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FIELD-EMISSION MICROSCOPIC OBSERVATION OF CATALYZED AMMONIA SYNTHESIS ON TUNGSTEN

By

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Abstract

Catalyzed ammonia synthesis on tungsten was investigated by means of field-emission microscope. Nitrogen, hydrogen, a mixture of nitrogen and hydrogen, and ammonia were severally allowed to be adsorbed on tungsten tip at liquid nitrogen temperature under a pressure gradually increased from 10^{-9} to 10^{-7} mmHg and then decreased by evacuation. After the beginning of the evacuation the tip was subjected to intermittent heat treatments at temperature successively raised from 500° to 3000°K. Field-emission pattern and the associated change of average work function of the tip were observed in course of adsorption as well as after each of the subsequent intermittent heat treatments.

The results were as follows: (i) The mixture of nitrogen and hydrogen gave the characteristic pattern of adsorbed nitrogen atoms, that of adsorbed hydrogen atoms or a superposition of the both. The presence of hydrogen accelerated the dissociative adsorption of nitrogen on tungsten as indicated by a rapid development of the characteristic pattern of adsorbed nitrogen atoms in this case. (ii) The pattern of ammonia did not give the characteristic of the adsorbed nitrogen atoms but that of hydrogen atoms. Besides, the pattern has shown a characteristic, from the period of the maximum pressure mentioned above as far as that of the heat treatment at 1700°K, which was distinguishable from either of the characteristics of adsorbed nitrogen and hydrogen atoms and accompanied by a decrease of the average work function; this result was adequately accounted for as due to the formation of adsorbed imino and/or amino radicals.

From these results it was concluded that the rate-determining step of the catalyzed ammonia synthesis was the formation either of these intermediates, *i. e.*

$$N(a) + H(a) \longrightarrow NH(a),$$
$$NH(a) + H(a) \longrightarrow NH_2(a),$$

but not the dissociative adsorption of nitrogen.

Introduction

Heterogeneous reaction on catalyst surface may be directly observed by means of the field-emission microscope technique*),1),2). Only a few investigations

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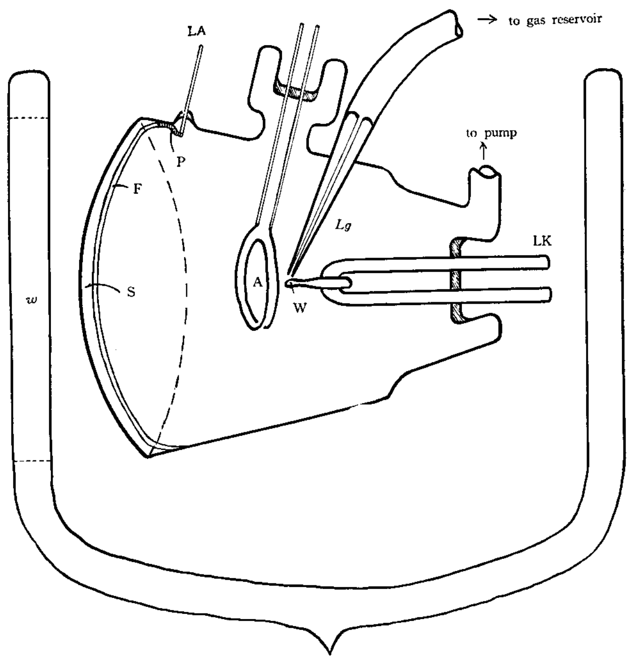
*) The field-emission microscopy was invented by E. W. MÜLLER in 1937 and developed by himself and others incorporated with recent ultra high vacuum techniques.

are reported3),4), however, notwithstanding powerful potentialities of this method, which might be due to the difficulties in stabilizing and identifying the field-emission patterns.

The present paper is concerned with an attempt to elucidate the mechanism of the ammonia synthesis on tungsten catalyst by this method. Clean surface of tungsten tip was allowed to adsorb nitrogen, a mixture of nitrogen and hydrogen, hydrogen and ammonia severally in four series at liquid nitrogen temperature and then in each series subjected, under evacuation, to intermittent heat treatments at successively elevated temperature. Observations were made simultaneously on the field-emission pattern and the average work function along with initial rise and subsequent fall of pressure around the tip as well as following the heat treatments.

The characteristic pattern of clean tungsten surface identifiable with that given by MÜLLER5) was reproduced with one and the same tip before every series by ultra high vacuum technique employed, hence it was admitted that the geometry of the point of the tip remained unchanged throughout the experiments. On this basis the conclusions were drawn from the experimental results obtained as above on the mechanism of the catalyzed reaction in question.



W : Tungsten tip.
A : Anode ring.
S : Screen.
F : Aluminum-backing.
P : Platinum foil.
LA : Screen lead.
LK : Tungsten loop.
Ig : Gas-inlet capillary.
w : Window of the Dewar vessel.

Fig. 1. Schematic diagram of the field-emission tube.

Chapter I. Experimental

§ 1. Field-emission microscope assembly

Fig. 1 shows the field-emission tube or the cell. The phosphorescent screen S of Zn_2SiO_4 : Mn was backed with evaporated aluminum film F and connected with the high voltage tungsten lead LA by a platinum foil P covered by the extension of F. The anode ring A of *ca.* 1.5 cm diameter was a coil of 0.2 mm thick tungsten wire mounted between the screen S and the tip W, with its centre *ca.* 5 mm apart from the tip. The tip was prepared by electrolytic etching of 0.15 mm diameter tungsten wire by 1~10 V ac in 10 g/l solution of NaOH[2]. The radius of curvature of the tip was estimated at $3\sim5\cdot10^{-5}$ cm by an optical microscope and coincidently by an empirical relation of DRECHSLER and HENKEL[6,7]. The tip was spotwelded to a 0.3 mm diameter tungsten loop LK of *ca.* 6 cm length, which served as the lead as well as the electric heater of the tip.

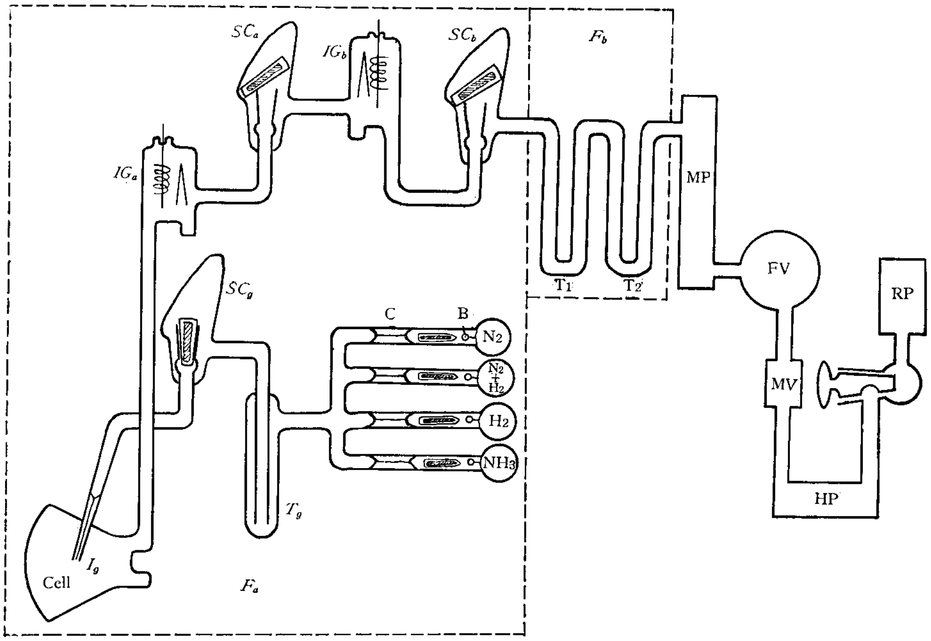


Fig. 2. Vacuum apparatus.

RP: Rotary pump. HP: Hickman pump. MV: Metal valve.
FV: Forevacuum. MP: Mercury-diffusion pump.
T_1, T_2 and T_g: Traps. SC_a, SC_b and SC_g: Greaseless stop-cocks.
F_a and F_b: Furnaces. IG_a and IG_b: B-A type ionization gauges.
I_g: Gas-inlet capillary. C: Capillary. B: Breakable joint.
N_2, N_2+H_2, H_2 and NH_3: Gases in gas-reservoirs.

§ 2. Vacuum apparatus

Fig. 2 shows the apparatus schematically, which consists of a rotary pump RP, a HICKMAN type oil-diffusion pump HP, a forevacuum FV, a mercury-diffusion pump MP*), [8], two traps T_1 and T_2 and two BAYARD-ALPERT type ionization gauges IG_a and IG_b[9]. Surface contaminations were eliminated as far as possible by ultra high vacuum techniques[9] accompanied by electric heating or electron bombardment of metallic parts of the cell and baking out of the glass walls at about 350°∼400°C in furnaces F_a and F_b for 10 hours or more. After the repetition of the above treatments a pressure of the order of 10^{-7} mmHg was attained in the apparatus, as mercury vapour was trapped by means of T_1 and T_2.

The evacuated apparatus was now shut off from the oil-diffusion pump HP by a metal high vacuum valve MV[9]. The preceding treatments for evacuation of the cell were further carried out with T_1 and T_2 immersed in liquid nitrogen until the pressure in the system attained to the order of 10^{-8} mmHg, while both the tip and the anode ring were kept at red heat. Greaseless stop-cocks SC_a and SC_b were now closed and the pressure was reduced to $2 \cdot 10^{-9}$ mmHg by the well-known pumping action beside the pressure indicating function of the ionization gauges (IG_a and IG_b).

§ 3. Preparation of gases

Nitrogen : sodium azide was heat-decomposed. The gas was passed through liquid nitrogen traps and stored in a flask.

Hydrogen : electrolytically prepared hydrogen was passed through an electrically heated palladium thimble and stored in a flask.

Ammonia : chemically pure concentrated aqueous solution of ammonia was fractionally distilled several times in vacuum from −30°C to −195°C and dry ammonia thus prepared was stored in a flask.

The three flasks, containing thus purified gases, were now set to a separate vacuum system comprising four reservoirs each of 10 cc capacity provided each with a breakable joint, and preliminarily baked out in high vacuum. Nitrogen, hydrogen, 1 : 5 mixture of nitrogen and hydrogen, and ammonia were now filled respectively in the reservoirs at about $10^{-3}\sim10^{-4}$ mmHg pressure, through liquid nitrogen trap for the former three gases and dry ice trap for the last one. The gas reservoirs thus filled were connected to the high vacuum system mentioned above each by a breakable joint B and a capillary C, as shown in

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*) Dr. Y. MIZUSHIMA, Elec. Communication Lab., Nippon Telegraph and Telephone Public Corp., has kindly bestowed the pump elaborated by himself on the present author.

Fig. 2, before the ultimate high evacuation of the cell described in §2 was carried out.

§4. High tension source

The high tension source is stable to about 50 parts per 10^4. The anode pole of the circuit and both the leads from the anode ring A and the screen S were earthed. Cathodic voltages of $3\cdot10^3\sim10^4$ V were applied to the tip through the tungsten loop LK against the anode ring[*]. The field-emission current was regulated manually at 10 μA.

§5. Procedure of measurements

The whole cell was immersed in liquid nitrogen. Field-emission patterns were observed through an unsilvered window of the Dewar vessel shown in Fig. 1 and photographically recorded by Nikon F camera with a lens of Nikkor, 5 cm f : 2, and Fuji tri-S film. Trouble of fog or dew on the window was fairly well avoided by spraying alcohol upon it.

Four series of experiments were conducted in turn respectively with nitrogen, 1 : 5 mixture of nitrogen and hydrogen, hydrogen and ammonia.

The experiment of each series was started by introducing gas into the cell, when the cell had been sufficiently outgassed until the pattern of Plate No. 8, Series 1[**], which was identified with that of clean tungsten surface as observed by MÜLLER[5], was steadily visible at least for 10 minutes running without any change of applied voltage for 10 μA field-emission current; Fig. 3 shows the appropriate map of MILLER indices of principal single crystal faces of a clean tungsten tip[***]. The gas was introduced into the cell by opening

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[*] *Cf.* Fig. 1.

[**] *Cf.* §8.

[***] Point of a tip of field-emission microscope consists practically of a single crystal, inasmuch as the point is much smaller than the average grain size of the crystallites, of which the tip is composed. Closely packed faces have now higher work functions than loosely packed ones [Ref. 10]. The difference of the work function results in that of emission from the respective faces giving rise to a pattern on the screen of a field-emission microscope. Principal crystal faces of tungsten tip surface can readily be identified each by the symmetry of its brightness as well as by its angular separation on the pattern, assuming a semispherical surface of the point of the tip. It was thus found in the present experiment that the (011)-face was just at the zenith of the semisphere. The work functions of the principal crystal faces of tungsten are given by MÜLLER [Ref. 11] as below;

face	(116)	(013)	(012)	(122)	(111)	(233)	(123)	(001)	(112)	(011)
work function (eV)	4.30	4.31	4.34	4.35	4.39	4.46	4.52	4.52†	4.65 ~4.88	5.70 ~5.99

†) The value reported by SMITH [Ref. 12].

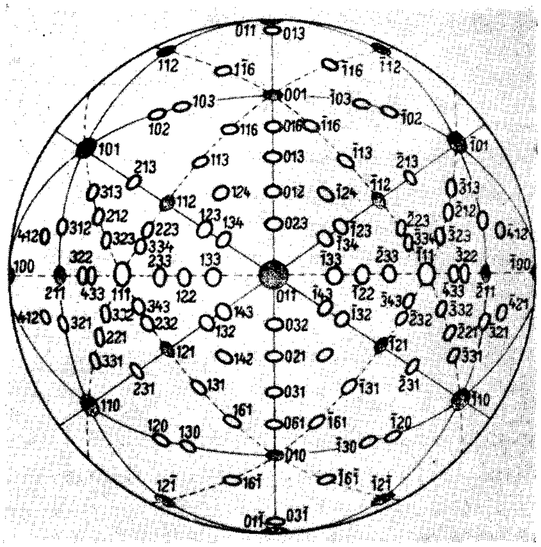

Fig. 3. Orthographic projection of hemispherical tungsten tip, body-centered cubic structure, with (011) in the axis (by MÜLLER [Ref. 5]).

the breakable joint B attached to the gas reservoir through the trap Tg in Fig. 2 immersed in liquid nitrogen (N_2, N_2+H_2 and H_2) or in dry ice (NH_3). The gas leaked through the greaseless stop-cock SC_g and effused from the capillary I_g, pointing at the tip W *ca.* 5 mm clear of it, into the cell. The gas thus expanded from the volume of 10 cc of the reservoir into that of about one litre. Changes of the field-emission pattern, the average work function*) and pressure were now followed simultaneously with time.

The pressure as observed by ionization gauge IG_a attained a maximum value $10^{-6}\sim10^{-7}$ mmHg about $20\sim80$ minutes after the start and then decreased gradually, inasmuch as gas cleaned up by the ionization gauges IG_a and IG_b and leaked out through the greaseless stop-cocks SC_a and SC_b. The cell was now pumped off by means of the mercury-diffusion pump through the greaseless stop-cocks SC_a and SC_b now opened. In course of pumping, the tip was subjected, by heating tungsten loop LK electrically, on which the tip was mounted, to intermittent heat treatments without high tension applied meanwhile, each followed by observations of the field-emission pattern, the average work function and the pressure while the cell kept at liquid nitrogen temperature. Temperature of the heat treatment was determined from the heating current preliminarily calibrated against the temperature observed by the optical pyrometer

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*) *Cf.* § 6, (c).

at the apex of the loop LK.

§ 6. Remarks on measurements

(a) The pressure was measured by the ionization gauge IG_a*), which was situated remote from the cell as shown in Fig. 2 and left at room temperature. The measured pressure may hence differ from that around the tip, especially in the case of the gas mixture or ammonia, where synthesis or decomposition might occur in the ionization gauge.

(b) Measured temperatures of the tip at heat treatments were not corrected for such factors as the emissivity of tungsten, the end-cooling effect and others. The temperature was observed in the calibration mentioned in § 5 with a fluctuation of about 50°K at the apex of tungsten loop LK by means of the optical pyrometer.

(c) The average work function of the tip surface was determined by the approximate form3) of the FOWLER-NORDHEIM equation1),13)

$$e\varphi = e\varphi_W (V/V_W)^{2/3} \text{ eV},$$

where V or V_W was the applied voltage (Volts) observed at common emission current (10 μA) respectively with or without adsorbate on the tip surface and $e\varphi$ or $e\varphi_W$ the relevant average work function. The $e\varphi_W$ was taken to be 4.50 eV7).

Chapter II. Results

§ 7. Presentation of results

Fig. 4 illustrates the simultaneous variations of the average work function and of pressure with time throughout the whole course of the respective series by points numbered the same as photographs of the field-emission patterns taken respectively at the points.

Results of the four series are summarized respectively in the Table 1~4 and commented upon in later sections.

§ 8. Nitrogen (Series 1)

No particular change of the pattern was observed by adsorption from Plate No. 8 of clean surface to Plate No. 16. The width of the dark (011)-region then became narrower towards the direction of the (001)-(011) zone as seen from Plates

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*) The B-A type ionization gauge was operated at the condition that the potentials of anode and filament were kept respectively at +200 and +45 volts against the ion collector and the electron current was maintained at 1 mA.

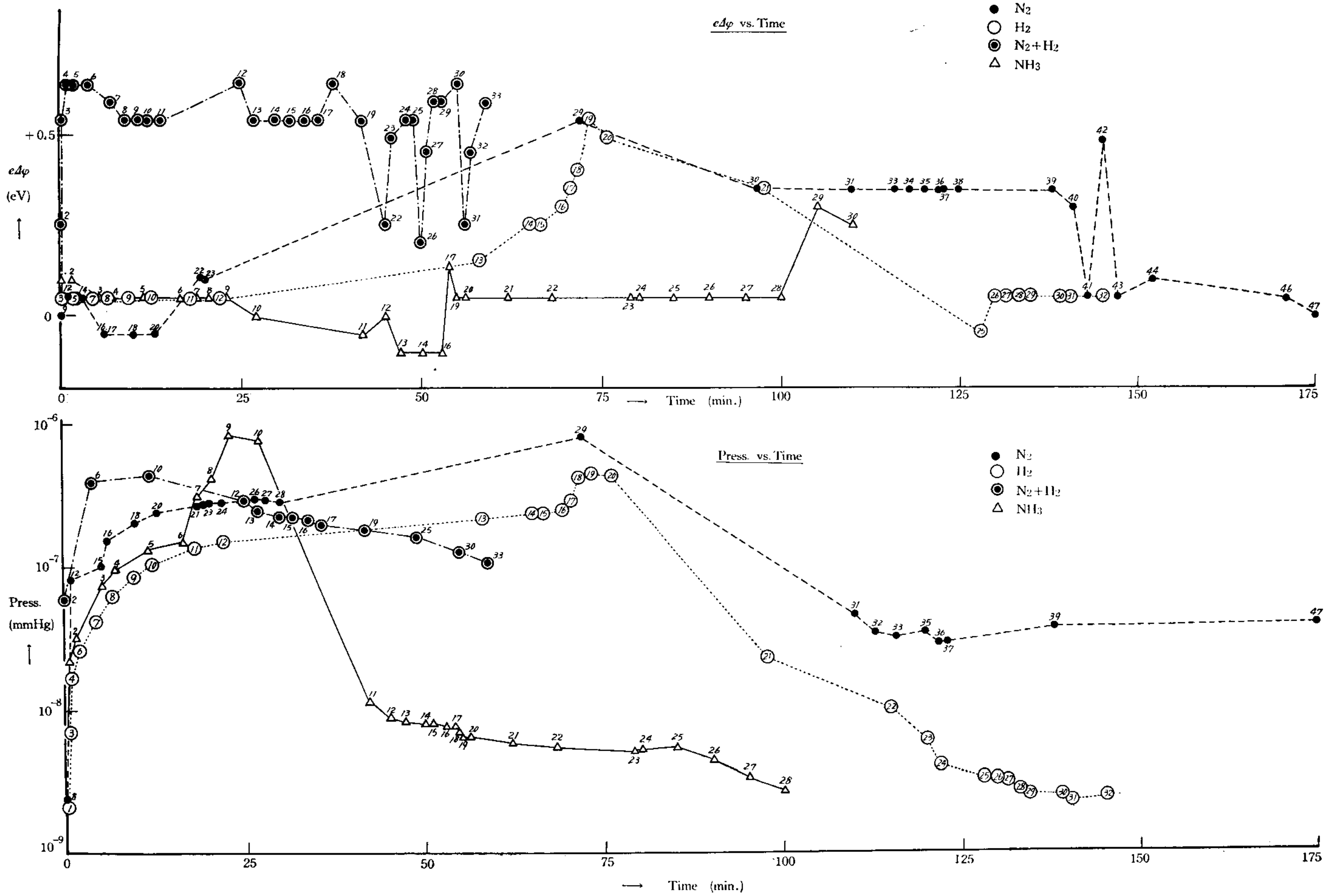


Fig. 4. Simultaneous variations of average work function and of pressure with time.

TABLE 1. (Nitrogen, Series 1)

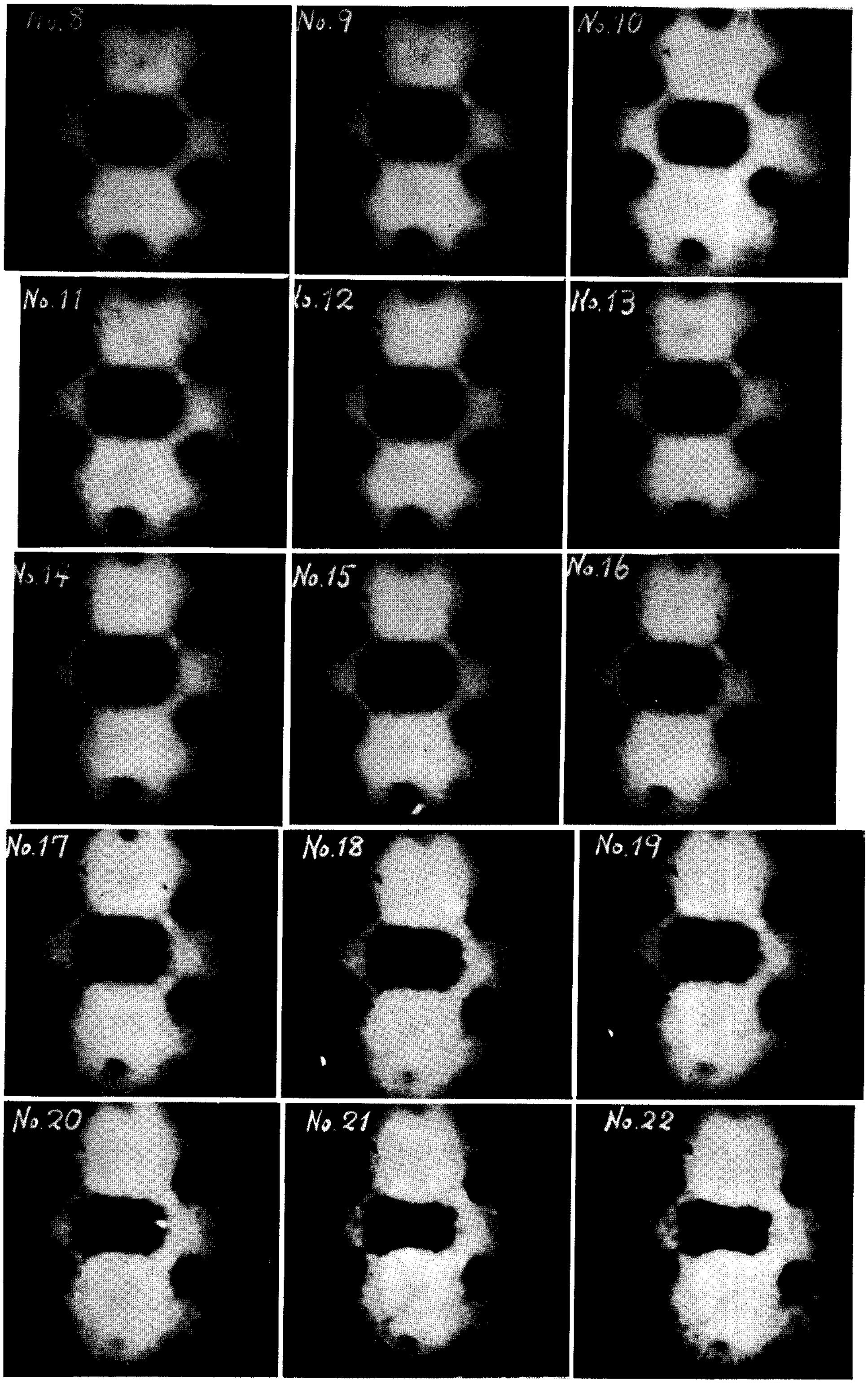
Points	Time (min.)	Press. (mmHg) $\times 10^{-8}$	Applied voltages (volts) $\times 10^{3}$	Behaviour of emission current	Condition of heat treatments	Remarks
No. 8	0	0.23	5.9	stable		before the introduction of N_2, clean surface
No. 9	15 sec.		5.9			after the introduction of N_2
No. 10			5.9			
No. 11			5.9			
No. 12	1	8	6.0	rather decreasing		
No. 13			6.0			
No. 14	3		6.0			
No. 15			6.0			
No. 16	6	15	5.8	rather increasing		
No. 17			5.8			
No. 18	10	20	5.8			
No. 19			5.8			
No. 20	13	24	5.8			
No. 21	18.5	27	6.0*) (9.8μA)			
No. 22	19	27	6.1	unstable, rather decreasing		
No. 23	20	28	6.1			
No. 24	22	29	6.1*) (7.4μA)	decreasing		
No. 25	25	30	6.1*) (5.6μA)			
No. 26	26	30	6.1*) (5.2μA)			
No. 27	28	30	6.1*) (4.6μA)			
No. 28	30	29	6.1*) (4 μA)			
No. 29	72	80	7.0			
No. 30	97		6.6			
No. 31	110	4.5	6.6			immediately after the beginning of evacuation
No. 32	113	3.4	6.6 (9.6μA)			
No. 33	116	3.2	6.6		500°K., 1 min.	

Points	Time (min.)	Press. (mmHg) $\times 10^{-8}$	Applied voltages (volts) $\times 10^3$	Behaviour of emission current	Condition of heat treatments	Remarks
No. 34	118		6.6		900°K., 1 min.	
No. 35	120	3.4	6.6		1100°K., 1 min.	
No. 36	122	3.0	6.6		1300°K., 1 min.	
No. 37	123	3.0	6.6		1430°K., 1 min.	
No. 38	125		6.6		1550°K., 1 min.	
No. 39	138	3.8	6.6	unstable increasing	1550°K., 12 more min.	
No. 40	141		6.5		1550°K., 12 more min.	
No. 41	143		6.0	unstable	1700°K., 1 min.	immediately after the sudden change of pattern
No. 42	145		6.9	unstable	1700°K., 1 more min.	
No. 43	147		6.0	stable	1700°K., 1.5 more min.	
No. 44	152		6.1		1700°K., 4 more min.	
No. 45	169				1700°K., 16 more min.	
No. 46	171		6.0		1800°K., 1 min.	
No. 47	177	4	5.9		1800°K., 5 more min.	
No. 48	298	4.2			1800°K., 2 hrs.	
No. 49	300					
No. 50	305		6.0		3000°K., 10 sec.	
No. 51	307	2.6	6.0		2050°K., 1 min.	
No. 52	313				2050°K., 5 more min.	
No. 53	319	2.1	6.0		3000°K., 10 sec.	
No. 54	324	2.6				

*) The field-emission current was accidentally not being controlled at 10 μA, of the value given in the parenthesis.

No. 21～31. The average work function, on the other hand, increased initially by *ca.* 0.05 eV (Points No. 12～15) but decreased after a few minutes by *ca.* 0.1 eV from the latter value (Points No. 16～20). It then increased up to the maximum value *ca.* 0.55 eV above the initial value as seen from Fig. 4 (Point No. 29). The maximum increase of the average work function is in good agreement with that 0.50 eV14) observed by MIGNOLET.

N_2 (Series 1)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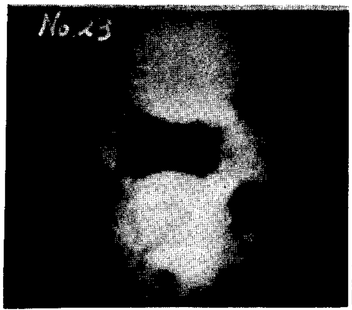
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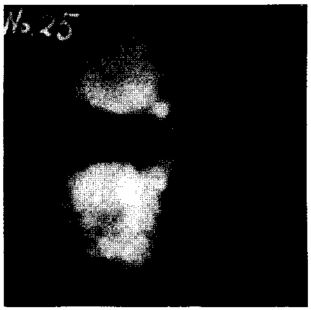
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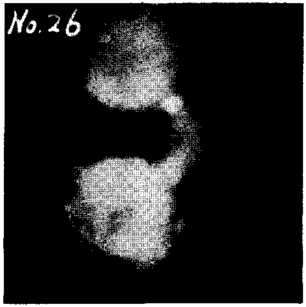
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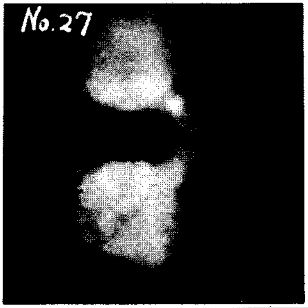
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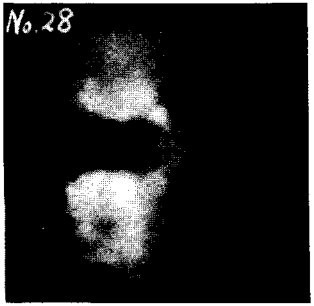
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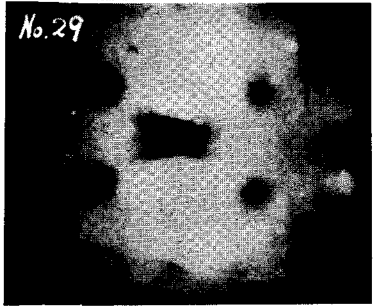
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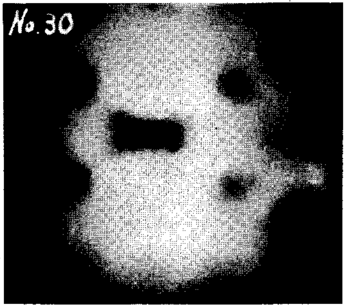
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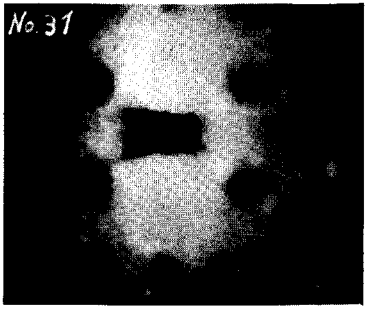
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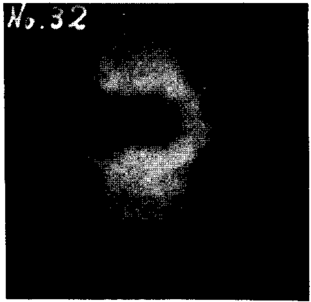
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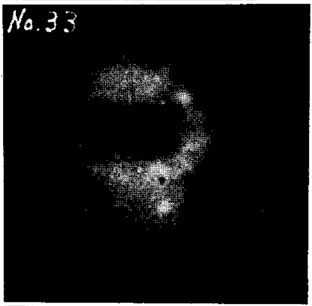
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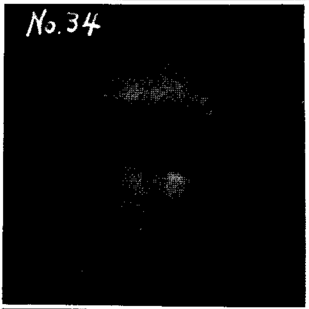
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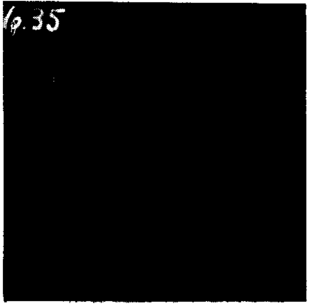
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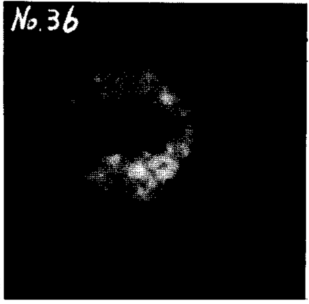
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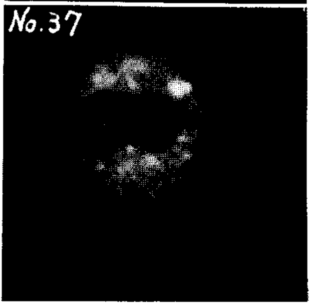
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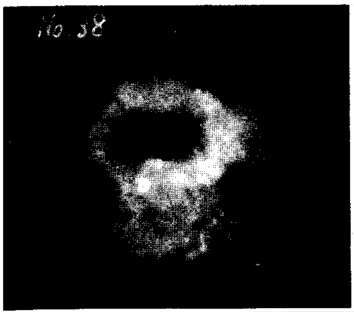
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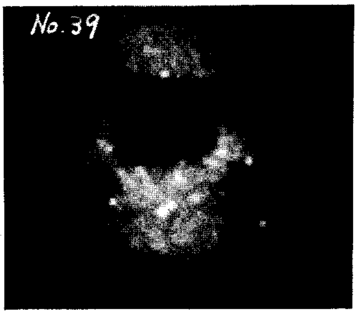
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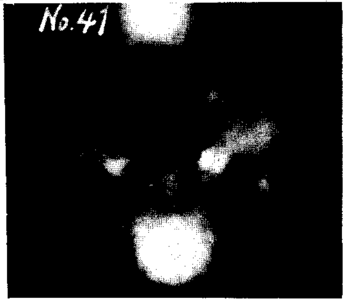
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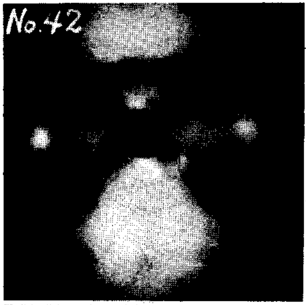
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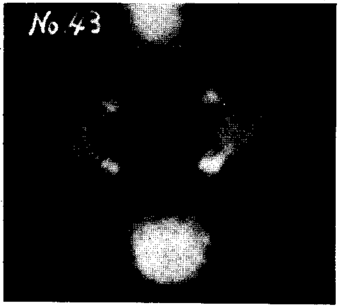
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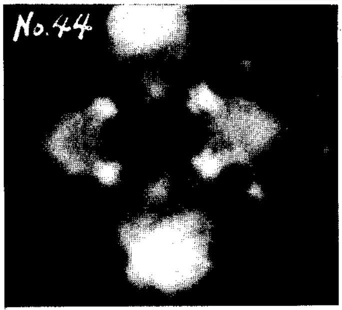
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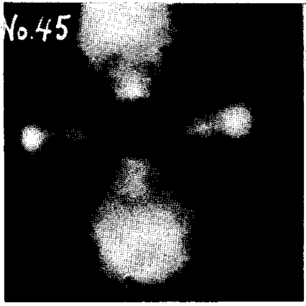
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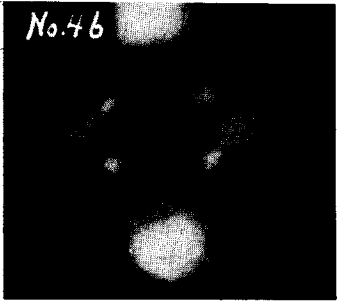
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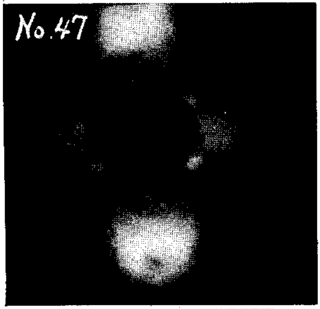
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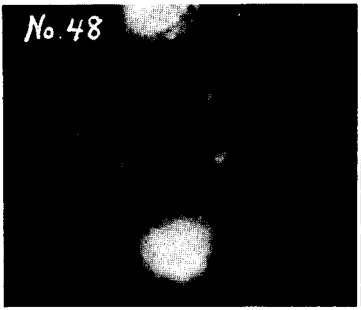
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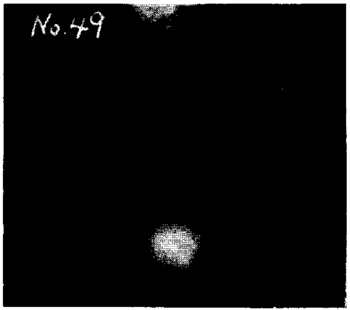
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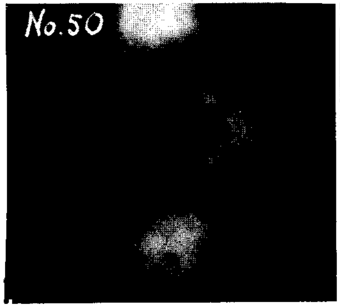
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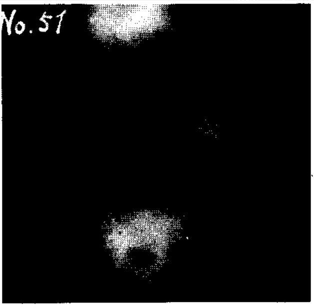
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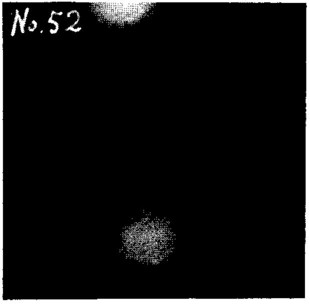

No.52

The average work function decreased then gradually as far as *ca.* 0.2 eV below the maximum value along with decrease of pressure until the point No. 30. The average work function then kept constant until after the heat treatment at 1700°K as seen from Fig. 4 (Points No. 30~40).

After the heat treatments at 1100°~1550°K bright spots were observed to migrate over the whole surface (Plates No. 35~40). The heat treatment at 1700°K changed the pattern altogether as seen from Plate No. 41, simultaneously decreasing the average work function by *ca.* 0.25 eV (Point No. 41). The subsequent heat treatments at higher temperatures, the above heat treatment as well, somewhat darkened the regions situated on the (001)-(011) zone such as (012)- and (013)-regions as compared with the surroundings of the (001)-region as seen from Plates No. 41 and 43 to 52, and remarkably brightened the (111)-region as seen from Plates No. 42, 45 and 52 while the average work function violently fluctuated. The former group of patterns has common characteristic of the bright surroundings of the (001)-region whereas the latter group that of the bright (111)-region.

§ 9. A 1 : 5 nitrogen-hydrogen mixture (Series 2)

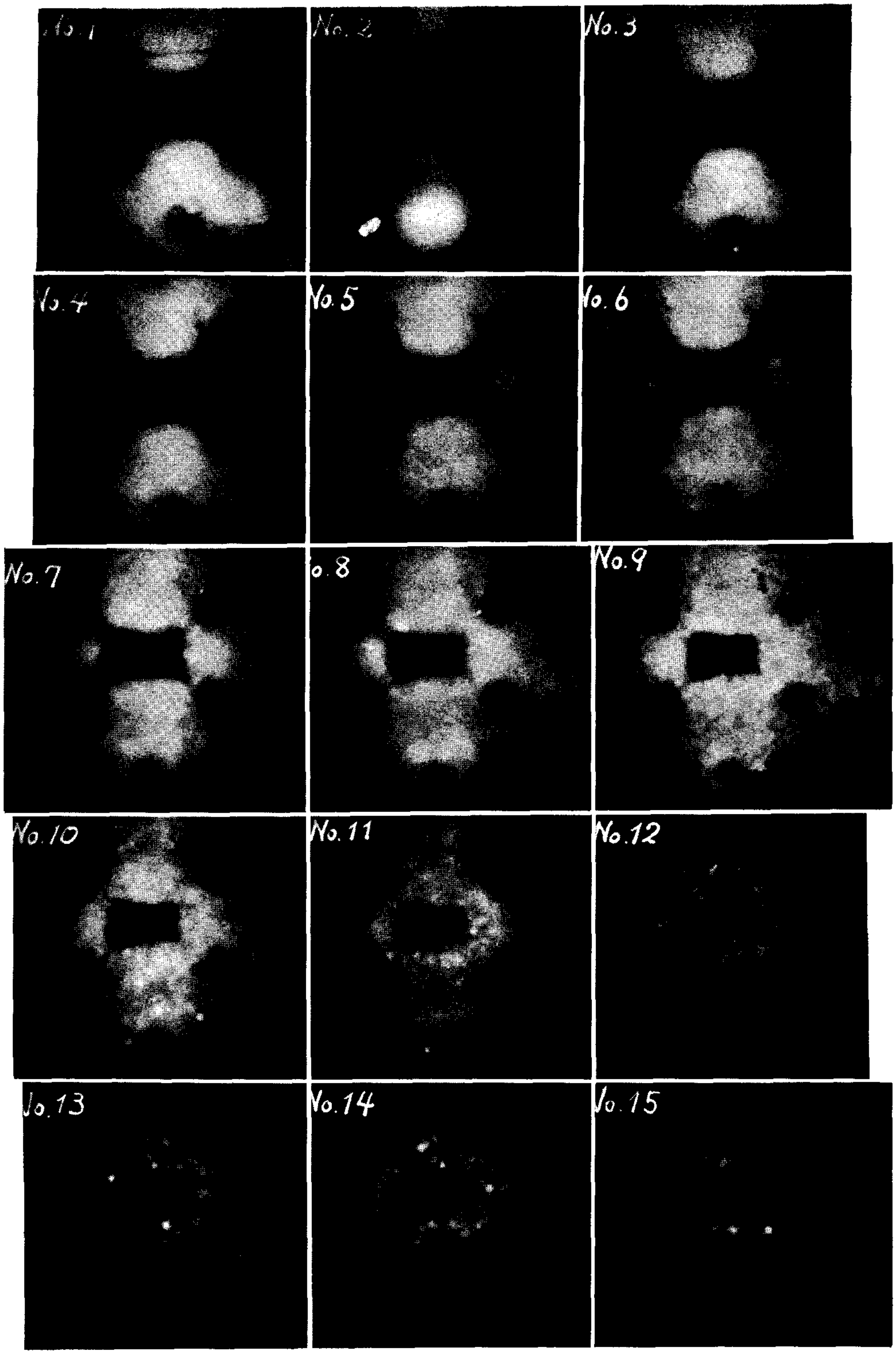
TABLE 2. (Nitrogen-Hydrogen mixture, Series 2)

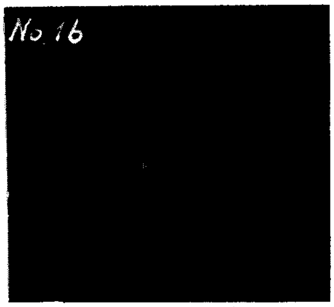
Points	Time (min.)	Press. (mmHg) $\times 10^{-8}$	Applied voltages (volts) $\times 10^3$	Behaviour of emission current	Condition of heat treatments	Remarks
No. 1	a few sec.	<6		rapidly decreased		immediately after the introduction of the gas
No. 2	a few sec.	6	6.4			*cf.* Plate No. 45, Series 1
No. 3	10 sec.		7.0			
No. 4	1		7.2			
No. 5	2		7.2			
No. 6	4	40	7.2			
No. 7	7		7.1			
No. 8	9		7.0			
No. 9	11		7.0			
No. 10	12	44	7.0			
No. 11	14		7.0			
No. 12	25	30	7.2			

Points	Time (min.)	Press. (mmHg) $\times 10^{-8}$	Applied voltages (volts) $\times 10^{3}$	Behaviour of emission current	Condition of heat treatments	Remarks
No. 13	27	24	7.0		900°K., 1 min.	immediately after the beginning of evacuation
No. 14	30	22	7.0		1100°K., 2 min.	
No. 15	32	21	7.0		1300°K., 1 min.	
No. 16	34	20.6	7.0		1430°K., 1 min.	
No. 17	36	19.7	7.0		1550°K., 1 min.	
No. 18	38		7.2		1550°K., 1 more min.	sudden change of the pattern; *cf.* Plate No. 41, Series 1
No. 19	42	18.7	7.0		1550°K., 3 more min.	*cf.* Plate No. 45, Series 1
No. 20	43			very much increased		
No. 21	44			rather increasing	1550°K., 1 more min.	*cf.* Plate No. 41, Series 1 and Plate No. 13, Series 3
No. 22	45		6.4			
No. 23	46		6.9			
No. 24	48		7.0			
No. 25	49	16.5	7.0	stable		
No. 26	50		6.3		1800°K., 30 sec.	
No. 27	51		6.8			
No. 28	52		7.05			
No. 29	53		7.05			
No. 30	55	13	7.2			
No. 31	56		6.4		1800°K., 30 more sec.	
No. 32	57		6.8			*cf.* Plate No. 45, Series 1
No. 33	59	11	7.1			

For the first few seconds the average work function increased by *ca.* 0.25 eV from the initial value, while the pattern changed from that of clean surface of Plate No. 8, Series 1 to those of Plates No. 1 and 2. The bright (122)-region and its surroundings then spread slightly toward the dark (011)-region as seen from Plates No. 4~8. After further several minutes, the migration of bright spots were observed (Plate No. 12), which survived the heat treatment at 1550°K for one minute as seen from Plate No. 17. Further heat treatment at 1550°K for one minute caused the change of pattern to that of

N_2+H_2 (Series 2)

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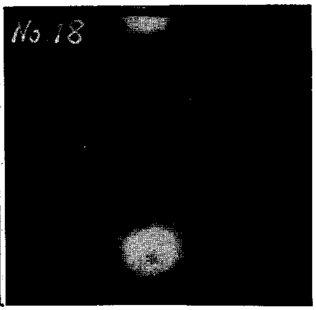
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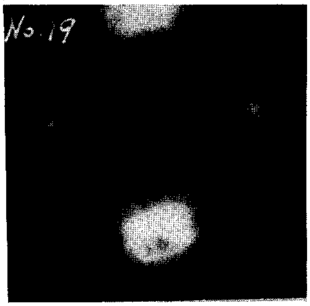
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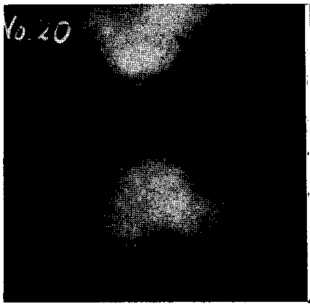
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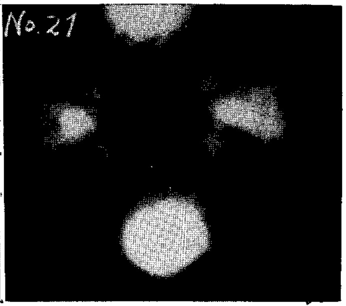
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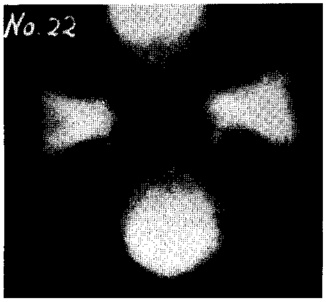
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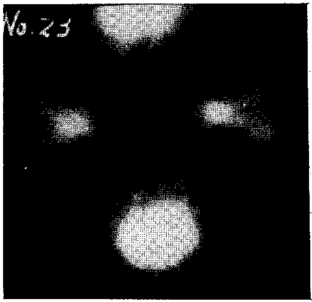
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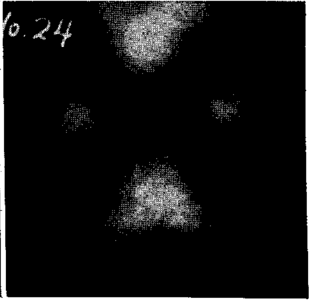
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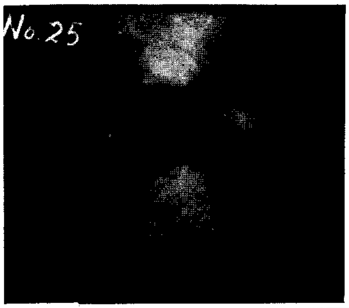
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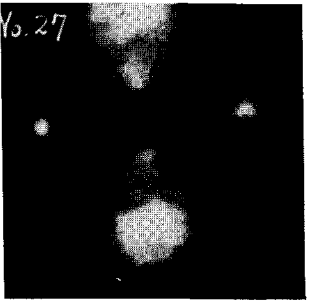
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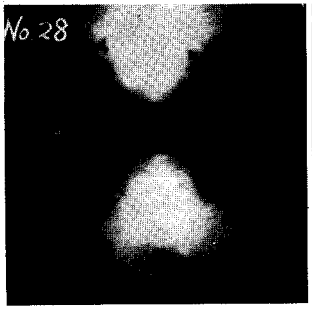
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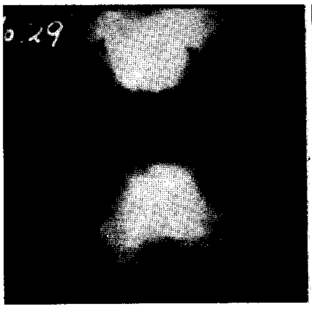
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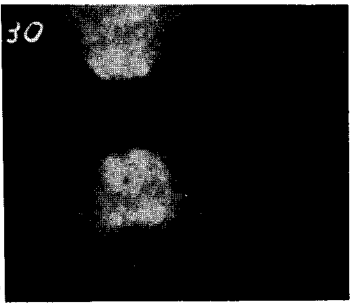
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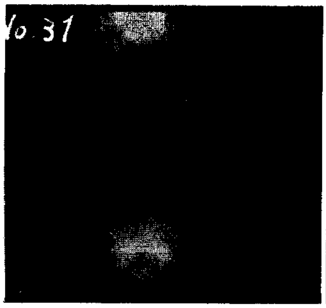
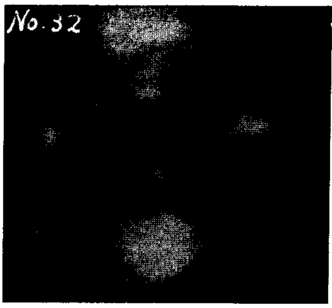




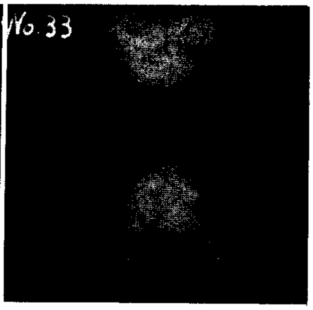


Plate No. 18, which was quite the same as that of Plate No. 41, Series 1. Subsequent changes of pattern by successive heat treatments were observed as shown by Plates No. 19, 21, 26 and 31.

§ 10. Hydrogen (Series 3)

TABLE 3. (Hydrogen, Series 3)

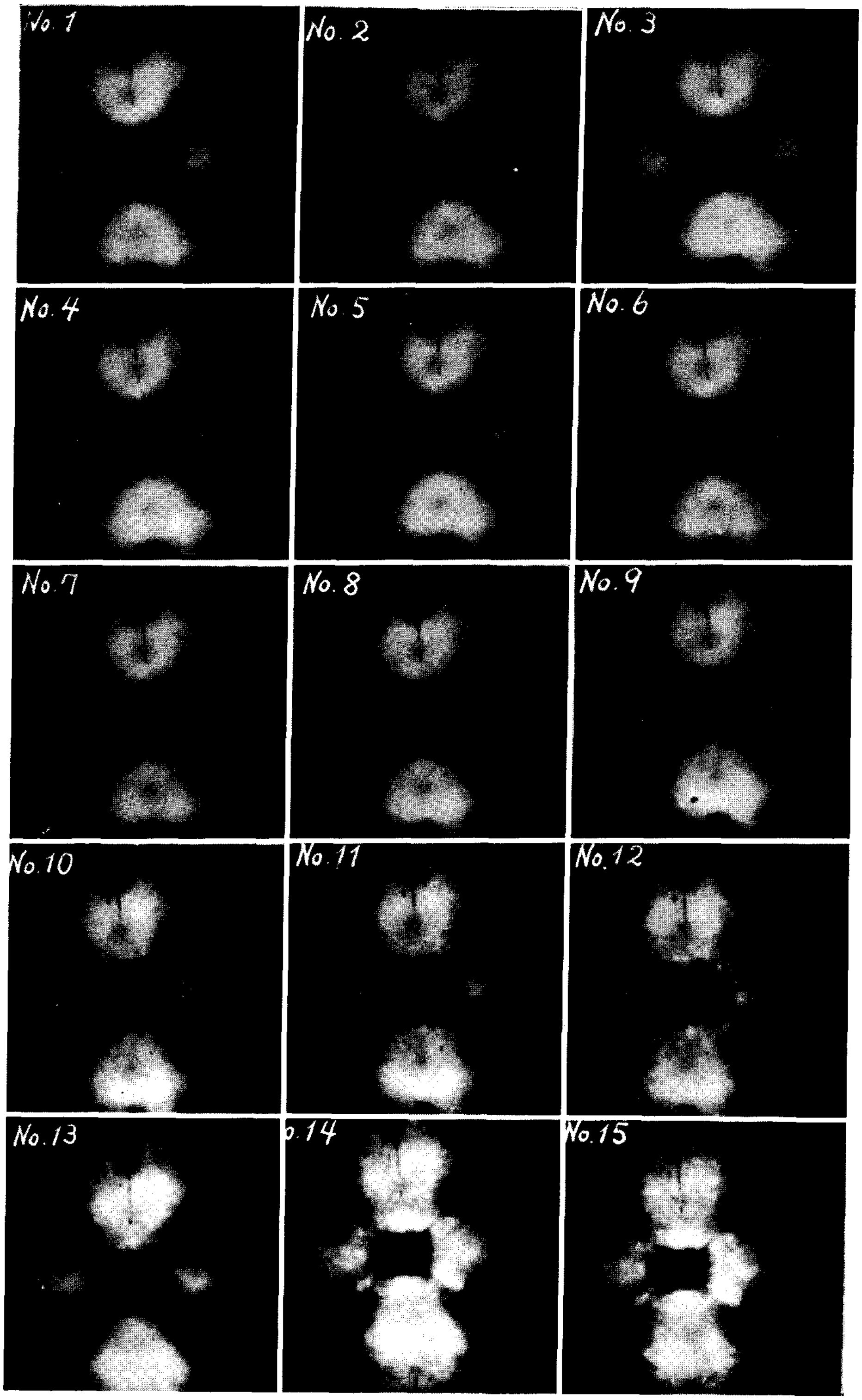
Points	Time (min.)	Press. (mmHg) $\times 10^{-8}$	Applied voltages (volts) $\times 10^{3}$	Behaviour of emission current	Condition of heat treatments	Remarks
No. 1		0.23	6.0			immediately after the introduction of H_2
No. 2	a few sec.	0.3	6.0	stable		
No. 3	40 sec.	0.7	6.0			
No. 4	50 sec.	1.7	6.0			
No. 5	1.5		6.0			
No. 6	2	2.8	6.0			
No. 7	4	4.2	6.0			
No. 8	6.5	6.3	6.0	rather increasing		
No. 9	9.5	8.8	6.0	increasing		
No. 10	12	10.6	6.0	increasing		
No. 11	18	14.5	6.0	increasing		
No. 12	22	16.5	6.0	rapidly increasing		The pattern vanished altogether after the observation of No. 12.
No. 13	58	22.5	6.2	decreasing	repeated heating at 1800°K.	The point No. 13 was observed after the restoration of the pattern.
No. 14	65	23	6.4	decreasing		

Points	Time (min.)	Press. (mmHg) $\times 10^{-8}$	Applied voltages (volts) $\times 10^3$	Behaviour of emission current	Condition of heat treatments	Remarks
No. 15	66.5	23	6.4	decreasing		
No. 16	69.5	26	6.5	decreasing		
No. 17	70	30	6.6	decreasing		
No. 18	71.5	41	6.6	decreasing		
No. 19	73	44	7.0	decreasing		
No. 20	76	43	6.9	increasing		
No. 21	97.5	23	6.6	unstable		
No. 22	115	10	6.0*) (5μA)	unstable		The evacuation started after the observation of No. 22.
No. 23	120	0.6	6.0*) (5μA)	unstable	1300°K., 2 min.	
No. 24	122	0.4	5.8*) (5μA)		1550°K., 1.5 min.	
No. 25	128	0.33	5.8		1800°K., 5 min.	*cf.* Plate No. 1, this series and No. 19, Series 4
No. 26	130	0.32	6.0	decreasing	1800°K., 1 more min.	
No. 27	131	0.31	6.0	decreasing	2050°K., 50 sec.	
No. 28	133	0.29	6.0	stable	2100°K., 1 min.	
No. 29	134	0.28	6.0	decreasing	2500°K., 30 sec.	
No. 30	139	0.27	6.0	decreasing	3000°K., 10 sec.	
No. 31	140	0.24	6.0	stable	1800°K., 10 min.	
No. 32	145	0.25	6.0	stable	3000°K., 10 sec.	
No. 33			6.0	stable		
No. 34			6.0	stable		

*) The field-emission current was accidentally not being controlled at 10 μA, of the value given in the parenthesis.

As soon as hydrogen was introduced into the cell, the pattern changed from Plate No. 8, Series 1 of clean surface to Plate No. 1, while the average work function increased from the initial value by *ca.* 0.05 eV. No particular change was observed up to Plate No. 12, where the bright region spread just perceptibly toward the dark (011)-region along the (111)-(011) zone. After the observation of Plate No. 12, several bright spots appeared twinkling and gamboling over the pattern. The field-emission current increased now extraordinarily

H_2 (Series 3)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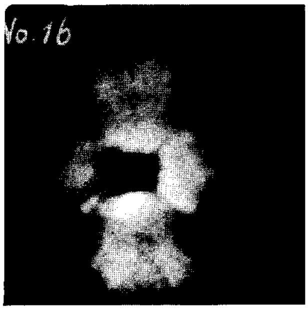
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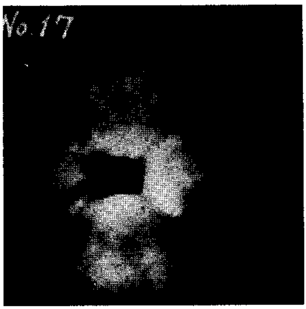
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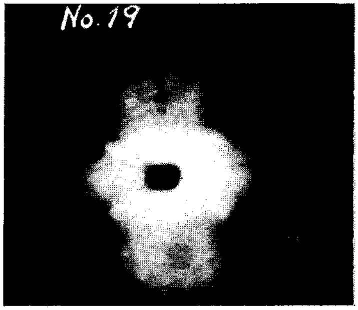
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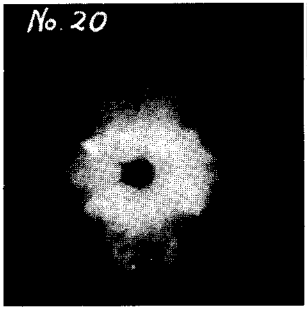
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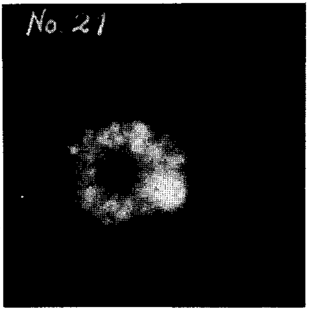
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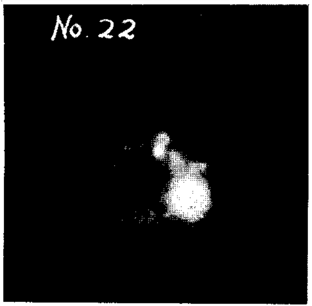
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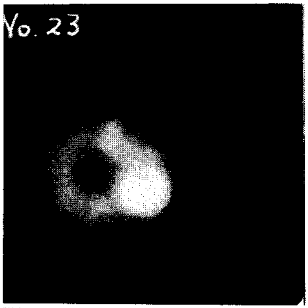
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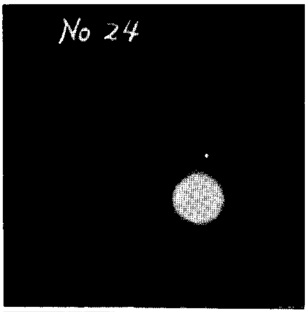
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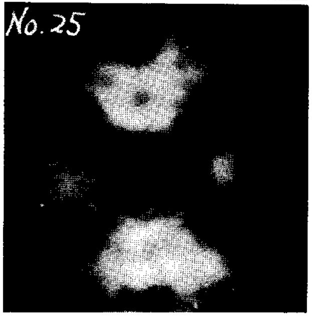
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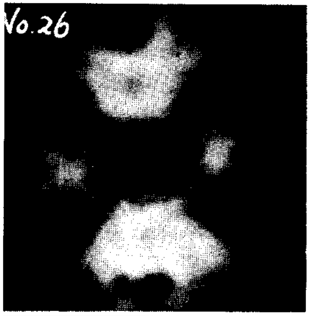
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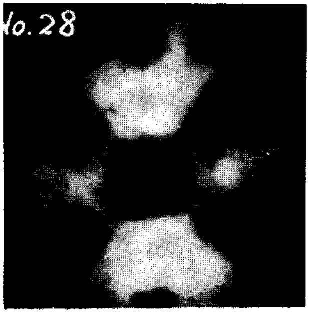
No. 27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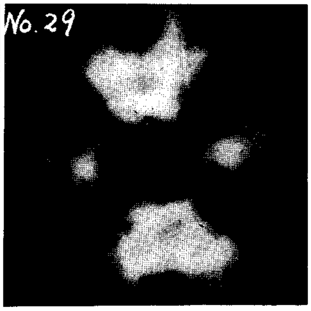
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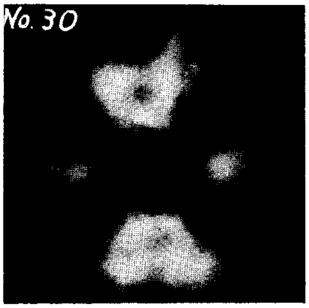
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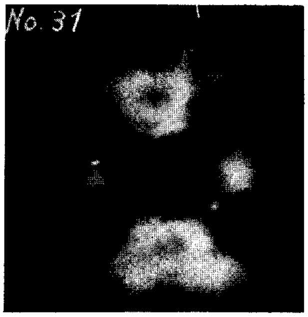
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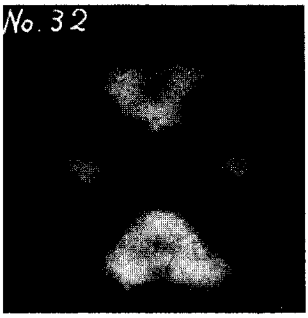
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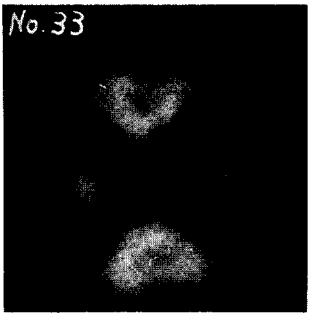
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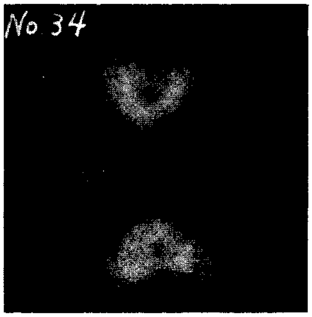
No. 34

to cause the micro-ammeter to scale out and the pattern to vanish altogether even at high tension of 10^4 V. The tip was heated repeatedly at above 1800°K for about 30 minutes as in heat treatments but without the mercury-diffusion pump being operated*). This procedure restored the pattern as Plate No. 13 and subsequently the average work function steadily increased to the maximum value *ca.* 0.55 eV above that of the clean surface with rise of pressure (Points No. 12~19). The maximum increase was in good agreement with that 0.48~0.65 eV14),15) observed by MIGNOLET, or 0.55 eV16) by GOMER.

Petal-like bright parts around the dark (011)-region apeared as shown in Plate No. 14. They drew near each other to diminish the dark area around the (011)-region as shown in Plate No. 19~21 and the point No. 22 was then observed after the evacuation as in the usual case*). After the subsequent heat treatment at 1300°K for two minutes the pattern of Plate No. 23 was observed. Another heat treatment at 1800°K for 5 minutes resulted in a pattern of Plate No. 25 resembling the earlier patterns, *e.g.* that of Plate No. 1. Further heat treatments caused no substantial change of pattern (Plates No. 26~32), but reproduced the average work function observed just after the introduction of hydrogen.

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*) *Cf.* § 5.

§ 11. Ammonia (Series 4)

TABLE 4. Ammonia, (Series 4)

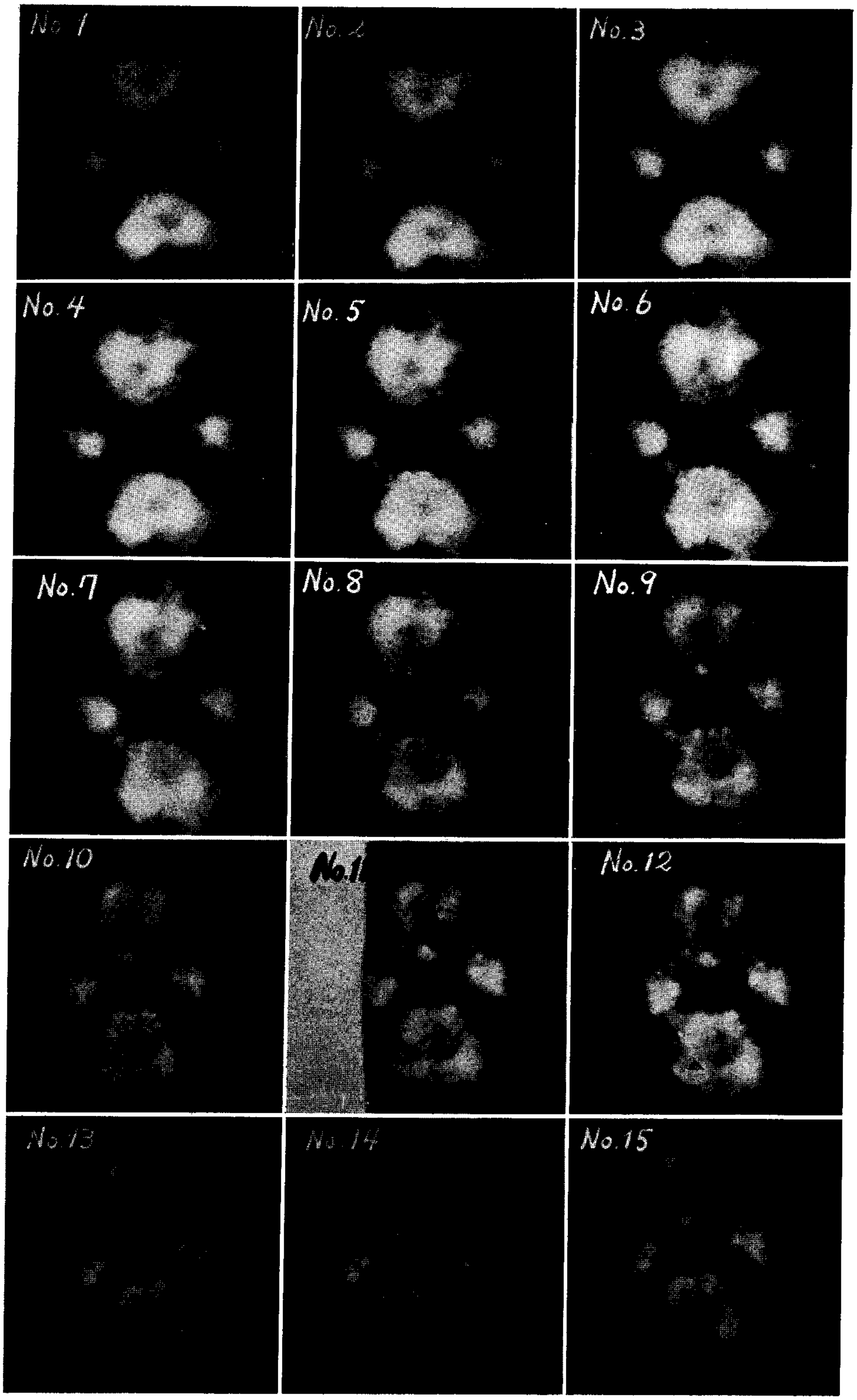
Points	Time (min.)	Press. (mmHg) $\times 10^{-8}$	Applied voltages (volts) $\times 10^{3}$	Behaviour of emission current	Condition of heat treatments	Remarks
No. 1	30 sec.	2.2	6.1	stable		after the introduction of NH_3, *cf.* Plates Nos. 1~10 and Nos. 25~34, Series 3
No. 2	1.5	3.2	6.1	stable		
No. 3	5	7.8	6.0	increasing		
No. 4	7.5	10	6.0	rather increasing		
No. 5	11.5	13	6.0	increasing		
No. 6	16.5	16	6.0			
No. 7	18.5	32	6.0	decreasing		
No. 8	20.5	42	6.0	increasing		
No. 9	23	83	6.0	increasing		*cf.* Plate No. 12, Series 3
No. 10	27	78	5.9	increasing		The evacuation started after the observation of No. 10.
No. 11	42	1.1	5.8	stable		
No. 12	45	0.84	5.85	stable	500°K., 1 min.	
No. 13	47	0.8	5.65	stable	900°K., 1 min.	
No. 14	50	0.78	5.65	stable	1300°K., 1 min.	
No. 15	51	0.8	5.7	decreasing	1550°K., 30 sec.	
No. 16	53	0.76	5.7	decreasing	1700°K., 1 min.	
No. 17	54	0.75	6.2	decreasing	1800°K., 10 sec.	*cf.* Plate No. 21, Series 2
No. 18	54.5	0.68	6.2	decreasing	1800°K., 10 more sec.	
No. 19	55	0.63	6.0	decreasing	1800°K., 30 more sec.	
No. 20	56	0.63	6.0	unstable	1800°K., 1 more min.	
No. 21	62	0.58	6.0		1800°K., 5 more min.	
No. 22	68	0.53	6.0		1800°K., 5 more min.	
No. 23	79	0.5	6.0		1800~1550°K., 10 min.	
No. 24	80	0.52	6.0		2050°K., 30 sec.	

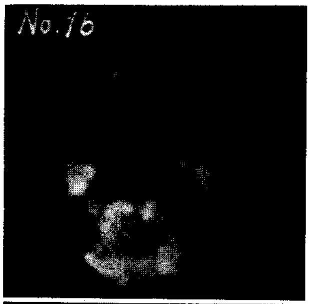
Points	Time (min.)	Press. (mmHg) $\times 10^{-8}$	Applied voltages (volts) $\times 10^3$	Behaviour of emission current	Condition of heat treatments	Remarks
No. 25	85	0.52	6.0		3000°K., 10 sec.	
No. 26	90	0.43	6.0		3000°K., 10 more sce.	
No. 27	95	0.33	6.0		3000°K., 10 more sec.	
No. 28	100	0.28	6.0		3000°K., 10 more sec.	
No. 29	105		6.5			*cf.* Plate No. 2, Series 2
No. 30	110		6.4		1800°K., 40 sec.	

The pattern changed during the first 30 seconds from Plate No. 8, Series 1 of clean surface to Plate No. 1 associated with increase of the average work function by *ca.* 0.1 eV from the initial value, spreading the slightly bright region along the (111)-(011) zone toward the dark (011)-region; the spread was quite the same as those of Plates No. 1～13 of Series 3 and continued to subsequent Plates No. 2～16. The area around the (013)-region on the latter patterns were darker than the surrounding region. The pattern changed scarcely by heat treatments up to Plate No. 16 taken subsequent to the heat treatment at 1700°K for one minute, whereas the average work function decreased as much as *ca.* 0.1 eV by the point No. 13 and kept then constant as far as the point No. 16.

The heat treatment at 1800°K for 30 seconds caused the surroundings of the (001)-region to become brighter as seen from Plate No. 17 than other regions along the (001)-(011) zone. The (001)-region became then darker than the latter regions as seen from Plate No. 19 by another two heat treatments at the same temperature for 10 and 30 seconds respectively. Further heat treatments resulted in Plates No. 20～30.

NH_3 (Series 4)


No.1
No.2
No.3
No.4
No.5
No.6
No.7
No.8
No.9
No.10
No.1
No.12
No.13
No.14
No.15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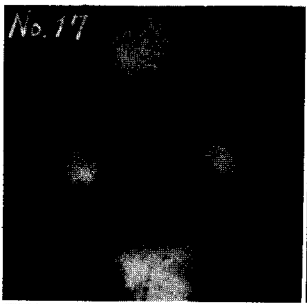
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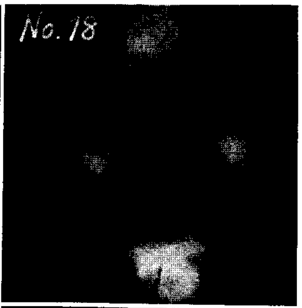
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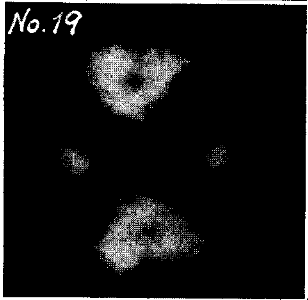
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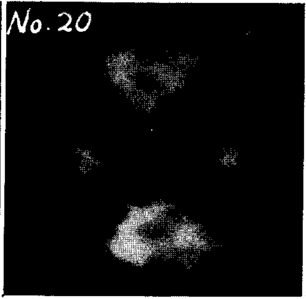
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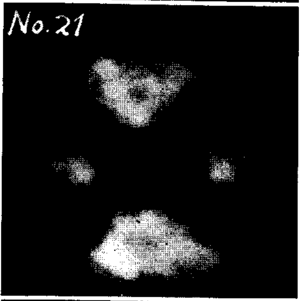
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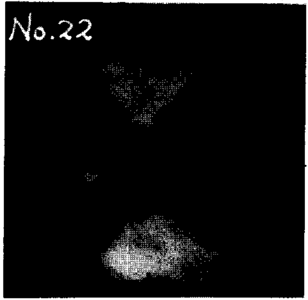
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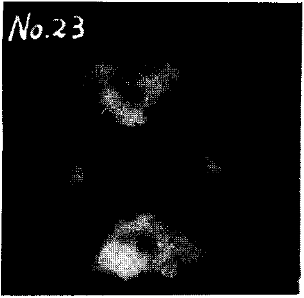
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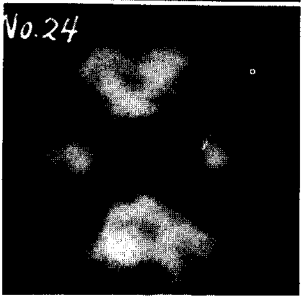
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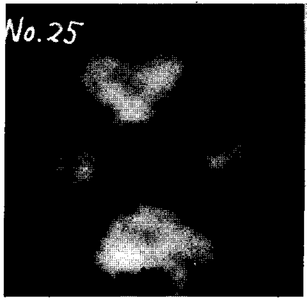
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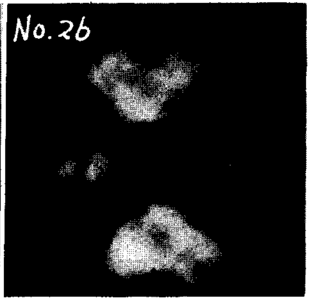
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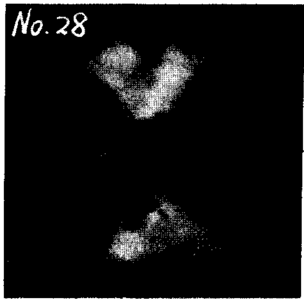
No.27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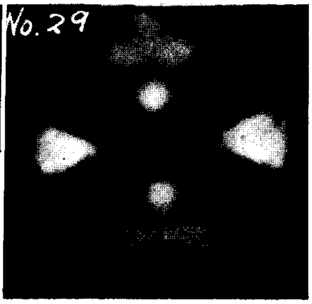
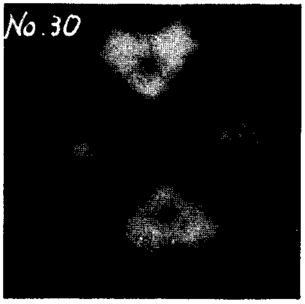

No.29


No.30

Chapter III. Discussion and Conclusion

§ 12. Discussion

The results described in the preceding chapter are now summarized and discussed as follows:

(i) *Nitrogen* (*Series 1*). Little change of the pattern was observed before heat treatments, except that the width of the dark (011)-region of the pattern grew narrower towards the direction of the (001)-(011) zone with rise of pressure as seen from Plates No. 8~29, whereas the average work function attained to considerably high a maximum value 0.55 eV above that of the clean tungsten surface after the smaller initial rise and drop. The pattern changed altogether by heat treatment at 1700°K under evacuation associated with a fairly large decrease (Point No. 41) or increase (Point No. 42) of average work function, but not appreciably by subsequent heat treatments, revealing instead common characteristics throughout as mentioned in § 8.

The dissociative adsorption of nitrogen should take place, if at all, later in the series on account of the appropriate chemical affinity. This must have more or less occured, however, because of the considerable increase of the average work function as much as 0.55 eV, since the molecular adsorption should decrease rather than increase it[*],[17]. We may duly attribute the patterns observed after the change caused by the heat treatment at 1700°K of the two characteristics to dissociatively adsorbed nitrogen N(a), which will be called N(a)-pattern in what follows. The N(a)-pattern is similar to the pattern observed at room temperature by BROCK[18] and attributed similarly to N(a) by him.

(ii) *Hydrogen* (*Series 3*). The pattern were not much changed after the initial variation even by heat treatments at 1800°K and above, as seen from Plate No. 25 or 32, whereas the average work function increased steadily after the point No. 12 up to maximum value 0.55 eV above that of the clean tungsten surface and then reduced, along with repetition of heat treatments accompanied by evacuation, to a value observed just after the introduction of hydrogen.

The noticeable characteristic of the pattern was that the bright regions spread radially toward the centre of the dark (011)-region[16] from the surroundings as observed initially on Plate No. 13 and 15 as well as after the heat treatment at 1800°K on Plate No. 32. The considerable increase of average work function is attributed to the formation of H(a) as in the case of nitrogen adsorption, hence the characteristic pattern of Plate No. 14, 15 or 32 is assigned

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[*]) The later decrease of the average work function is understood as due to the desorption caused by evacuation carried on throughout the heat treatments.

to H(a) on tungsten and called H(a)-pattern in what follows.

(iii) *A 1:5 nitrogen-hydrogen mixture* (*Series 2*). The pattern for instance of Plate No. 2 or 18 was identified with N(a)-pattern of Plate No. 45 or 41 of Series 1, that of Plate No. 24 with H(a)-pattern of Plate No. 13 of Series 3 and that of Plate No. 21 with the superposition both of the characteristic patterns. The N(a)-pattern appeared as soon as the gas was introduced, as seen from Plate No. 2, while the average work function increased by *ca.* 0.25 eV, which then continued to increase up to the maximum value *ca.* 0.65 eV above that of the clean surface. The maximum increment was larger than that *ca.* 0.55 eV in the case of nitrogen or hydrogen*). The heat treatments at 1550° and 1800°K caused the patterns unstable, which likely implied the characteristic attributed to NH(a) and/or NH_2(a) in (iv), § 12 and was associated with decrease of the average work function by *ca.* 0.3～0.4 eV from the maximum value*).

It is inferred from the rapid development of the N(a)-pattern in this case a) that the presence of hydrogen accelerates the adsorption of N(a) on tungsten, which is, besides, compatible with the rapid increase of the average work function. From the unstable pattern associated with the decrease of the average work function, it is inferred b) that intermediates, *e.g.* NH(a) and/or NH_2(a) with positive dipole moment are formed, which desorb rapidly to form ammonia rendering the pattern unstable. The inference a) is in conformity with the conclusion arrived at from the observation of the isotopic exchange of nitrogen on iron catalyst by KUMMER and EMMETT[19] and that from the measurement of adsorption in course of ammonia synthesis on a doubly promoted iron catalyst by TAMARU[20].

(iv) *Ammonia* (*Series 4*). The characteristics of H(a)-pattern prevailed throughout the observation. On the other hand, that of the N(a)-pattern was not initially observed but just after the heat treatment at 1800°K as seen from Plate No. 17, in spite of the larger proportion of nitrogen for hydrogen (1 : 3) as compared with that 1 to 5 in the case of the nitrogen-hydrogen mixture, Series 2. A stable pattern, *e.g.* of Plate No. 13, was observed between successive heat treatments at 500°, 900° and 1300°K, which embraced no characteristic of N(a)- but that of H(a)-pattern as well as that distinguishable from the former two ones, while the average work function attained to the maximum value *ca.* 0.1 eV below that of the clean tungsten surface**).

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*) *Cf.* Fig. 4.

**) Present author and KOBAYASHI observed that the average work function of evaporated nickel film similarly decreased by *ca.* 0.07 eV by adsorption of the mixture of hydrogen (1 mmHg) and ammonia (31 mmHg) [Ref. 21].

The latter characteristic of the pattern associated with the decrease of the average work function may be attributed to NH(a) and/or NH_2(a) in conformity with the inference in (iii), §12. It is inferred from the above results that ammonia does not decompose into H(a) and N(a) completely[22)] at temperatures below 1800°K, but only partially into intermediates H(a) and NH(a) and/or NH_2(a).

§ 13. Mechanism of the catalyzed synthesis of ammonia

Admitting that the catalyzed ammonia synthesis, $N_2+3H_2=2NH_3$, proceeds through the elementary steps,

(1) $N_2 \longrightarrow N(a) + N(a)$,
(2) $H_2 \longrightarrow H(a) + H(a)$,
(3) $N(a) + H(a) \longrightarrow NH(a)$,
(4) $NH(a) + H(a) \longrightarrow NH_2(a)$,
(5) $NH_2(a) + H(a) \longrightarrow NH_3$,

it is now induced that the step (3) or (4) is rate-determining, which fits in with the results discussed in §12 as shown below.

I) In the case of nitrogen-hydrogen mixture of Series 2, both the N(a)- and H(a)-patterns should be readily developed while considerably increasing the average work function as mentioned in (iii), §12 through steps other than, hence quicker than, the rate-determining step. The rate-determining step is surmounted just by heat treatment at elevated temperature to produce the intermediate NH(a) or NH_2(a), decreasing the average work function, but the appropriate pattern may be unstable as observed owing to its ready conversion through steps other than the rate-determining one into ammonia initially absent.

II) Ammonia of Series 4 should readily form H(a) and NH_2(a) through the reverse of the step (5) provided that the step (4) is rate-determining. Alternatively H(a), NH_2(a) and NH(a) are to be formed through the reverse of steps (4) and (5) in case of (3) being the rate-determining step. Patterns of H(a) as well as of NH_2(a) and/or NH(a) may hence be observed, associated in either case with the decrease of the average work function as remarked in (iv), §12. The pattern of the intermediates may be stable as actually observed, being sustained by ammonia initially present through steps other than the rate-determining one. The N(a)-pattern should just appear, as the rate-determining step is reversely surmounted by heat treatment at elevated temperature as actually observed.

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