-band effect does not seem to be the sole factor in the decomposition of formic acid vapor (see Section VI-D), it might be of interest to study the reaction on a series such as evaporated copper, silver and gold. Because pure copper will not chemisorb hydrogen²⁰ a new method of surface measurement would have to be developed. Wooten and Brown's variation of the BET method²¹ might prove satisfactory.

20. O. Beeck, Disc. Faraday Soc., 8, 118 (1930).

21. L. A. Wooten and C. G. Brown, J. Am. Chem. Soc., 65, 113 (1943).

A separation of the d-band effect from the effect shown on the copper, silver, and gold series could then be made by studying the copper-nickel alloy system. The evaporation of an alloy presents a problem. By using two filaments, one of copper and one of nickel, and by controlling the rates of evaporation, alloys of various compositions might be formed. The use of large diameter filaments is necessary so that the amount of metal evaporated will change the filament diameter negligibly and the rate of evaporation will remain uniform throughout the evaporation. A combination of methods of surface area measurement might prove useful here. The amount of nickel surface can be measured by hydrogen chemisorption and the total surface area can be measured by the BET method.

Results along these lines could prove important in the advancement of fundamental knowledge of catalysis.

VII SUMMARY

The rate of decomposition of formic acid vapor on evaporated nickel films has been studied manometrically in a static system from 125 to 190° C. and from 10 to 100 mm. pressure.

The nickel films, ranging in weight from 10 to 100 mg., were prepared in a spherical 500 ml. Pyrex flask having an internal surface of 300 cm.² in a high vacuum and in 1 to 2 mm. of nitrogen, and sintered at 190° C. The experimental examination of the films was carried out by X-ray and electron diffraction. The average crystallite size, as determined by X-ray measurements, was 270 Å for the high vacuum films and 160 Å for the nitrogen type films, both sintered at 190° C. Electron diffraction studies showed that both the high vacuum and the nitrogen evaporated films were randomly oriented on both soft and Pyrex glass backing. After use, the high vacuum films appeared to have an amorphous substance on the surface but no carbon or nickel oxide lines were detectable. Samples made when the flask was not thoroughly degassed before evaporation showed nickel oxide lines.

The surface area of the films was determined by measuring the amount of hydrogen rapidly chemisorbed at 0° C. Surface areas of the films sintered at 190° C. were reproducible, but were not proportional to the weight of the nickel evaporated. The area showed a decreasing increment with increasing amounts of nickel up to 100 mg. For the same weight of nickel, the nitrogen evaporated films have four times the area of the high vacuum films. The catalytic activity per unit surface area is the same for the two types.

The products of decomposition--hydrogen, carbon dioxide, carbon monoxide, water vapor, and methane--were identified by mass spectrographic analysis; no other gases were detected. Hydrogen, carbon dioxide and carbon monoxide were measured by gas analysis, and the small amount of methane (<1 per cent) was determined from mass spectrograms. Water vapor was determined indirectly in the products of reactions which went to completion, and was found to be present in amounts equal to the amount of carbon monoxide formed. The ratio of carbon dioxide to carbon monoxide is constant at about 3 to 1 throughout the main course of a single reaction, and at all the temperatures studied.

No reaction occurred at 190° C. in the absence of a nickel film.

The initial rate of decomposition of formic acid vapor on evaporated nickel films is zero order with respect to the formic acid vapor pressure from 10 to 50 mm., and over the temperature range studied, 125 to 190° C. The rate decreases with time in individual experiments.

Variation of the temperature indicates that there is no difference between temperature coefficients of reactions on the high vacuum and nitrogen type nickel films, and the activation energy for the combined data is 16.5 ± 1.3 kcal./mole.

The addition of a product gas causes the initial rate to decrease inversely with the pressure of the added gas. The general shape of all the curves, giving pressure increase with time, is similar for all the experiments in which product gases are added, except carbon dioxide which acts as a strong poison after the first few minutes of the reaction. Oxygen is a strong poison for the reaction.

The degree of degassing, before and during the evaporation of nickel, affects the initial activity of the films. Films evaporated at 10^{-7} mm. are about 2 to 3 times as active as those evaporated at 10^{-6} mm.

The first decomposition experiment on a nickel film has the highest initial rate. The initial rates of the slower subsequent decompositions on the same film depend upon the evacuation pressure reached between experiments; i.e., the initial rate is slower when the flask is evacuated to 10^{-6} mm. between experiments than when evacuated to 10^{-5} mm.

There is no significant difference between the Low Carbon and the 99 Alloy nickel used as catalysts in this research.

The mechanism is discussed, and may involve an inhibited bimolecular surface reaction with a formate-like intermediate.

APPENDIX

In this section the complete rate data of the experiments are given. The experiments are given as a series of numbers separated by dashes. The first number refers to the data book, the next number is the page of the experiment, and if more than one experiment was performed on a nickel film, the number of the experiment is given by the final number. The reaction temperature ($^{\circ}\text{C}.$) and the initial formic acid vapor pressure (mm. Hg) are given in all of the tables. The weight (mg.) and kind of nickel evaporated are not repeated when more than one experiment was performed on a film. The average pressure (mm. Hg) during evaporation of the nickel is given starting with experiment 5-26-1. In the case of the high vacuum films the average pressure is $1/2$ (pressure at the beginning of the evaporation + pressure at the end of the evaporation). For the nitrogen type films, the pressure of the nitrogen is given. In experiments where a gas was added before the formic acid vapor, the pressure of the gas (mm. Hg) is given. In experiments where the surface was measured by the rapid chemisorption of hydrogen at $0^{\circ}\text{C}.$, the number of hydrogen atoms adsorbed is given.

The reaction rate data are tabulated in parallel columns entitled pressure and time. The pressure units are given either as mm. of mercury or, in experiments where the sloping manometer was used, mm. of mercury divided by the sloping manometer factor 0.432. The time units are given either in seconds or in minutes. The initial pressure,

the pressure at zero time, is an extrapolated and not a measured value, and is placed in parentheses. When a gas was added before the formic acid vapor, the pressure of the gas and the time it was admitted to the reaction flask is listed. The taking of samples is also recorded and, where available, the times at which the samples were taken are noted.

In some experiments the data, taken directly from the tables, were fitted by the method of least squares to a cubic equation of the form

$$P = A + B \times 10^{-2}t + C \times 10^{-4}t^2 + D \times 10^{-8}t^3$$

where P is the pressure either in mm. of mercury or in mm. of mercury divided by the sloping manometer factor 0.432, t is the time in seconds, and A, B, C, D are constants. These constants are given in the tables whenever the data were fitted to the cubic equation. Only the points taken during the first 5 or 6 minutes of the reaction were used for these calculations. A line is drawn in the pressure and time columns under the last pressure and time reading used in the calculations.

APPENDIX

TABLE I

Experiment 4-79-1
 Temperature 187° C.
 9.7 mg. A Nickel from tungsten filament
 10.0 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	18.4	100.0
(10.0)	0.0	18.7	105.0
10.0	0.5	18.9	110.0
10.0	1.0	19.1	115.0
10.0	2.0	19.3	120.0
10.0	3.0	19.4	125.0
9.9	4.0	19.5	130.0
9.9	5.0	19.5	133.0
9.9	9.0	19.6	136.0
10.0	12.0	19.7	137.0
10.1	15.0	19.7	139.0
10.2	20.0	19.7	140.0
10.5	25.0	19.7	145.0
11.1	35.0	19.8	150.0
11.6	40.0	19.9	155.0
12.1	45.0	20.0	160.0
12.8	50.0	20.0	165.0
13.4	55.0	21.0	170.0
14.0	60.0	21.0	180.0
14.6	65.0	21.0	190.0
15.3	70.0	22.0	198.0
15.8	75.0	23.0	205.0
16.5	80.0	23.0	210.0
17.1	85.0	23.0	220.0
17.6	90.0	23.0	228.0
18.0	95.0		

APPENDIX
TABLE II

Experiment 4-79-2
Temperature 177° C.
6.8 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	9.8	74.0
(6.8)	0.0	9.8	75.0
6.8	0.5	10.1	80.0
6.8	1.0	10.4	85.0
6.8	2.0	10.8	92.0
6.8	3.0	11.0	95.0
6.8	4.0	11.2	100.0
6.7	5.0	11.4	105.0
6.7	6.0	11.7	110.0
6.7	7.0	12.0	115.0
6.7	9.0	12.4	121.0
6.7	10.0	12.5	125.0
6.7	12.0	12.6	132.0
6.8	13.0	12.8	139.0
6.8	14.0	13.0	146.0
6.9	15.0	13.1	155.0
7.0	19.0	13.2	166.0
7.0	20.0	13.4	176.0
7.1	25.0	13.4	185.0
7.2	30.0	13.4	198.0
7.6	37.0	13.5	202.0
7.8	42.0	13.5	205.0
8.0	45.0	13.5	209.0
8.4	52.0		
8.6	55.0		
9.0	60.0		
9.6	70.5		

APPENDIX
TABLE III

Experiment 4-79-3
Temperature 167° C.
8.4 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	12.1	250.0
(8.4)	0.0	12.2	257.0
8.4	0.5	12.4	260.0
8.3	3.0	12.6	270.0
8.2	8.0	12.7	274.0
8.2	13.0	12.8	275.0
8.2	18.0	12.9	280.0
8.1	23.0	13.1	288.0
8.1	28.0	13.2	295.0
8.1	33.0	13.4	300.0
8.1	38.0	13.6	305.0
8.1	43.0	13.8	315.0
8.2	53.0	14.0	320.3
8.2	63.0	14.0	325.0
8.3	73.0	14.1	330.0
8.6	98.0	14.2	335.0
9.0	118.0	14.4	340.0
9.2	130.0	14.6	347.0
9.4	144.0	14.7	350.0
9.6	153.0	14.8	355.0
9.9	167.0	15.0	361.0
10.2	177.0	15.0	365.0
10.6	194.0	15.1	370.0
11.0	207.0	15.2	375.0
11.2	223.0	15.3	380.0
11.7	239.0	15.4	390.0
11.8	242.0	15.6	400.0
11.9	244.0		
12.0	246.0		

APPENDIX
TABLE IV

Experiment 4-79-4
Temperature 189° C.
7.6 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	7.8	80.0
(7.6)	0.0	7.8	85.0
7.6	0.5	7.9	90.0
7.5	2.0	8.0	95.0
7.4	4.0	8.0	100.0
7.4	5.0	8.2	105.0
7.4	7.0	8.2	110.5
7.4	9.0	8.3	115.0
7.4	10.0	8.4	122.0
7.4	14.0	10.4	216.0
7.4	15.0	10.4	220.0
7.4	20.0	10.6	225.0
7.4	25.0	10.8	233.0
7.4	28.0	10.9	235.0
7.4	30.0	11.0	240.0
7.4	35.0	11.2	247.0
7.4	40.0	11.2	255.0
7.5	50.0	11.6	265.0
7.6	55.0	12.0	280.0
7.6	60.0	12.4	295.0
7.6	65.0	12.7	311.0
7.7	70.0	13.2	332.0
7.8	75.0		

APPENDIX TABLE V

Experiment 4-87-1
Temperature 190° C.
6.8 mg 99 Alloy Nickel from tungsten filament
5.0 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	7.2	18.0
(5.0)	0.0	7.4	19.0
5.0	0.5	7.6	20.0
5.1	2.0	7.7	21.0
5.2	3.0	8.2	23.0
5.2	4.0	8.4	25.0
5.3	5.0	8.7	27.0
5.4	6.0	8.8	28.0
5.4	7.0	9.0	29.0
5.6	8.0	9.1	30.0
5.6	9.0	9.3	32.0
5.8	10.0	9.4	33.0
6.3	14.0	9.6	35.0
6.6	15.0		
6.9	17.0		

Experiment 4-87-2
33 mm. more formic acid vapor
introduced at 35.5 minutes

12.9	36.0	15.8	70.0
13.2	37.0	16.2	73.0
13.3	38.0	16.5	76.0
13.4	39.0	16.5	80.0
13.6	42.0	16.8	83.5
13.8	47.0	17.1	85.0
14.0	50.0	17.2	90.0
14.2	55.0	17.5	95.0
14.7	60.0	17.8	100.0
15.0	64.0	18.1	106.0
15.2	65.0	18.5	110.0
15.4	67.0	18.7	115.0
15.7	69.0		

APPENDIX TABLE VI

Experiment 4-87-3
Temperature 189° C.
10.7 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	10.0	48.0
(10.7)	0.0	10.0	50.0
10.7	0.5	10.0	61.0
10.7	1.0	10.0	71.0
10.6	2.0	10.1	81.0
10.6	3.0	10.2	85.0
10.5	4.0	10.3	90.0
10.5	5.0	10.4	95.0
10.4	7.0	10.5	100.0
10.3	9.0	10.6	105.0
10.3	10.0	10.8	114.0
10.3	12.0	10.9	117.0
10.3	15.0	11.0	120.0
10.2	18.0	11.1	127.0
10.2	20.0	11.3	137.0
10.2	22.0	11.4	139.0
10.2	24.0	11.4	140.0
10.1	25.0	11.5	146.0
10.0	30.0	11.6	150.0
10.0	33.0	11.9	162.0
10.0	34.0	12.0	164.0
10.0	35.0	12.0	165.0
10.0	41.0		

Experiment 4-87-4
Temperature 190° C.
12.0 mm. more formic acid vapor
introduced at 166.0 minutes

24.0	166.5	23.2	270.0
23.9	167.0	23.2	276.0
23.8	168.0	23.2	284.0
23.8	169.0	23.3	290.0
23.7	170.0	23.4	301.0
23.7	172.0	23.5	308.0
23.6	175.0	23.6	320.0
23.4	176.0	23.8	336.0
23.4	180.0	24.0	345.0
23.4	185.0	24.1	355.0
23.4	190.0	24.3	363.0
23.2	200.0	24.4	368.0
23.2	208.0	24.6	377.0
23.2	217.0	24.6	380.0
23.2	220.0	24.9	392.0
23.2	225.0	25.0	395.0
23.2	230.0	25.0	400.0
23.2	235.0	25.2	410.0
23.2	240.0	25.4	417.0
23.2	253.0	25.6	420.0
23.2	262.0	25.6	430.0

APPENDIX
TABLE VII

Experiment 4-93-1
Temperature 189° C.
24.6 mg. 99 Alloy Nickel from tungsten filament
5.0 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	8.5	69.0
(5.0)	0.0	8.7	70.0
5.0	0.5	8.8	72.0
5.3	1.0	9.0	74.0
5.5	1.5	9.1	75.0
5.7	2.0	9.5	82.0
5.8	2.5	9.7	84.0
5.9	3.0	9.8	86.0
6.2	4.0	10.0	88.0
6.2	5.0	10.7	99.0
6.2	9.0	10.9	100.0
6.3	12.0	11.1	103.0
6.3	20.0	11.5	105.0
6.3	25.0	11.9	108.0
6.4	30.0	12.1	111.0
6.6	35.0	12.1	116.0
6.7	40.0	12.2	118.0
6.9	45.0	12.3	121.0
7.1	51.5	12.3	125.0
7.3	55.0	12.4	130.0
7.6	60.0	12.5	140.0
8.1	65.0	12.6	153.0
8.3	67.0	12.6	176.0
8.4	68.0		

APPENDIX
TABLE VIII

Experiment 4-93-2
Temperature 190° C.
10.4 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
00.0	----	13.5	130.0
(10.4)	0.0	13.7	133.0
10.4	0.5	13.8	135.0
10.5	1.0	14.1	141.0
10.5	2.0	14.3	145.0
10.4	3.0	14.7	150.0
10.3	4.0	14.9	156.0
10.3	6.0	15.5	168.0
10.2	8.0	15.7	170.0
10.2	10.0	16.0	176.0
10.1	12.0	16.1	180.0
10.1	14.0	16.6	190.0
10.1	18.0	16.9	195.0
10.1	21.0	17.2	203.0
10.2	27.0	17.3	205.0
10.2	30.0	17.7	210.0
10.3	33.0	17.8	212.0
10.3	35.0	17.9	218.0
10.4	40.0	18.0	221.0
10.5	45.0	18.1	223.0
10.7	58.0	18.2	225.0
10.8	60.0	18.3	231.0
10.9	65.0	18.5	238.0
11.2	72.0	18.6	240.0
11.3	74.0	18.9	247.0
11.5	80.0	19.0	251.0
11.7	85.0	19.3	265.0
12.3	100.0	20.4	360.0
12.4	105.0	20.5	375.0
12.9	117.0	20.6	385.0
13.1	122.0	20.7	412.0

APPENDIX TABLE IX

Experiment 5-15-1
Temperature 188° C.
16.2 mg. 99 Alloy Nickel from tungsten filament
25.0 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	33.4	396.0
(25.0)	0.0	33.6	402.0
25.0	0.5	33.7	405.0
24.5	1.0	33.8	410.0
24.0	2.0	34.0	420.0
23.8	3.0	34.1	425.0
23.6	4.0	34.2	430.0
23.6	5.0	34.5	445.0
23.6	6.0	34.8	460.0
23.6	8.0	35.0	465.0
23.7	13.0	35.2	476.0
23.8	15.0	35.4	489.0
23.8	18.0	35.4	490.0
24.0	26.0	35.5	493.0
24.1	28.0	35.6	495.0
24.2	32.0	35.8	500.0
24.3	35.0	35.8	506.0
24.5	40.0	35.9	514.0
24.7	47.0	36.1	523.0
25.0	53.0	36.2	528.0
25.5	69.0	36.4	534.0
26.1	88.0	36.6	544.0
26.6	100.0	36.7	550.0
26.8	106.0	36.8	555.0
32.1	320.0	36.8	560.0
32.2	330.0	36.9	561.0
32.4	335.0	37.0	564.0

APPENDIX TABLE X

Experiment 5-15-2
Temperature 189° C.
19.4 mm. initial pressure

Pressure mm. Hg	Time minutes	Pressure mm. Hg	Time minutes
0.0	----	20.0	45.0
(19.4)	0.0	20.2	60.0
19.4	0.5	20.3	75.0
19.5	1.0	20.4	85.0
19.5	2.0	20.8	145.0
19.5	3.0	20.9	150.0
19.6	4.0	21.0	155.0
19.6	5.0	21.0	160.0
19.6	10.0	21.0	165.0
19.7	15.0	22.0	310.0
19.7	20.0	22.0	315.0
19.8	25.0	22.0	320.0
19.8	30.0	22.2	340.0
19.8	35.0		
20.0	40.0		

APPENDIX TABLE XI

Experiment 5-26-1
 3×10^{-6} mm. average evaporation pressure
39.4 mg. Low Carbon Nickel
14.2 mm. initial pressure
Temperature 192° C.

Pressure mm. Hg/0.432	Time minutes
00.0	0.0
(32.5)	0.0
36.5	2.0
51.7	4.6
55.5	8.0
61.5	12.0
65.5	19.0

APPENDIX
TABLE XII

Experiment 5-26-2
Temperature 192° C.
24.0 mm. initial pressure

Pressure mm. Hg/0.432	Time minutes
0.0	--
(55.5)	0.0
56.5	0.5
58.5	1.5
63.0	6.5
65.0	10.0
68.0	15.0
75.5	22.75
79.0	29.5
83.5	35.6
84.5	42.0
88.0	51.0
92.0	64.0
95.5	70.0
96.0	80.0
103.2	103.0
107.5	114.0
108.5	125.0
112.5	141.0
112.5	143.0
113.0	145.0
113.5	150.0
119.0	165.0
119.5	170.0
121.5	185.0
125.0	281.0

APPENDIX
TABLE XIII

Experiment 5-26-3
20.1 mm. initial pressure
Temperature 192° C.

Pressure mm. Hg/0.432	Time minutes
0.0	----
(46.5)	0.0
47.0	0.5
49.5	6.0
51.7	16.0
55.2	46.0
56.0	57.0
56.5	64.0
57.0	70.0
58.0	80.0
59.0	91.0
59.5	100.0
61.8	122.0
63.5	134.0
64.5	145.0
65.8	158.0
66.8	168.5
80.0	252.0
80.8	270.0
83.0	289.0
83.8	310.0
85.0	331.0
88.0	363.0
98.5	525.0
98.5+	545.0
99.0	558.0
102.0	593.0
102.0	600.0
102.3	610.0
102.3	625.0

APPENDIX
TABLE XIV

Experiment 5-33
 1.6×10^{-6} mm. average evaporation pressure
 50.7 mg. Low Carbon Nickel
 20 mm. initial pressure
 Temperature 190° C.

Pressure mm./0.432	Time minutes
0.0	--
--	0.0
48.0	0.5
52.0	1.5
56.0	4.0
58.0	5.25
66.0	10.5
70.0	16.5
72.5	21.5
76.0	26.5
78.0	31.5
79.0	35.5
80.5	40.5
82.5	48.5
85.0	56.5
86.5	68.5
88.0	81.5
92.5	84.5
93.0	208.5
94.0	240.0
95.0	269.5
96.0	298.5
96.5	348.5
Sample taken	

APPENDIX
TABLE XV

Experiment 5-37
 2.1×10^{-6} mm. average evaporation pressure
 28.3 mg. Low Carbon Nickel
 26.4 mm. initial pressure
 Temperature 190°C.

Pressure mm. Hg/0.432	Time minutes
0.0	---
--	0.0
63.0	0.5
70.5	6.0
73.0	8.0
75.5	10.5
78.0	13.7
80.5	18.0
83.0	23.0
86.0	28.0
88.5	35.0
90.5	40.0
92.5	46.0
94.5	53.0
97.1	59.0
99.0	66.0
101.7	84.0
117.5	188.0
122.0	214.0
124.5	240.5
126.0	252.0

APPENDIX
TABLE XVI

Experiment 5-42
 7.7×10^{-7} mm. average evaporation pressure
 64.0 mg. 99 Alloy Nickel
 31.5 mm. initial pressure
 Temperature 187°C.

Pressure mm. Hg/0.432	Time minutes
0.0	---
--	0.0
75.5	0.75
78.0	2.0
82.0	5.0
85.2	8.0
88.2	11.5
92.0	17.0
96.0	23.0
101.8	32.0
106.0	43.0
118.5	69.0
123.0	81.0
126.8	91.0
129.0	100.0
131.5	110.0
135.5	130.0
138.2	140.0
141.0	152.0
145.5	178.0
147.7	195.0
152.5	230.0
156.0	260.0
159.5	300.0
162.0	330.0
162.7	340.0
163.2	351.0
164.2	366.0
165.2	390.0
167.5	420.0
168.8	450.0
169.0	480.0
169.5	495.0
170.0	510.0
170.5	525.0
170.5	540.0
Sample taken	

APPENDIX TABLE XVII

Experiment 5-52
 9.1×10^{-7} mm. average evaporation pressure
 50.5 mg. 99 Alloy Nickel
 14.5 mm. initial pressure
 Temperature 188°C.

Pressure mm. Hg/0.432	Time minutes
0.0	--
--	0.0
36.0	0.5
38.5	1.1
46.0	5.0
48.5	7.0
50.0	9.0
54.0	12.0
Sample taken	12.25

APPENDIX TABLE XVIII

Experiment 5-55
 7.8×10^{-7} mm. average evaporation pressure
 26.6 mg. 99 Alloy Nickel
 51.0 mm. initial pressure
 Temperature 189°C.

Pressure mm. Hg/0.432	Time minutes
0.0	--
--	0.0
118.0	0.5
123.5	3.0
125.5	4.75
128.0	7.20
130.6	10.25
132.0	12.0
135.6	18.0
Sample taken	19.25

APPENDIX
TABLE XIX

Experiment 5-58
 7.9×10^{-7} mm. average evaporation pressure
 37.4 mg. 99 Alloy Nickel
 14.0 mm. initial pressure
 Temperature 188°C.

Pressure mm. Hg/0.432	Time minutes
0.0	--
--	0.0
35.0	0.5
38.2	1.5
40.5	2.5
42.5	3.5
45.0	4.5
47.0	6.0
48.5	7.0
Sample taken	8.0

APPENDIX
TABLE XX

Experiment 5-60
 7.4 mm. average evaporation pressure
 24.0 mg. 99 Alloy Nickel
 10.3 mm. initial pressure
 Temperature 188°C.

Pressure mm. Hg/0.432	Time minutes
0.0	--
--	0.0
26.5	0.5
28.5	1.0
32.0	2.0
34.5	3.0
37.0	5.0
38.5	7.5
Sample taken	8.0

APPENDIX
TABLE XXI

Experiment 5-65
 4.6×10^{-7} mm. average evaporation pressure
 33.8 mg. 99 Alloy Nickel
 20.3 mm. initial pressure
 Temperature 187.9°C .

Pressure mm. Hg/0.432	Time Seconds
00.0	--
(47.2)	0.0
51.0	65.5
54.5	134.2
60.5	255.0
62.0	327.5
63.5	386.6
67.3	624.0
Sample taken	720.0

APPENDIX
TABLE XXII

Experiment 5-72
 4.5×10^{-7} mm. average evaporation pressure
 27.6 mg. 99 Alloy Nickel
 23.2 mm. initial pressure
 Temperature 188.5°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(53.4)	0
57.0	44
58.5	79
61.5	111
63.2	147
66.0	196
67.7	239
69.8	293
<u>72.0</u>	<u>352</u>
74.0	411
76.0	488
79.9	600
82.6	804
87.2	1235
90.2	1626
Sample taken	1650

$$A = 53.4$$

$$B = 7.85$$

$$C = -0.857$$

$$D = 3.38$$

APPENDIX
TABLE XXIII

Experiment 5-77
 3×10^{-7} mm. average evaporation pressure
 30.3 mg. 99 Alloy Nickel
 17.4 mm. initial pressure
 Temperature 188.5°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(40.2)	0
43.2	22
47.5	61
51.2	99
54.0	149
56.2	197
58.2	253
59.5	311
<u>61.8</u>	<u>416</u>
63.0	550
65.5	888
68.6	1633
Sample taken	1665

A = 40.2

B = 14.5

C = 4.16

D = 48.3

APPENDIX
TABLE XXIV

Experiment 5-81
 2.8×10^{-7} mm. average evaporation pressure
 27.4 mg. 99 Alloy Nickel
 27.9 mm. initial pressure
 Temperature 188.2°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
(64.6)	0
67.7	39
70.5	68
71.6	98
74.5	123
76.5	153
77.8	190
81.0	233
82.6	280
<u>83.9</u>	<u>323</u>
85.5	371
87.0	427
88.6	492
90.6	553
92.6	646
94.8	737
96.8	871
100.0	1068
Sample taken	1090

A = 64.6

B = 8.31

C = -0.328

D = -12.0

APPENDIX
TABLE XXV

Experiment 5-86
Reaction flask evacuated to 5×10^{-7} mm.
at 187.5°C. reaction temperature
No nickel film
17.3mm. initial pressure

Pressure mm. Hg/0.432	Time seconds
0.0	--
(40.0)	0
40.0	39
40.0	82
40.0	180
40.0	300
40.0	600
40.0	900
40.0	1200

APPENDIX
TABLE XXVI

Experiment 5-92
 2.2×10^{-7} mm. average evaporation pressure
 35.2 mg. 99 Alloy Nickel
 0.05 mm. CO added before initial 23.2 mm.
 of formic acid vapor
 Temperature 188.7°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
0.12 CO	(8 min. before start)
(53.6)	0
58.0	31
61.5	66
64.5	97
67.5	136
70.0	181
70.6	212
73.0	274
75.5	347
79.5	474
82.5	699
88.5	1333
Sample taken	1358

A = 53.6

B = 15.1

C = -4.40

D = 53.9

APPENDIX
TABLE XXVII

Experiment 5-96-1
 2.5×10^{-7} mm. average evaporation pressure
 44.9 mg. 99 Alloy Nickel
 0.09 mm. CH₄ added before initial 19.2 mm.
 of formic acid vapor
 Temperature 187.8°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
0.2 CH ₄	(6 min. before start)
(44.4)	0
48.5	23
53.5	62
56.5	87
59.0	114
61.0	149
63.0	199
65.5	270
68.5	368
71.0	537
73.0	726
74.0	1235
77.0	1813
Sample taken	

$$A = 44.6$$

$$B = 18.0$$

$$C = -5.78$$

$$D = 71.8$$

APPENDIX
TABLE XXVIII

Experiment 5-96-2
After 2 hrs. evacuation
19.2 mm. initial pressure
Temperature 187.8°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
(44.5)	0
49.5	58
53.0	100
55.0	149
56.5	188
58.0	260
59.5	290
61.0	316
62.2	349
64.0	399
65.5	462
67.1	532
68.7	612

APPENDIX
TABLE XXIX

Experiment 5-96-3
Reaction flask evacuated to 2.8×10^{-6} mm. Hg.
16.0 mm. initial pressure
Temperature 187.8°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
(37.0)	0
38.0	20
39.0	51
41.5	107
44.8	170
46.5	201
48.0	240
49.5	282
51.0	323
52.5	377
54.0	434
55.5	506
57.0	587

APPENDIX
TABLE XXX

Experiment 5-96-4
Reaction flask evacuated to 1.5×10^{-5} mm. Hg.
15.1 mm. initial pressure
Temperature 187.8°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(35.0)	0
37.5	30
40.0	57
42.6	80
44.3	106
45.5	136
47.0	170
48.5	198
52.0	312
52.8	336
54.5	376
56.0	445
57.2	529
58.0	560

APPENDIX
TABLE XXXI

Experiment 5-96-5
Reaction flask evacuated to 1.1×10^{-5} mm. Hg.
14.9 mm. initial pressure
Temperature 187.8°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(34.5)	0
35.5	19
37.0	46
38.6	76
40.5	117
42.0	157
43.5	198
45.5	254
47.0	311
48.5	366
50.2	436
51.5	505
53.0	597

APPENDIX

TABLE XXXII

Experiment 5-96-6

Reaction flask evacuated to 1.8×10^{-5} mm. Hg.

16.0 mm. initial pressure

Temperature 189.8°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(37.0)	0
40.0	36
42.5	64
44.5	91
46.5	129
48.0	163
49.5	210
51.5	266
53.0	315
54.0	389
55.7	465
57.0	557
57.5	583

APPENDIX

TABLE XXXIII

Experiment 5-96-7

Reaction flask evacuated to 1.6×10^{-6} mm. Hg.

14.5 mm. initial pressure

Temperature 188.8°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(33.5)	0
35.0	53
35.8	74
36.5	94
36.8	119
37.0	148
38.5	183
40.0	220
40.5	243
41.5	273
42.5	360
44.5	464
46.0	551

APPENDIX
TABLE XXXIV

Experiment 5-96-8
Reaction flask evacuated to 2×10^{-6} mm. Hg.
17.9 mm. initial pressure
Temperature 188.8°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(41.5)	0
43.0	59
44.5	97
46.4	140
47.6	203
49.5	260
50.8	337
52.5	424
53.6	510
54.9	561

APPENDIX
TABLE XXXV

Experiment 5-96-9
Reaction flask evacuated to 1.2×10^{-5} mm. Hg.
13.4 mm. initial pressure
Temperature 189.2°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(31.0)	0
32.0	27
33.5	60
34.8	103
37.0	147
38.6	211
40.5	276
42.2	364
43.5	463
45.2	575

APPENDIX
TABLE XXXVI

Experiment 5-96-10a
Reaction flask evacuated to 1.7×10^{-5} mm. Hg.
13.6 mm. initial pressure
Temperature 189.0°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
(31.5)	0
39.5	34
42.0	64
43.0	93
44.5	126
46.5	177
47.5	267
50.0	370
51.5	446
53.5	543

APPENDIX
TABLE XXXVII

Experiment 5-96-10b
Temperature 189.0°C.
Approximately 4 mm. more formic acid vapor added
at 570 seconds

Pressure mm. Hg/0.432	Time seconds
62.5	587
63.0	616
65.0	678
66.5	788

Experiment 5-96-10c
Temperature 189.0°C.
A few mm. of gas were pumped off and more
formic acid vapor was added to reaction flask
at about 850 seconds

Pressure mm. Hg/0.432	Time seconds
69.5	873
71.0	902
72.5	1012
74.0	1095

APPENDIX
TABLE XXXVIII

Experiment 5-96-11
Reaction flask evacuated to 1.3×10^{-5} mm. Hg.
16.0 mm. initial pressure
Temperature 147.6°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
(37.0)	0
37.0	30
38.0	331
38.7	512
39.6	875
40.5	1189
41.3	1690

APPENDIX
TABLE XXXIX

Experimental 5-111
 312×10^{-7} mm. average evaporation pressure
 42.7 mg. 99 Alloy Nickel
 5.8 mm. CO₂ added before initial 12.7 mm.
 of formic acid vapor
 Temperature 189.0°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
13.5 CO ₂	(7 min. before start)
(42.9)	0
46.5	23
48.5	47
52.0	80
54.5	110
56.5	174
58.0	223
59.5	282
61.0	473
60.0	596
61.0	691
Sample taken	750

A = 42.9

B = 15.5

C = -5.87

D = 87.0

APPENDIX
TABLE XL

Experiment 6-2
 3.0×10^{-7} mm. average evaporation pressure
 39.5 mg. 99 Alloy Nickel
 17.3 mm. CO₂ added before initial 5.0 mm.
 of formic acid vapor
 Temperature 189.0°C.

Pressure mm. Hg/0.432	Time seconds
0.0	--
40.0 CO ₂	{11 min. before start)
(51.6)	0
53.0	19
54.5	57
56.5	102
57.0	170
57.0+	481
57.5+	590
Add more HCOOH	620
82.5	702
84.0	738
85.0	770
86.0	806
88.0	869
89.5	956
91.5	1050
93.0	1290
Sample taken	1320

A = 51.6

B = 7.06

C = -2.85

D = 33.7

APPENDIX TABLE XLI

Experiment 6-b
 1.9×10^{-7} mm. average evaporation pressure
 45.6 mg. 99 Alloy Nickel
 14.7 mm. H_2 added before initial 17.1 mm.
 of formic acid vapor
 Temperature $189.0^\circ C$.

Pressure mm. Hg/0.432	Time Seconds
0.0	--
34.0 H_2	(13 min. before start)
(73.7)	0
77.0	28
79.5	67
81.7	90
85.5	128
88.0	162
90.5	234
94.0	317
97.0	457
98.5	573
Sample taken	590

$$A = 73.7$$

$$B = 10.5$$

$$C = -1.34$$

$$D = 0.579$$

APPENDIX
TABLE XLII

Experiment 6-10
 2.2×10^{-7} mm. average evaporation pressure
 36.5 mg. 99 Alloy Nickel
 11.6 mm. H_2O vapor added before initial 24.2 mm.
 of formic acid vapor
 Temperature $189.0^\circ C$.

Pressure mm. Hg/0.432	Time seconds
0.0	--
27.0 H_2O	(18 min. before start)
(82.8)	0
85.5	25
89.5	58
90.5	88
92.5	118
93.6	151
96.4	190
99.1	244
100.5	296
<u>102.8</u>	<u>375</u>
105.0	459
106.5	517
107.0	558
107.5	601
Sample taken	635

A = 82.8

B = 9.07

C = -1.66

D = 17.6

APPENDIX
TABLE XLIII

Experiment 6-14-1
 1.9×10^{-7} mm. average evaporation pressure
 33.5 mg. 99 Alloy Nickel
 4.3 mm. O_2 added before initial 21.2 mm.
 of formic acid vapor
 Temperature $188.8^\circ C$.

Pressure mm. Hg/0.432	Time seconds
0.0	--
10.0 O_2	(12 min. before start)
(58.0)	0
58.0	42
59.0	129
59.0	741
59.0	880

Experiment 6-14-2
 Flask evacuated and 21.6 mm. of formic acid
 vapor introduced

0.0	--
50.0	23
50.0	214
50.0	305
50.0	723

APPENDIX
TABLE XLIV

Experiment 6-25
 2.2×10^{-7} mm. average evaporation pressure
 41.2 mg. 99 Alloy Nickel
 17.7 mm. CO added before initial 8.4 mm. of
 formic acid vapor
 Temperature 189.0°C .

Pressure mm. Hg/ 0.432	Time seconds
0.0	--
41.0 CO	(13 min. before start)
(60.5)	0
61.0	27
63.0	147
64.5	434
67.0	1320
71.0	1760
72.0	2048

APPENDIX
TABLE XLV

Experiment 6-31
 2.1×10^{-7} mm. average evaporation pressure
 39.8 mg. 99 Alloy Nickel
 13.2 mm. initial pressure
 Temperature 150.5°C .

Pressure mm. Hg/0.432	Time seconds
0.0	--
(30.5)	0
31.5	33
33.5	87
34.7	183
36.5	320
36.9	400
37.6	482
<u>38.5</u>	<u>620</u>
40.0	895
42.0	1400
43.6	1856
45.2	2313
47.6	3240
51.6	5505
Sample taken	5755

A = 30.5

B = 3.70

C = -0.830

D = 7.61

APPENDIX
TABLE XLVI

Experiment 6-45
 1.8×10^{-7} mm. average evaporation pressure
 30.2 mg. 99 Alloy Nickel
 28.9 mm. initial pressure
 Temperature 146.4°C .

Pressure mm. Hg.	Time seconds
0.0	--
(28.90)	0
29.40	43
29.70	90
30.00	114
30.25	154
30.50	206
30.75	254
31.00	322
31.80	466
<u>32.10</u>	<u>575</u>
32.50	670
32.75	772
33.40	1013
33.65	1143
33.85	1247
34.10	1410
34.50	1584
35.50	2086
36.50	2700
37.00	3142
38.50	4585
39.10	5020
Sample 1	5100
31.6	5210
32.1	5968
33.0	6483
33.6	7263
35.0	8848
35.3	9283
Sample 2	9330
28.5	9400
29.4	10662
33.1	17739
33.4	19900
33.7	20860
Sample 3	--
A = 28.9	
B = 1.12	
C = -0.224	
D = 2.47	

APPENDIX
TABLE XLVII

Experiment 6-53
 2.6×10^{-7} mm. average evaporation pressure
 44.5 mg. 99 Alloy Nickel
 12.1 mm. initial pressure
 Temperature 168.3°C.

Pressure mm. Hg.	Time seconds
0.0	--
(12.1)	0
12.7	21
13.7	56
14.5	93
14.85	127
15.35	161
16.00	213
16.60	309
17.60	482
18.10	605
Sample 1	--
15.40	644
16.80	1126
17.60	1496
18.10	1621
18.35	2069
19.00	2653
19.40	3203
19.60	3703
20.00	4670
20.05	5360
20.10	6020
20.55	11830
20.55	12020
Sample 2	12052

A = 12.1
 B = 3.29
 C = -0.922
 D = 10.7

APPENDIX
TABLE XLVIII

Experiment 6-59
 1.9×10^{-7} mm. average evaporation pressure
 28.9 mg. 99 Alloy Nickel
 25.3 mm. initial pressure
 Temperature 167.4°C .

Pressure mm. Hg.	Time seconds
0.0	--
(25.3)	0
25.85	21
26.80	61
27.45	95
28.20	135
28.70	179
29.20	209
29.55	245
30.00	278
30.40	318
30.70	365
31.45	458
32.00	565
Sample 1	584
26.00	650
26.90	725
27.30	820
28.75	1080
29.90	1389
30.80	1613
31.50	1965
32.60	2385
33.70	2950
34.30	3150
34.60	3310
34.90	3642
Sample 2	3708
28.90	3740
29.50	4065
30.20	4690
30.80	5276
31.70	6000
32.50	6955
33.30	9170
34.30	13840
34.50	15215
34.70	20645
34.75	25500
34.75	35470
Sample 3	--
A = 25.3	
B = 2.84	
C = -0.675	
D = 9.36	

APPENDIX
TABLE XLIX

Experiment 6-65
 9 mm. of CO contaminated with O₂ added to
 reaction flask 19 min. before addition of
 24.6 mm. of formic acid vapor
 37.4 mg. 99 Alloy Nickel
 Temperature 189.0°C.

Pressure mm. Hg.	Time seconds
0.0	--
9.0 CO(+O ₂)	(19 min. before start)
X	0.0
33.6	47
33.7	211
33.6	334
33.6	516
56.0	20020
56.2	20567
57.2	34440
58.0	35940

APPENDIX TABLE L

Experiment 6-69
 2×10^{-7} mm. average evaporation pressure
38.0 mg. 99 Alloy Nickel
51.1 mm. initial pressure
Temperature 168.6°C .

Pressure mm. Hg.	Time seconds
0.0	--
(51.1)	0
52.3	47
53.4	87
54.0	121
54.3	150
54.9	192
55.4	228
56.3	286
56.8	343
57.3	384
57.6	426
58.2	490
58.9	558
59.2	603
60.0	701
61.9	985
62.5	1124

A = 51.1
B = 3.05
C = -0.695
D = 8.68

APPENDIX
TABLE LI

Experiment 6-71
 1.8×10^{-7} mm. average evaporation pressure
 38.3 mg. 99 Alloy Nickel
 25.4 mm. initial pressure
 Temperature 188.8°C .

Pressure mm. Hg.	Time seconds
0.0	--
(25.4)	0
27.6	42
29.6	81
30.6	114
31.9	156
32.8	200
33.7	239
34.5	276
<u>35.0</u>	<u>324</u>
35.6	366
36.5	443
37.3	499
38.0	566
38.5	598

$$A = 25.4$$

$$B = 5.95$$

$$C = -1.36$$

$$D = 13.8$$

APPENDIX
TABLE LII

Experiment 6-74
 2.2×10^{-7} mm. average evaporation pressure
 31.7 mg. 99 Alloy Nickel
 8.2 mm. CO added before initial 19.8 mm.
 of formic acid vapor
 Temperature 188.5°C.

Pressure mm. Hg.	Time seconds
0.0	--
8.2 CO	(8 min. before start)
(27.0)	0
29.3	40
31.2	77
32.5	112
33.2	154
34.2	194
34.9	238
35.5	279
36.2	337
37.3	445
38.0	528
38.3	583

A = 27.0
 B = 6.75
 C = -2.06
 D = 25.9

APPENDIX TABLE LIII

Experiment 6-77
1.3 mm. N₂ during evaporation
19.3 mg. 99 Alloy Nickel
Approximately 16 mm. initial pressure
Temperature 189.2°C.

Pressure mm. Hg.	Time seconds
0.0	--
--	0
27.2	30
31.0	78
31.9	119
32.5	226
32.5	460
32.5	600
Sample taken	

TABLE LIV

Experiment 6-81
1.3 mm. N₂ during evaporation
18.1 mg. 99 Alloy Nickel
Approximately 18 mm. initial pressure
Temperature 169.2°C.

Pressure mm. Hg.	Time seconds
0.0	--
--	0
23.5	29
27.6	97
28.5	124
29.0	152
30.0	191
30.6	231
31.2	276
32.0	333
32.6	421
33.5	550
33.8	655
34.5	1014
Sample taken	--

APPENDIX
TABLE LV

Experiment 6-87
1.3 mm. N₂ during evaporation
20.4 mg. 99 Alloy Nickel
11.8 mm. initial pressure
Temperature 146.0°C.

Pressure mm. Hg.	Time seconds
0.0	--
(11.8)	0
12.2	23
12.5	50
12.8	76
13.2	101
13.5	126
13.8	166
14.2	215
<u>14.5</u>	<u>262</u>
14.8	320
15.3	400
15.8	477
16.1	588
16.6	754
17.6	1120
sample taken, more HCOOH added	1200
24.5	1248
24.8	1324
25.2	1416
26.0	1600
26.5	1730
27.3	1905
27.8	2080
28.8	2429
29.9	2700
30.4	2970

A = 11.8
B = 1.43
C = -0.113
D = -1.90

APPENDIX TABLE LVI

Experiment 6-91
1.7 mm. N₂ during evaporation
34.9 mg. 99 Alloy Nickel
32.0 mm. initial pressure
Temperature 125.3°C.

Pressure mm. Hg.	Time seconds
0.0	--
(32.0)	0
32.5	35
33.0	73
33.5	105
33.7	140
34.0	172
34.4	222
34.8	260
<u>35.0</u>	<u>333</u>
35.4	414
35.8	519
36.3	600
37.6	1040
37.8	1150
38.3	1348

A = 32.0
B = 1.44
C = -0.148
D = -0.469

APPENDIX
TABLE LVII

Experiment 6-95
1.7 mm. N₂ during evaporation
19.8 mg. 99 Alloy Nickel
22.4 mm. initial pressure
Temperature 147.2°C.

Pressure mm. Hg.	Time seconds
0.0	--
(22.4)	0
23.9	38
25.6	92
26.3	130
27.3	164
27.5	192
28.1	238
28.5	274
<u>29.1</u>	<u>336</u>
30.0	419
30.3	475
30.8	553
31.8	649

A = 22.4
B = 4.37
C = -1.11
D = 11.9

APPENDIX
TABLE LVIII

Experiment 6-97
1.5 mm. N₂ during evaporation
13.4 mg. 99 Alloy Nickel
27.1 mm. initial pressure
Temperature 155.2°C.

Pressure mm. Hg.	Time seconds
0.0	--
(27.1)	0
28.3	29
29.3	60
30.5	96
31.4	132
32.3	170
32.9	207
33.7	265
34.6	333
<u>35.8</u>	<u>422</u>
Sample 1	438
29.8	485
30.6	554
32.3	721
34.3	1036
35.6	1360
38.0	1891
39.5	2409
45.5	10560
45.7	11600
45.9	12110
46.2	12983
46.4	13250
Sample 2	13300
A = 27.1	
B = 4.43	
C = -0.979	
D = 9.86	

APPENDIX
TABLE LIX

Experiment 6-101
1.0 mm. N₂ during evaporation
21.0 mg. 99 Alloy Nickel
24.7 mm. initial pressure
Temperature 124.7°C.

Pressure mm. Hg.	Time seconds
0.0	--
(24.7)	0
25.0	65
25.4	164
25.8	320
26.2	433
26.5	563
27.1	700
27.8	1085
28.2	1365
28.5	1595
Sample taken	1650

APPENDIX
TABLE LX

Experiment 6-106
1.7 mm. N₂ during evaporation
15.1 mg. 99 Alloy Nickel
13.1 mm. initial pressure
Temperature 153.3°C.

Pressure mm. Hg.	Time Seconds
0.0	--
(13.1)	0
13.5	10
15.6	65
16.2	90
16.8	117
17.3	148
18.0	190
18.6	240
<u>19.5</u>	<u>346</u>
20.5	510
21.2	595
Sample taken	640

A = 13.1
B = 4.45
C = -1.27
D = 15.0

APPENDIX
TABLE LXI

Experiment 6-111
 2×10^{-7} average evaporation pressure
 31.3 mg. 99 Alloy Nickel
 0.89×10^{18} H atoms adsorbed
 14.9 mm. initial pressure
 Temperature 189.2°C.

Pressure mm. Hg.	Time seconds
0.0	--
(14.9)	0
16.8	37
18.6	72
19.3	107
20.2	147
21.1	203
22.1	277
<u>22.6</u>	<u>317</u>
23.2	403
23.8	469
24.5	563
Sample taken	590

A = 14.9
 B = 6.15
 C = -2.16
 D = 31.3

APPENDIX
TABLE LXII

Experiment 7-3
1.4 mm. N₂ during evaporation
45.9 mg. 99 Alloy Nickel
3.86x10¹⁸ H atoms adsorbed
26.2 mm. initial pressure
Temperature 146.0°C.

Pressure mm. Hg.	Time seconds
0.0	--
(26.2)	0
27.3	33
28.7	77
29.6	113
30.3	143
31.2	178
32.1	223
32.6	270
<u>33.5</u>	<u>333</u>
34.1	378
34.7	435
35.2	491
36.0	546
36.3	607
Sample taken	640

A = 26.2
B = 3.61
C = -0.491
D = 2.01

APPENDIX
TABLE LXIII

Experiment 7-9
 2×10^{-7} mm. average evaporation pressure
 71.0 mg. 99 Alloy Nickel
 1.04×10^{18} H atoms adsorbed
 21.0 mm. initial pressure
 Temperature 156.3°C .

Pressure mm. Hg.	Time seconds
0.0	--
(21.0)	0
21.3	27
21.7	70
22.0	112
22.4	167
22.8	255
<u>23.1</u>	<u>364</u>
24.0	710
24.5	950
25.0	1231

A = 21.0
 B = 1.05
 C = -0.154
 D = 0.585

APPENDIX
TABLE LXIV

Experiment 7-15
 2×10^{-7} mm. average evaporation pressure
 100.8 mg. 99 Alloy Nickel
 1.32×10^{18} H atoms adsorbed
 24.7 mm. initial pressure
 Temperature 171.1°C .

Pressure mm. Hg.	Time seconds
0.0	--
(24.7)	0
25.2	32
26.0	68
26.5	125
26.9	290
27.2	471
27.8	565
28.4	800
28.7	1025
28.9	1150
29.0	1232

APPENDIX
TABLE LXV

Experiment 7-18
 2×10^{-7} mm. average evaporation pressure
 29.1 mg. 99 Alloy Nickel
 0.84×10^{18} H atoms adsorbed
 25.8 mm. initial pressure
 Temperature 188.5°C.

Pressure mm. Hg.	Time seconds
0.0	--
(25.8)	0
28.1	43
29.3	78
30.6	112
31.0	136
31.5	163
32.1	190
32.7	223
33.4	258
<u>34.0</u>	<u>296</u>
34.5	337
35.1	387
36.0	465
36.4	496
36.7	527
37.1	565
37.3	598
38.8	792
40.4	1040

A = 25.8
 B = 6.11
 C = -2.18
 D = 36.9

APPENDIX
TABLE LXVI

Experiment 7-21
 2×10^{-7} mm. average evaporation pressure
 40.5 mg. ⁹⁹Alloy Nickel
 0.89×10^{18} H atoms adsorbed
 19.3 mm. initial pressure
 Temperature 159.0°C.

Pressure mm. Hg.	Time seconds
0.0	--
(19.3)	0
20.2	53
20.7	92
21.2	127
21.4	155
21.7	216
22.3	291
<u>22.8</u>	<u>405</u>
23.1	536
23.5	690
23.9	860
24.0	940

A = 19.3
 B = 1.92
 C = -0.454
 D = 4.77

APPENDIX
TABLE LXVII

Experiment 7-24
 2×10^{-7} mm. average evaporation pressure
 13.7 mg. ⁹⁹Alloy Nickel
 0.60×10^{18} H atoms adsorbed
 12.2 mm. initial pressure
 Temperature 173.3°C.

Pressure mm. Hg.	Time seconds
0.0	--
(12.2)	0
12.8	30
13.2	63
13.8	90
14.4	137
14.7	170
15.4	231
<u>15.8</u>	290
16.2	347
17.1	440
17.5	516
17.8	601
18.4	756

A = 12.2
 B = 1.94
 C = -0.285
 D = 1.68

APPENDIX
TABLE LXVIII

Experiment 7-27
1.9 mm. N_2 during evaporation
14.9 mg. 99 Alloy Nickel
 2.58×10^{18} H atoms adsorbed
16.2 mm. initial pressure
Temperature $153.5^\circ C$.

Pressure mm. Hg.	Time seconds
0.0	--
(16.2)	0
17.3	40
18.0	74
18.8	106
19.4	140
19.8	176
20.4	210
20.9	249
<u>21.4</u>	<u>290</u>
22.0	332
22.3	385
22.9	466
23.4	548
23.9	622
24.9	792
25.7	930

A = 16.2
B = 3.08
C = -0.694
D = 8.92

APPENDIX
TABLE LXIX

Experiment 7-30
 1.8 mm. N_2 during evaporation
 41.6 mg. $^{69}\text{Alloy Nickel}$
 3.94×10^{18} H atoms adsorbed
 19.3 mm. initial pressure
 Temperature 132.1°C .

Pressure mm. Hg.	Time seconds
0.0	--
(19.3)	0
19.6	25
20.2	63
20.8	102
21.4	135
21.8	165
22.5	210
22.8	244
23.2	301
23.5	<u>340</u>
23.9	388
24.3	432
24.5	483
24.8	530
25.2	600
26.7	910
36.6	9851
37.6	5 hr. 30 min.
38.0	19 hr. 8 min.
37.8	23 hr. 31 min.

A = 19.3
 B = 1.33
 C = 0.328
 D = -11.1

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AUTOBIOGRAPHY

I, Dean Kirkland Walton, was born in Canton, Ohio, on November 11, 1925. I received my elementary and high school education in the public schools of Coshocton, Ohio. I graduated from high school in June 1943. From June 1943 to March 1944 I attended the College of Wooster in Wooster, Ohio. After spending the following two years in the Army, I returned to Wooster and finished college in 1949 with a Bachelor of Arts degree. Since September, 1949, I have been enrolled in the Graduate School of The Ohio State University. I was employed by The Ohio State University Research Foundation as a Research Assistant from 1950-1952. In the school year 1952-1953, I was a General Electric Fellow. The following school year, 1953-1954, I held an Allied Chemical and Dye Corporation Fellowship. During the 1954-1955 school year, I held a fellowship granted by the Department of Chemistry.