

CHEMISORPTION OF NITROGEN ON IRON CATALYSTS IN CONNECTION WITH AMMONIA SYNTHESIS

PART 2.—THE RATE-DETERMINING STEP IN AMMONIA SYNTHESIS

J. J. F. SCHOLTEN, J. A. KONVALINKA AND P. ZWIETERING

Central Laboratory, Staatsmijnen in Limburg, Geleen, The Netherlands

Received 4th August, 1959

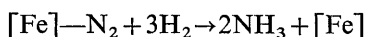
A comparison is made of the rate of nitrogen chemisorption on a singly-promoted iron catalyst with the rate of ammonia synthesis over the same sample. During synthesis the amount of nitrogen chemisorbed on the catalyst is determined gravimetrically.

It is shown that the chemisorption and synthesis rates were equal at the same temperature, nitrogen pressure and nitrogen coverage. Moreover, the nitrogen coverages calculated by means of the nitrogen fugacity $P^*_{N_2}$ and the chemisorption isotherm were in accordance with the coverages found gravimetrically. These results are in agreement with the well-known supposition of Emmett and Brunauer that nitrogen chemisorption is the rate-determining step in ammonia synthesis.

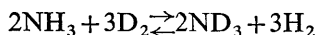
In addition a hydrogen chemisorption isobar was measured on the highly reduced catalyst. Only one type of hydrogen chemisorption was detected, as distinct from the result of Emmett and Harkness who found two types of chemisorption on a doubly promoted catalyst.

There are several indications that nitrogen chemisorption is the rate-determining step in ammonia synthesis. Brunauer and Emmett¹ and Zwietering and Roukens,² found synthesis rates on their catalysts which were of the same order of magnitude as the nitrogen chemisorption rate. Compare also the work of Kozhenova and Kagan³ who showed that the hydrogenation of pre-chemisorbed nitrogen proceeded much faster than the normal synthesis reaction starting from gaseous nitrogen+hydrogen mixture.

In agreement with these results, Temkin *et al.*⁴ proved that the reaction



attained equilibrium at very low temperatures. Our own experiments (unpublished) confirm this. Taylor and Jungers⁵ found that the exchange reaction



occurs over an iron catalyst at room temperature.

However, Horiuti *et al.*⁶ found the stoichiometric number⁶ of the ammonia synthesis to be 2, from which they concluded that some hydrogenation step must be rate-determining. However, Bokhoven, Gorgels and Mars,⁷ repeating and extending this work, obtained a stoichiometric number of unity, which points to the nitrogen chemisorption being rate-determining.

In the present paper we give a direct comparison of the rate of nitrogen chemisorption with the rate of ammonia synthesis on the same catalyst sample and show that the nitrogen chemisorption is rate-determining. Such a comparison has to be made not only at the same temperature and nitrogen pressure, but also at the same nitrogen coverage, on which the nitrogen chemisorption rate is strongly dependent. The problem of the determination of the nitrogen coverage during synthesis was solved by weighing the catalyst during the synthesis experiments.

EXPERIMENTAL

APPARATUS, AND PURIFICATION OF THE SYNTHESIS GAS

The high-vacuum balance used in this study has already been described in a previous publication.⁸

The synthesis gas, a 1 : 3 nitrogen+hydrogen mixture containing traces of CO, CO₂, O₂ and oil, was purified in the way described by Bokhoven, Gorgels and Mars⁷ and then passed through a cold trap, cooled with liquid nitrogen to -196°C , in order to freeze out any remaining condensable gases.

The oxygen content of the purified gas was only 0.01 p.p.m. This low oxygen content was determined by means of a Cd-Ag cell.⁹

REDUCTION OF THE CATALYST, DETERMINATION OF THE SURFACE AREA AND OF THE AMOUNT OF ADSORBED NITROGEN AT FULL COVERAGE

The experiments were performed with the same singly promoted catalyst as used in our chemisorption experiments.¹⁰ The available surface area was determined from the physical adsorption of nitrogen at -196°C (B.E.T. method), using for the cross-sectional area of a nitrogen molecule Livingston's value of 15.4 \AA^2 . The results are given in table 1, column no. 1, for different series of measurements; the surface area was found to remain constant in each series, so that it was not seriously reduced by sintering.

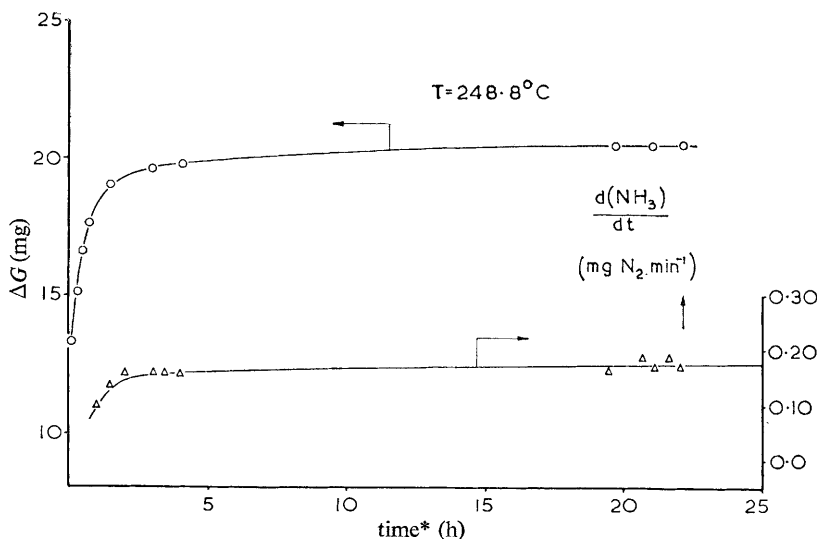


FIG. 1.—Weight increase of the catalyst and simultaneous increase of the ammonia synthesis rate, as functions of time. $T=248.8^{\circ}\text{C}$; O, catalyst weight; Δ , NH_3 synthesis rate.

For the maximum adsorption capacity of N_2 , half the maximum adsorption capacity of CO was taken.^{2, 10} The maximum adsorption capacity of CO was determined at the end of the third series of measurements; in the other series, it was calculated assuming that the free iron part of the catalyst is reduced proportionally to the total surface area. The value of $(g_{\text{N}_2})_{\text{max}}$ found in this way is in accordance with the value found if one tries to saturate the surface completely with nitrogen.¹⁰ An error in the coverage definition will not invalidate the comparisons to be made, as in all calculations the same definition is used.

BUOYANCY CORRECTIONS AND FLOW CORRECTIONS

When working with streaming gases, buoyancy corrections* alone do not suffice; the apparent catalyst weight is influenced also by the flowing of the gas along the catalyst basket. The flow corrections were determined both with the purified hydrogen+nitrogen

* For the determination of the buoyancy corrections, see ref. (10).

mixture and with pure argon, the catalyst basket being filled with a passivated iron catalyst or with corundum particles to avoid chemical interaction between gases and catalyst.

Calculation showed that the Stokes force on the upper surface of the cylindrical basket (see ref. (8), fig. 1) could be neglected (correction <0.01 mg) and that the flow corrections could be described in good approximation by Poiseuille's law for a tube of annular section.¹¹ The sum of buoyancy and flow corrections never exceeded 7.5% of the total weight change of the catalyst and was known with an accuracy of about 10 %.

METHOD OF EXPERIMENTATION

As our highly active catalyst sample (having the same activity as the sample used in our chemisorption experiments¹⁰) was rather sensitive to small variations in the degree of reduction,¹⁰ it was decided always to measure the nitrogen chemisorption rate immediately before performing the synthesis rate measurement at the same temperature. Between these two experiments nitrogen was removed by desorption, not by reduction; in this way the activity of the catalyst remained constant. In one experiment (at 165.4°C) the chemisorption rate was moreover measured after the synthesis experiment (which lasted more than 160 h) and appeared to be equal to the rate measured before the synthesis.

The synthesis experiments were performed in the following way. The highly purified nitrogen+hydrogen mixture was led past the reduced catalyst at the rate of 10-30 l./h. Then the catalyst was rapidly brought to the desired reaction temperature by pushing the pre-heated furnace FI (see ref. (8), fig. 1) around the catalyst tube and both the weight of the catalyst and the ammonia content of the exit-gases were registered at regular intervals. The ammonia content was determined titrimetrically with 0.1 or 0.01 N sulphuric acid.

When the catalyst weight and the ammonia production had remained constant for a few hours, the experiment was regarded as completed; in experiments below 200°C these values remained constant for over 20 h.

RESULTS

During synthesis experiments a slow rise of the catalyst weight and a simultaneous rise of the synthesis rate are observed; both become constant at the same time (fig. 1 and 2). The total weight increase ΔG of the catalyst compared with that in vacuum conditions comprises the following terms:

$$\Delta G = g_{N_2} + g_{H_2} + g_{NH_3} + c, \quad (1)$$

where g_{N_2} is the weight increase due to nitrogen chemisorption,
 g_{H_2} is the amount of adsorbed hydrogen,
 g_{NH_3} is the amount of adsorbed ammonia,
 c is the sum of the corrections for buoyancy and flow.

Hence, if ΔG and c are determined experimentally and g_{H_2} and g_{NH_3} are known, we calculate g_{N_2} , the amount of nitrogen chemisorbed during synthesis.

From

$$g_{N_2} = \theta_s (g_{N_2})_{\max}, \quad (2)$$

we calculate θ_s , the nitrogen coverage during synthesis. θ_s can subsequently be compared with θ_{ch} , the nitrogen coverage found in a chemisorption experiment at the same temperature and nitrogen pressure. θ_{ch} is the coverage at the point where the nitrogen chemisorption rate is equal to the ammonia synthesis rate:

$$\frac{d(NH_3)}{dt} = \left[\frac{d(N_2)}{dt} \right]_{\theta=\theta_{ch}}, \quad (3)$$

where $d(NH_3)/dt$, expressed in mg nitrogen per min, is the constant ammonia synthesis rate eventually reached.

If θ_s is equal to θ_{ch} , it is experimentally proved that (3) applies and hence that nitrogen chemisorption was rate-determining under the experimental conditions used.

DETERMINATION OF g_{H_2} AND g_{NH_3}

g_{NH_3} may be neglected as compared with g_{H_2} . This follows from the low heat of adsorption (NH_3 , 16 kcal/mole; rapidly declining with coverage¹²); H_2 , initial heat of adsorption 35 kcal/mole^{13, 14}) and from the fact that the max. partial NH_3 pressure in our experiments was more than 100 times smaller than the partial H_2 pressure.

g_{H_2} was calculated from the relation found both on "unpromoted" catalysts (0.24 % Al_2O_3)¹⁵ and on evaporated iron films,¹⁶ which indicates that at full coverage and at room temperature the sum of the number of adsorbed H atoms and N atoms remains constant. In this case,

$$g_{H_2} = ((g_{N_2})_{max} - g_{N_2})/14. \quad (4)^*$$

The amount of hydrogen adsorbed at the experimental temperature, $(g_{H_2})_T$, was calculated from the hydrogen isobar found on the nitrogen-free catalyst (fig. 3), assuming the same temperature dependence of g_{H_2} in the presence of nitrogen. The assumption made in the calculation of g_{H_2} are justified by the low atomic weight of H_2 with respect to

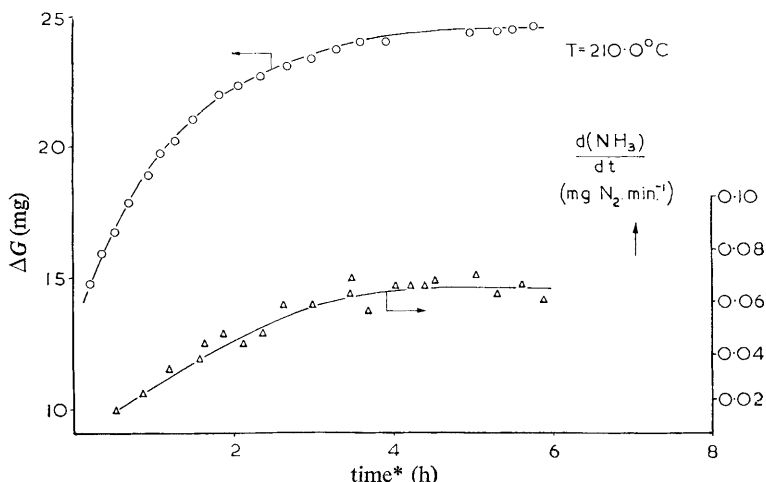


FIG. 2.—Weight increase of the catalyst and simultaneous increase of the ammonia synthesis rate, as functions of time. $T = 210.0^\circ C$; \circ , catalyst weight; \triangle , NH_3 synthesis rate.

nitrogen and by the weak temperature dependence of g_{H_2} . Emmett and Harkness¹⁷ obtained with a catalyst promoted with 1.3 % Al_2O_3 and 1.6 % K_2O two types of hydrogen chemisorption, whereas only one type was detected by us (see fig. 3). This can perhaps be explained from the difference in promotor content (see Podgurski and Emmett¹⁸), but also the degree of reduction may play a part in the occurrence of two types of hydrogen chemisorption, as was found by Schuit and de Boer¹⁹ with Ni-on-silica catalysts.

CHEMISORPTION AND SYNTHESIS EXPERIMENTS

Fig. 4 gives an example of the rate of chemisorption in mg N_2 /min as a function of coverage at $248.8^\circ C$. Because of the high activity of the catalyst, the measurement was performed at the low nitrogen pressure of 1.86 cm Hg, but as the rate is strictly proportional to the pressure, as shown in previous publications^{8, 10} the experimental rate was recalculated for a nitrogen pressure of 19 cm Hg, which is equal to the partial nitrogen pressure in the 1 : 3 $N_2 + H_2$ mixture.

After termination of this run, the catalyst was degassed at gradually rising temperature; after final degassing for a few hours at $525^\circ C$, the weight of the catalyst had returned to its original value. The catalyst was then cooled to room temperature and the 1 : 3 $N_2 + H_2$

* In our opinion¹¹ relation (4) is only an empirical rule, which in first approximation gives a description of simultaneous nitrogen+hydrogen adsorption on iron and is not based on the fact that hydrogen will fully occupy the free sites in simultaneous adsorption with nitrogen. However, we chose this relation for our calculations because it has an experimental basis. With a singly promoted catalyst, Brunauer and Emmett¹⁵ found that previous chemisorption of nitrogen increased the subsequent hydrogen chemisorption by 30-50 %; this result was obtained, however, with a sample containing 10.2 % Al_2O_3 .

mixture was led past the catalyst at a space velocity of 200 h^{-1} .* Next the sample was rapidly brought to the desired reaction temperature (248.8°C) and the weight increase ΔG and the synthesis rate $d(\text{NH}_3)/dt$, as functions of time were registered (see fig. 1). Fig. 2 gives an example of an analogous experiment at 210°C .

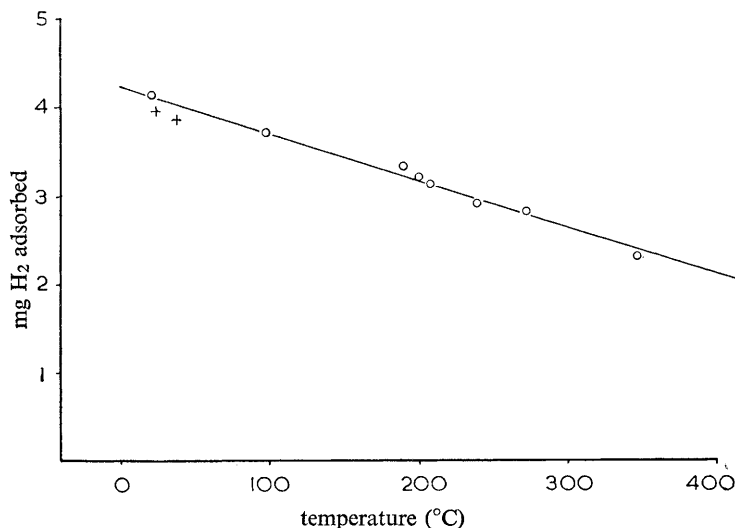


FIG. 3.—Hydrogen chemisorption isobar at 56 cm Hg pressure on a highly reduced, singly promoted iron catalyst. Total surface area 350 m^2 ; O, first measurement; +, second measurement.

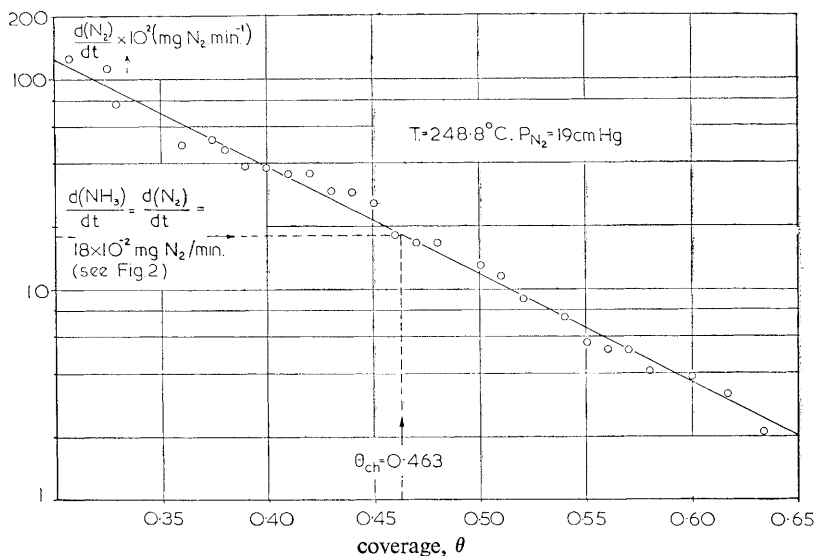


FIG. 4.—Chemisorption rate of nitrogen as a function of coverage, on a semilog scale. $T = 248.8^\circ\text{C}$; $P_{\text{N}_2} = 19 \text{ cm Hg}$.

Fig. 4 shows the method used for finding θ_{ch} ; i.e. the coverage at the point where the final, constant, ammonia synthesis rate is equal to the nitrogen chemisorption rate.

The result of all experiments are listed in table 1.

* The space velocity is defined as in ref. (10).

DISCUSSION

From table 1, for experiments above 200°C (rows no. 3-7 incl.) the agreement between θ_s and θ_{ch} is satisfactory, the deviations being within the experimental error. The results of all experiments performed far from equilibrium are a direct proof that the nitrogen chemisorption rate determines the rate of the synthesis reaction. Expt. 6 and 7 were made slightly closer to equilibrium conditions; the efficiencies η of the synthesis reaction, given in column 11 of table 1, reaches values of about 10 %. From Temkin's theory it follows that

$$v_{decomp}/v_{synth.} = \eta^2,$$

so that this ratio equals 0.8 % for expt. 6 and 1.7 % for expt. 7. These ratios are in very good agreement with the ratios

$$v_{desorption}/v_{adsorption} = 0.9 \% \text{ and } 2.2 \%,$$

calculated from the chemisorption experiments¹⁰ at the pressures and coverages used in expt. 6 and 7. These experiments also prove that the rates of the synthesis and decomposition of ammonia are determined by the rates of ad- and desorption of nitrogen.

There is yet another way to calculate the coverage during synthesis. The Temkin theory²⁰ assumes that during synthesis all reaction stages are in equilibrium with one another, with the exception of the nitrogen chemisorption. If this assumption is right, it follows that²⁰

$$P_{N_2}^* = K^{-1} P_{NH_3}^2 / P_{H_2}^3, \quad (5)$$

where $P_{N_2}^*$ = the fugacity of the chemisorbed nitrogen,

K is equal to the equilibrium constant of the gas equilibrium, and

P_{H_2} and P_{NH_3} are the hydrogen and ammonia pressures during synthesis respectively.

With the efficiency of the reaction defined as

$$\eta = P_{NH_3} / P_{NH_3, \text{equil.}},$$

(5) rearranges to

$$P_{N_2}^* = \eta^2 P_{N_2} (1-x)^4 \text{ atm}, \quad (6)$$

where x is the NH_3 mole fraction in the 1:3 $N_2 + H_2$ equilibrium mixture.

By substituting the calculated value of $P_{N_2}^*$ in the isotherm equation for the synthesis temperature, found by equalizing the equations describing the adsorption and desorption kinetics,¹⁰ we should find θ_s , the nitrogen coverage during synthesis.

TABLE 1.—COMPARISON OF THE NITROGEN COVERAGE DURING SYNTHESIS (θ_s) WITH THE COVERAGE FOLLOWING FROM A CHEMISORPTION EXPERIMENT AT THE SAME TEMPERATURE AND N_2 PRESSURE (θ_{ch}) AND WITH θ_{isoth} , THE COVERAGE FOLLOWING FROM THE CHEMISORPTION ISOTHERM AND THE N_2 FUGACITY

| column no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|------------|-----------------------------------|-----------|-------------------------|-------------------------------|------------------|-----------|---------------------|-----------------|------------|---------------|----------------------|------------------------|------------------|
| row no. | surface area m ² /g | T °C | s.v. h ⁻¹ | $d(NH_3)/dt$ mg N_2 /min | ΔG mg | C mg | $(g_{H_2})_T$ mg | g_{N_2} mg | θ_s | θ_{ch} | η % | $f \cdot N_2$ cm Hg | θ_{isoth} |
| 1 | 5.24 | 64.7 | 200 | 1.5×10^{-4} | 7.44 | 0.13 | 2.00 | 5.57 | 0.16 | 0.22 | 8.2×10^{-5} | 8.0×10^{-17} | 0.15 |
| 2 | 5.24 | 165.4 | 100 | 3.4×10^{-3} | 11.53 | -0.64 | 1.51 | 9.38 | 0.27 | 0.50 | 1.1×10^{-2} | 4.8×10^{-6} | 0.27 |
| 3 | 7.14 | 210.0 | 220 | 6.5×10^{-2} | 24.20 | -1.32 | 1.48 | 21.40 | 0.44 | 0.45 | 0.25 | 6.7×10^{-5} | 0.40 |
| 4 | 5.86 | 248.8 | 200 | 1.8×10^{-1} | 20.48 | -1.51 | 1.15 | 17.82 | 0.45 | 0.46 | 1.64 | 4.0×10^{-3} | 0.47 |
| 5 | 7.14 | 275.5 | 240 | 4.8×10^{-1} | 27.35 | -1.84 | 1.16 | 24.35 | 0.51 | 0.53 | 6.17 | 6.3×10^{-2} | 0.55 |
| 6 | 5.86 | 294.9 | 200 | 4.2×10^{-1} | 23.80 | -1.79 | 0.86 | 21.14 | 0.54 | 0.52 | 9.08 | 1.5×10^{-1} | 0.57 |
| 7 | 5.86 | 294.9 | 100 | 3.0×10^{-1} | 25.89 | -1.35 | 0.73 | 23.81 | 0.60 | 0.57 | 13.00 | 2.9×10^{-1} | 0.60 |

The result of a calculation, for each of our experiments, of the coverage during synthesis by the method described above, is given in column 11, 12 and 13 of table 1. In this,

x and $P_{\text{NH}_3 \text{ equil.}}$ were taken from Haber's tables;²¹

$$P_{\text{NH}_3} = \frac{d(\text{NH}_3)/dt \text{ (cm}^3 \text{ s.t.p./min)}}{\text{flow rate of the gas (cm}^3 \text{ s.t.p./min)}};$$

$P_{\text{N}_2}^*$ (column 12) has been calculated by means of eqn. (9).

The values of θ calculated from the isotherm equation¹⁰ at the temperature of the experiment are listed in column 13 of table 1 and indicated as θ_{isoth} .

Comparing columns 9 and 13 in table 1, we see that in all experiments there was perfect agreement between θ_s and θ_{isoth} . Thus the starting assumption made in the calculation of θ_{isoth} , namely that all reaction stages were in equilibrium with one another, except for the N_2 chemisorption, was proved correct by these experiments.

The experiment listed in row no. 7 was performed at the same temperature as no. 6, but the space velocity was twice as low. In accordance with Temkin's theory, the coverage during synthesis (column 9) increases with increasing efficiency, owing to a decrease in space velocity.

The experiments listed in rows no. 1 and 2 show a discrepancy between θ_s and θ_{ch} ; in both experiments the ammonia synthesis rate was lower by a factor of about 30 compared with that expected from the chemisorption run at the same temperature and nitrogen pressure. Yet there is a good agreement between θ_s and θ_{isoth} in these experiments.

The cause of this discrepancy is not clear. It is possible that in these low-temperature experiments the nitrogen chemisorption was poisoned by the relatively large amount of hydrogen. One of the premises of the Temkin theory, namely that the nitrogen chemisorption rate is not influenced by the presence of hydrogen on the surface, is perhaps not fulfilled in this case. However, a better insight into the kinetics at low temperature requires further research.

The authors wish to express their thanks to Prof. Dr. J. H. de Boer and Dr. C. van Heerden for valuable discussions in the course of this investigation.

¹ Brunauer and Emmett, *J. Amer. Chem. Soc.*, 1934, **56**, 35.

² Zwietering and Roukens, *Trans. Faraday Soc.*, 1954, **50**, 178.

³ Kozhenova and Kagan, *J. Physic. Chem. U.S.S.R.*, 1940, **14**, 1250.

⁴ Romanushkina, Kiperman and Temkin, *J. Physic. Chem. U.S.S.R.*, 1953, **27**, 1181.

⁵ Taylor and Jungers, *J. Amer. Chem. Soc.*, 1935, **57**, 660.

⁶ Enomoto and Horiuti, *J. Res. Inst. Cat. Hokkaido Univ.*, 1953, **2**, 87.

⁷ Bokhoven, Gorgels and Mars, *Trans. Faraday Soc.*, 1959, **55**, 315.

⁸ Scholten and Zwietering, *Trans. Faraday Soc.*, 1957, **10**, 1363.

⁹ Hersch, *Nature*, 1952, **169**, 792.

¹⁰ Scholten, Zwietering, Konvalinka and de Boer, J. H., *Trans. Faraday Soc.*, 1959, **55**, 2166.

¹¹ Scholten, *Thesis* (Delft, 1959).

¹² Dew and Taylor, *J. Physic. Chem.*, 1927, **31**, 277.

¹³ Kwan, *J. Res. Inst. Cat. Hokkaido Univ.*, 1957, **4**, 207.

¹⁴ Beeck, *Advances in Catalysis* (Academic Press Inc., New York, N.Y.), vol. 2, p. 177.

¹⁵ Brunauer and Emmett, *J. Amer. Chem. Soc.*, 1940, **62**, 1732.

¹⁶ Beeck, *Advances in Catalysis*, vol. 2, p. 181.

¹⁷ Emmett and Harkness, *J. Amer. Chem. Soc.*, 1953, **57**, 1631.

¹⁸ Podgurski and Emmett, *J. Physic. Chem.*, 1953, **57**, 164.

¹⁹ Schuit and de Boer, N. H., *Rec. trav. chim.*, 1951, **70**, 1067.

²⁰ Temkin and Pyzhev, *Acta physicochim.*, 1940, **12**, 327.

²¹ Haber, Gmelin's *Handbuch der Anorganischen Chemie*, 1936, **4**, 320.