

metastable. As in the case of all the simple alkali iodides (as distinct from the addition products) the solubility of ammonium iodide in sulfur dioxide decreases with rising temperature.

Summary

The composition of the solid addition products and the vapor pressure curves limiting the stability of these compounds have been determined between the maximum limits of -25 and $+25^{\circ}$ for the 2-component systems of sulfur dioxide with sodium, potassium, rubidium, cesium and ammonium iodides.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE KINETICS OF THE DECOMPOSITION OF AMMONIA ON COPPER

By J. K. DIXON¹

RECEIVED FEBRUARY 27, 1931

PUBLISHED MAY 6, 1931

The decomposition of ammonia on the surfaces of certain metals has been studied by Hinshelwood and Burk, Schwab and Kunsman.² In each case the metal in the form of a hot filament has been used to decompose the ammonia. In order to obtain a true conception of a heterogeneous reaction a knowledge of the following is necessary: (1) the heats of adsorption of the gases involved in the reaction; (2) the amount of each gas adsorbed, as a function of its pressure; (3) the rates of adsorption of the gases; and (4) the law expressing the relation between the velocity of reaction and the pressures of the gases above the surfaces.³ Except at low pressures, the use of a filament as a surface precludes any attempts to make measurements on the first three quantities. The object of the present work has been to study the kinetics of the decomposition of ammonia on copper, using enough of the metal to make later measurements on the first three factors possible.

Elöd and Banholzer⁴ have studied the decomposition of ammonia on copper and iron by a dynamic method. Their results on copper agree with those given here and can now be interpreted in a quantitative way.

Experimental

About fifty experiments on the decomposition of ammonia on forty grams of granular copper (see below) were performed in a static system.

¹ National Research Council Fellow.

² (a) Hinshelwood and Burk, *J. Chem. Soc.*, 127, 1105 (1925); (b) Schwab, *Z. physik. Chem.*, 128, 161 (1927); (c) Schwab and Schmidt, *ibid.*, B3, 337 (1929); (d) Kunsman, *THIS JOURNAL*, 50, 2100 (1928); 51, 688 (1929).

³ Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," Oxford University Press, 1929.

⁴ Elöd and Banholzer, *Z. Elektrochem.*, 32, 555 (1926).

The experiments were reproducible, but it was not possible to obtain an equation which would explain the rate of decomposition correctly. As only the general conclusions and a possible explanation of these experiments will be reported here, the details of the experiments will be omitted.

Experiments were then carried out in a dynamic system, from which it has been possible to set up an equation which expresses the rate of decomposition correctly.

Materials.—Ammonia from a tank was passed over fused potassium hydroxide and then through two tubes of anhydrous barium oxide. The latter removes water efficiently and does not react with ammonia. The gas obtained was completely absorbed by dilute sulfuric acid. Tank nitrogen (99.9%) was passed over copper turnings at 450°, then over solid potassium hydroxide and finally through phosphorus pentoxide. Tank hydrogen was passed over copper turnings at 350°, over potassium hydroxide and over phosphorus pentoxide.

Copper oxide, Kahlbaum's "pea-size," was sieved to 10–16 mesh and reduced in oxygen-free hydrogen. Since the temperature range studied in the catalytic reaction was 500–625°, the final twelve hours of reduction was made at 700°. The copper was strongly sintered, characterized by a true copper color.⁵

Apparatus and Experimental Procedure.—Ammonia passed from its purification train through a flowmeter and then over the copper catalyst. Hydrogen, nitrogen, or both, were added to the ammonia stream, as desired, before the latter entered the catalyst chamber. The amounts of added nitrogen and hydrogen were determined by suitable flowmeters. The amount of ammonia escaping decomposition in a definite length of time was found by absorbing it in dilute sulfuric acid of known concentration and titrating the excess acid with sodium hydroxide. The quantity of ammonia entering the catalyst chamber was known from the calibration of the ammonia flowmeter; hence, the percentage decomposition was easily calculated. It was possible to divert the "off" gases to a gas analysis apparatus by means of a three-way stopcock. The entire apparatus was constructed of Pyrex glass, the only rubber connection being used to lead the exit gases to the absorbing bottle.

Gas outlet



Gas inlet

Fig. 1.

The type of capillary used in the flowmeters is shown in Fig. 1. It is recommended because it is easily made, does not become clogged, gives a gas flow proportional to the pressure head and can be made to give small flow rates when the pressure head (mercury) is appreciable. For each of the gases, the pressure head on the flowmeter was kept constant by means of an overflow in the gas purification train. The hydrogen and nitrogen flowmeters were standardized by "displacing" water and, in the case of small flow rates, by using mercury in place of water. The accuracy was $\pm 1.0\%$. The ammonia flowmeter was standardized by titration, the accuracy being $\pm 0.3\%$. Since the ammonia flow rate decreased as the room temperature increased, the flowmeter was calibrated three or four times a day and hence it was unnecessary to calculate the corrections to be applied on account of these temperature variations.

Thirty-five grams of the copper catalyst, with an apparent volume of 15 cc., was held in an unfused quartz vessel, whose volume was 25 cc. and to which were attached inlet and outlet tubes. Connection with the rest of the apparatus was made by means of graded quartz to Pyrex seals. The inlet gases passed down through the furnace

⁵ When the oxide is reduced at 180–200°, it has a purple appearance.

and then entered at the bottom of the catalyst chamber. A furnace, wrapped with nichrome wire and electrically heated, was drawn up about the catalyst tube and the free space in the furnace filled with iron rods in order to equalize the temperature. A chromel-alumel thermocouple was fixed against the catalyst tube at the mid-point of the catalyst and the temperature determined in this way has been taken as that of the catalyst. The furnace was well insulated with asbestos; consequently the maximum temperature variation during an experiment was $\pm 1^\circ$.

The experimental procedure was, first, to pass a suitable gas mixture over the catalyst for ten to fifteen minutes at the temperature of the experiment in order to assure constant conditions above the surface. Then the ammonia in the "off" gases was absorbed in approximately 50 cc. of standard sulfuric acid for a suitable length of time and the excess acid determined by titrating back with sodium hydroxide, using methyl orange as indicator. A small correction was determined and made for the amount of ammonia escaping absorption in the acid. This correction proved to be negligible except for high rates of flow of nitrogen or hydrogen. Three or four runs were performed for each gas mixture and the mean of these results has been used in subsequent calculations. In any experiment the values of the percentage decomposition vary among themselves by not over 1%. When the mean is compared with that for the same experiment performed at a different date, the variation is not over $\pm 5\%$.

Results and Interpretation

The rate of decomposition has been studied at 495.5, 542.5, 581.5 and 619.5°. In Table I are given the results of the experiments at 542.5 and 581.5°; the results at 495.5 and 619.5° are analogous. The flow rates throughout are expressed in cc. per minute reduced to 25° and 760 mm. pressure. In the first column is given the experiment number, in the second the temperature in degrees centigrade, and in the third the volume of ammonia entering the catalyst tube per minute. The fourth column gives the percentage of ammonia decomposed, the fifth the hydrogen inlet flow rate and the sixth the inlet flow rate of nitrogen.

If we consider any small element of length of the catalyst tube containing an amount of surface, dA , then the rate of disappearance of ammonia per minute is proportional to this surface area. The composition of the gas above this surface is assumed to be constant. If we let V be the total flow rate of gas over dA , v the flow rate of ammonia, v_H the flow rate of hydrogen and v_N that for nitrogen, each in cc. per minute, then

$$V = v'_H + v'_N + 2v - v \quad (1)$$

The primed quantities refer to the flow rates of the inlet gases. The pressures of ammonia, hydrogen and nitrogen are

$$p = \frac{v}{V} P \quad p_H = \frac{v_H}{V} P \quad p_N = \frac{v_N}{V} P \quad (2)$$

where P is the total pressure, which is the barometric pressure in this case. The experiments indicate that the rate of decomposition of the ammonia is proportional to p and inversely proportional to p_H . If dv is the amount of ammonia decomposed *per minute* on the surface dA , then

$$-dv = k dA \frac{p}{p_H} = k dA \frac{v}{v_H} \quad \text{or} \quad -\frac{v_H dv}{v} = k dA$$

TABLE I
 THE DECOMPOSITION OF AMMONIA ON COPPER

Expt.	Temp., °C.	Inlet NH ₃ , cc./min.	% NH ₃ decomposed	Inlet H ₂ , cc./min.	Inlet N ₂ , cc./min.	Barometric pressure, cm.	k_1
1	580.5	20.2	23.50	0.00	0.00	75.3	0.65
3	581.0	20.2	13.60	8.30	.00	75.3	1.01
4	581.0	20.2	26.00	0.00	.00	75.1	0.82
7	581.5	20.2	14.45	4.80	.00	75.9	.74
8	581.5	22.0	19.25	2.40	.00	75.9	.81
10	581.5	31.7	21.60	0.00	.00	75.7	.87
11	581.5	43.2	20.10	.00	.00	75.2	1.06
16	581.5	21.7	19.95	4.80	14.5	74.2	1.19
17	581.5	21.7	23.95	2.40	16.9	74.4	1.18
18	581.5	21.7	28.10	0.00	18.6	74.5	1.07
19	581.5	21.7	29.95	.00	43.0	75.4	1.21
20	581.5	21.7	27.80	.00	22.9	75.8	1.06
21	581.5	22.0	23.85	.00	0.00	76.0	0.75
29	581.5	43.2	21.65	.00	.00	76.3	1.18
33	581.5	43.2	23.50	.00	25.4	75.8	1.40
34	581.5	43.2	17.45	5.30	25.4	75.7	1.41
35	581.5	43.2	16.65	5.30	0.00	75.6	1.31
37	581.5	43.2	2.35	52.9	.00	75.6	0.84
39	580.5	10.4	33.25	0.00	.00	75.5	.75
42	581.5	10.4	40.85	.00	47.1	75.8	1.22
45	581.5	22.0	32.65	.00	47.0	74.2	1.52
47	582.0	43.2	25.90	.00	47.3	75.2	1.72
51	581.5	22.0	5.68	25.3	0.00	77.1	1.01
52	581.5	22.0	3.08	40.2	.00	77.0	0.85
12	543.5	43.2	10.80	0.00	.00	75.0	.30
13	542.0	43.2	8.43	2.40	.00	74.6	.34
14	542.5	43.2	6.33	4.80	.00	74.5	.30
23	542.5	22.0	13.40	0.00	11.4	75.8	.23
24	542.5	22.0	12.80	.00	0.00	75.8	.20

k representing the number of cc. of ammonia decomposed per minute on unit surface when $p = p_H = 1$ atmosphere. When $A = 0$, $v = v'$, $v_H = v'_H$ and $v_N = v'_N$; when $A = A_1$, the total area of the catalyst, then $v = v_t$, which is calculated from the percentage decomposition. Therefore

$$\begin{aligned}
 - \int_{v'}^{v_t} \frac{v_H dv}{v} &= - \int_{v'}^{v_t} \frac{(2/3 v'_H + v' - v) dv}{v} = 2/3 k A_1, \text{ or} \\
 (2/3 v'_H + v') \ln \frac{v'}{v_t} - v' + v_t &= 2/3 k A_1 = k_1
 \end{aligned}
 \tag{3}$$

The barometric pressure is given in the seventh column of Table I and the calculated values of k_1 in the eighth column. The latter are not quite constant, but increase with the flow rate, as illustrated in Fig. 2. If the velocity of decomposition is assumed to be proportional to $p/(1 + k_2 p)$ instead of p , it is possible to account for the increase of k_1 as we add nitrogen, that is, increase the total flow rate. Since the activity of the catalyst increased slightly with time and the experimental accuracy of the determina-

tion of the percentage decomposition was about $\approx 5\%$, the introduction of a second constant, k_2 , is not warranted. If, for example, in Expt. 10, Table I, we assume that the percentage decomposition is 23.6, then k_1 becomes 1.06. That is, an error of 10% in the percentage decomposition makes an error of 20 to 25% in k_1 . In Expt. 37, where the amount of added hydrogen is large and the percentage decomposition small, the experimental error may be greater than 5%, hence the agreement of the constant with those from other experiments is satisfactory.

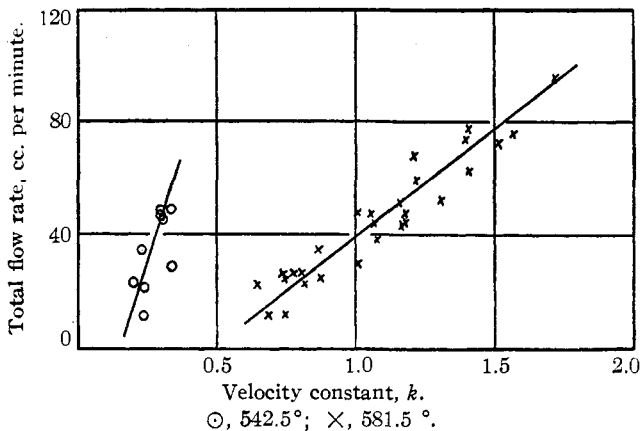


Fig. 2.—The dependence of the velocity constant on the total flow rate.

In Expts. 11, 37 and 42 the average ammonia pressures are 62, 22 and 10 and the average hydrogen pressures 10, 53 and 3.7, respectively, in centimeters of mercury. The pressure range for ammonia is from 10 to 60 cm. and the range of hydrogen pressures 4 to 50 cm.

The results of the experiments in the static system agree in some respects with those of the dynamic method. Nitrogen had no effect on the rate of decomposition of the ammonia. A number of experiments were made with the same initial pressure of ammonia, but varying initial pressures of added hydrogen. The results are given in Table II, in which the first column gives the initial pressure of ammonia, the second the *initial* pressure of hydrogen, and the third the initial slope of the pressure–time curve.

The reaction velocity is seen to be very nearly inversely proportional to the hydrogen pressure. The velocity constants, k , calculated from the results of the static experiments by means of the equation

$$-\frac{d p_{\text{NH}_3}}{dt} = \frac{k (p_{\text{NH}_3})^n}{(p_{\text{H}_2})^m} \tag{4}$$

with $n = m = 1$, drop off as the reaction proceeds. It would be necessary to assume that $n > 2$ and $m > 1$, and neither a whole number, in order to obtain a true constant. Such a procedure has been adopted by Schwab and

TABLE II
THE EFFECT OF HYDROGEN ON THE RATE OF DECOMPOSITION OF AMMONIA ON
COPPER IN A STATIC SYSTEM

$p_0, \text{NH}_3,$ cm.	p_0, H_2 cm.	$t = 619^\circ$ \dot{p} (initial), cm. per minute
10.5	0.0	(3.50) ^a
10.8	5.4	1.32
10.2	9.9	0.74
9.7	24.7	.40
11.2	34.0	.30

^a When (p_0, H_2) is zero the rate at the start is so fast that this value has very little significance.

Schmidt in order to explain their results on the decomposition of ammonia on a platinum filament, above 25 mm. pressure.^{2c} They were the first to point out the complexity of the reaction mechanism and their experiments showed the same rapid decrease in velocity with time which we have observed in a static system.

It seems more plausible to assume a simpler reaction mechanism and that the falling off in rate is partly due to a covering of the surface by an unstable nitride or other compound. In the case of copper it is known that copper oxide and ammonia react to form a nitride,⁶ and Beilby and Henderson⁷ report the formation of copper nitride by the action of ammonia on copper at high temperatures. The question of a nitride formation was investigated in the dynamic system. An analysis of the "off" gas from the catalyst was carried out at various times during the kinetic studies. Table III shows that the ratio of the hydrogen formed to the sum of hydrogen and nitrogen is that which we would expect if none of the nitrogen were disappearing to form a nitride.

TABLE III
ANALYSIS OF THE "OFF" GAS FROM THE DECOMPOSITION OF AMMONIA ON COPPER

$\text{N}_2 + \text{H}_2, \text{cc.}$	$\text{H}_2, \text{cc.}$	$\text{H}_2/(\text{H}_2 + \text{N}_2)$
37.85	28.50	0.753
39.00	29.00	.743
36.30	27.65	.763
35.10	25.80	.735

Theoretical, 0.780

Since the amount of nitrogen held by the copper might have been very small compared with the total set free by decomposition or since the nitride might have formed and remained in a nearly constant amount,⁸ a different procedure was adopted to detect a possible nitride formation under the conditions of the kinetic studies. A sample of Kahlbaum's

⁶ Guntz and Bassett, *Bull. soc. chim.*, [3] 35, 201 (1906).

⁷ Beilby and Henderson, *J. Chem. Soc.*, 79, 1245 (1901).

⁸ Compare with Mittasch, Kuss and Emert, *Z. Elektrochem.*, 34, 829 (1928).

copper oxide, 17.7756 g., was reduced completely in pure hydrogen at 300°. The weight of copper expected was 14.201 g. and the value found was 14.229 g. Pure ammonia was then passed over this heated catalyst, decomposition beginning at 410°. The temperature was raised to 500–550°, where the rate of decomposition of the ammonia was high. The copper with its containing tube was cooled from time to time and weighed, but there was no increase in weight. Finally, the ammonia was passed over the copper continuously for three days and the weight was again determined and found to be the same. During the course of the treatment with ammonia the weight of the copper decreased 0.002 g.

The negative results of these experiments do not disprove that a trace of some compound might be formed on the surface which would inhibit the reaction considerably. Experiments of the type described by Mittasch and Frankenburger⁹ might yield information with regard to compound formation.

The Temperature Coefficient.—The heat of activation, E , of the decomposition on copper has been determined from the reaction velocity constants at 495.5, 542.5, 581.5 and 619.5°. E in calories per mole has been calculated by means of the equation

$$E = 2.303 \left(\log_{10} \frac{k_2}{k_1} \right) \left(\frac{T_1 \times T_2}{T_2 - T_1} \right) \quad (5)$$

R is the gas constant expressed in calories per mole per degree; k_2 and k_1 are the velocity constants at the absolute temperatures, T_2 and T_1 , respectively. The values of $\log_{10} k$ corresponding to a certain total flow rate of gas have been plotted against $1/T$, the resulting curve being a straight line. The slope of the curve was used to calculate E . In Table IV the first column gives the temperature in degrees centigrade, the second the total gas flow rate, the third the velocity constant and the fourth column the energy of activation, E .

TABLE IV

THE ENERGY OF ACTIVATION FOR THE DECOMPOSITION OF AMMONIA ON COPPER

t , °C.	V , cc./min.	k	E , cal./mole
542.5	12	0.20	42,000
581.5	12	.65	
495.5	25	.041	46,500
542.5	25	.24	
581.5	25	.82	
619.5	25	2.80	
495.5	50	0.041	
542.5	50	.32	47,500
581.5	50	1.15	
619.5	50	3.90	

The most probable value of E is 46,000 = 2000 calories per mole.

⁹ Mittasch and Frankenburger, *Z. physik. Chem.*, A139, 386 (1928).

The Results of Elöd and Banholzer

Elöd and Banholzer¹⁰ have made measurements on the decomposition of ammonia on copper by a dynamic method which was essentially the same as we have used here. Their results may now be explained by assuming the same reaction mechanism, that is, by using equation (3) to calculate velocity constants. A few typical calculations of their results are given in Table V. The first column gives the table number and the second column the experiment number from their paper. The notation in the other columns is consistent with that used in our Table I, except that the flow rates are in terms of cc. per hour, hence k_1 is expressed in these units.

TABLE V

THE DECOMPOSITION OF AMMONIA ON COPPER ACCORDING TO ELÖD AND BANHOLZER

		$t = 700^{\circ a}$									
Table	Expt.	v'	v'_H	v'_N	k_1	Table	Expt.	v'	v'_H	v'_N	k
2	1	180	0.0	0.0	28	3	1	1191	0.0	0	26
2	4	2260	.0	.0	33	3	3	1292	.0	1000	35
2	7	5340	.0	.0	37	3	4	1292	.0	5000	31
2	8	7700	.0	.0	23	3	5	1353	.0	10000	35
2	9	11400	.0	.0	35	3	6	1212	.0	16000	31 ^b

^a The temperature is not given, but a comparison with their Table VIII shows that it is probably 700°.

^b Experiments 7-10 give values of $k_1 = 15-20$, but the value for the percentage decomposition in Expt. 9, with $v'_N = v'_H = 0$, does not agree with Expt. 7 of Table II.

The heat of activation calculated from the values of k_1 at 600 and 700° is 63,000 calories per mole (Ref. 4, Expts. 5 and 6, Table VIII). The percentage decomposition measured at 600° was 3.7, too small to be accurate, and this may account for the high value of the heat of activation.

In Table VI are given some of the values of k_1 , according to Equation 3, calculated from the experiments of Elöd and Banholzer for the decomposition of ammonia on an iron catalyst in a flowing system.

TABLE VI

THE DECOMPOSITION OF AMMONIA ON IRON ACCORDING TO ELÖD AND BANHOLZER

		$t = 700^{\circ}$							
Table	Expt.	v'	v'_H	k_1^a	Table	Expt.	v'	v'_H	k_1
1	2	554	0.0	826	6	7 and 8	1135	10000	1495
1	4	2438	.0	1055	7	2	2229	2000	1070
1	6	4480	.0	1365	7	5 and 4	3504	3500	1005
1	9	10015	.0	1805	7	6 and 7	5513	5500	1275
6	2	1063	1000	1150	7	8	8333	8000	1320
6	5 and 6	1129	5000	1305					

^a Nitrogen has no effect.

The heat of activation calculated from the values of k_1 at 600 and 700° is 37,900 calories per mole. It should be noted that k_1 increases as the flow rate increases in the same general way as we have found for copper.

¹⁰ Elöd and Banholzer, *Z. Elektrochem.*, **32**, 555 (1926).

The Poisoning Effects of Carbon Monoxide

It is known that carbon monoxide has a higher heat of adsorption on copper than hydrogen and ammonia¹¹ and, therefore, in small traces, should have a pronounced inhibiting effect on the decomposition of ammonia. Carbon monoxide from formic acid and sulfuric acid was purified and dried carefully and then added to the ammonia stream before the latter reached the copper catalyst. The percentage decomposition of the ammonia was determined in the usual way. Carbon monoxide reacts with ammonia to form hydrogen cyanide and water. The "effect" of carbon monoxide which has been measured is due to the sum of the effects of carbon monoxide, water and hydrogen cyanide. The results of the experiments are given in Table VII and are interesting because the first trace of carbon monoxide produced an appreciable lowering of the rate of decomposition; but subsequent increase in the amount had little added effect.

TABLE VII

THE EFFECT OF CARBON MONOXIDE ON THE DECOMPOSITION OF AMMONIA ON COPPER

NH ₃ per minute, cc.	CO per minute, cc.	% NH ₃ decomposed	t = 581.5°	
			Expt.	
32.3	0.00	21.60	1	
32.3	.30	18.00	2	
32.3	.79	18.20	3	
32.3	1.34	18.00	4	
43.8	0.00	18.40	5, 9, 10, 12	
43.8	.35	15.65	8, 11	
43.8	.70	15.40	7	
43.8	1.20	14.85	13	
43.8	1.35	14.85	6	

The copper used had been sintered at 700° (see Materials) and consequently possessed a nearly uniform surface. A very small partial pressure of carbon monoxide was sufficient to cover the few active patches remaining on the catalyst; but further increase in its pressure required that the carbon monoxide compete for a portion of the uniform surface and its effect was then necessarily very similar to that of adding hydrogen. The discussion which follows throws some doubt on this explanation, but it is presented nevertheless.

Discussion

Since the rate of decomposition of ammonia has been found to be proportional to the ammonia pressure and inversely proportional to the hydrogen pressure, we can say that the surface of the copper is almost completely covered with hydrogen and that the amount of surface available for ammonia adsorption is small. The fraction of this available surface which is covered with ammonia is proportional to the ammonia pressure.

¹¹ Taylor, *Z. Elektrochem.*, **35**, 542 (1929).

It is surprising that this simple explanation fits the facts over wide ranges of pressures. The observed heat of activation of 46,000 calories per mole is probably the true value since Beebe and Taylor,¹² and Dew and Taylor,¹³ have found nearly the same values for the heats of adsorption of hydrogen and ammonia on copper, 9600 and 9200 calories per mole, respectively. The results of the experiments with carbon monoxide, which show a small fraction of the surface is abnormally active, will not alter this conclusion materially.

The use of heats of adsorption to predict catalytic activity meets with serious objections in the light of recent experimental work. When pure ammonia was passed over copper at 581.5°, the average ammonia pressure above the metal was about 60 cm. and the average hydrogen pressure about 10 cm. In the ratio of 6:1, the hydrogen nearly completely covers the surface of the metal. Hence, if the accommodation coefficients of the two gases are the same, the rate of evaporation of hydrogen from the surface must be very much smaller than that of ammonia. To consider this particular case more closely, let k_2 and k'_2 be the rates of evaporation of ammonia and hydrogen, respectively, at 581.5°, each for unit area of covered surface. It is easily shown that k'_2/k_2 has the values 1/54, 1/114, 1/594 when the ratio of the fraction of the total surface covered by hydrogen to that covered by ammonia has the values 9:1, 19:1 and 99:1, respectively.¹⁴ The pressure of hydrogen has been taken as one-sixth that of the ammonia. Hinshelwood¹⁵ assumes that

$$k_2 = b_2 e^{-\lambda/RT} \quad \text{and} \quad k'_2 = b'_2 e^{-\lambda'/RT} \quad (6)$$

where λ and λ' are the heats of desorption and the b 's are constants. Using the ratios of k'_2/k_2 as given above and letting $b_2 = b'_2$, it is found that $\lambda' = \lambda + 2200$, $\lambda + 8100$ and $\lambda + 10,900$, respectively. The constant b_2 must be 10^3 to 10^4 times as large as b'_2 in order for λ' to equal λ . Although measurements cannot be made at high temperatures, it does not seem probable that the heats of adsorption differ by such values at high pressures. For practical purposes at least the use of equation (6) is doubtless incorrect.

Further evidence that these equations are not correct has been discussed by Taylor.¹⁶ In some cases a gas with a higher heat of adsorption can be pumped off a metal much more easily than a gas with a lower heat of adsorption. Unless the constant b varies enormously from gas to gas, the rate of evaporation is influenced by some other factors besides the heat of adsorption. Recently Benton and White¹⁷ have reached the conclusion that when

¹² Beebe and Taylor, *THIS JOURNAL*, **46**, 45 (1924).

¹³ Dew and Taylor, *J. Phys. Chem.*, **31**, 277 (1927).

¹⁴ Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," p. 206.

¹⁵ Ref. 14, p. 233.

¹⁶ G. B. Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, **34**, 799 (1930).

¹⁷ Benton and White, *THIS JOURNAL*, **52**, 2325 (1930).

hydrogen is adsorbed by nickel above -100° the adsorbed gas is activated, possibly existing as atomic hydrogen. In this case the rate of evaporation would not be determined solely by the heat of desorption. The same conclusion is probably true for copper.

From three different viewpoints we are led to the conclusion that the equations (6) are not correct and, therefore, it is not correct to assume that the true heat of activation of a heterogeneous reaction is equal to the observed heat of activation, minus the heats of adsorption of the reactants, plus the heats of adsorption of the products which retard. Experiments on the rate of adsorption of gases by copper are in progress, from which we should be able to draw more definite conclusions with regard to various points in the foregoing discussion.

I wish to thank Professor Hugh S. Taylor for suggesting this problem and for his constant advice and criticism.

Summary

The kinetics of the decomposition of ammonia on copper have been studied by a dynamic method. The experiments were made on a large amount of catalyst between 495 and 620° with ammonia and hydrogen partial pressures between 4 and 50, and 10 and 60 centimeters of mercury, respectively. The rate of decomposition was proportional to the ammonia pressure and inversely proportional to the hydrogen pressure. Experiments in a static system confirmed the facts that the rate was inversely proportional to the hydrogen pressure and independent of the nitrogen pressure. There was no appreciable formation of copper nitride under the conditions of the experiments. The heat of activation of the reaction was $46,000 \pm 2000$ calories per mole. Carbon monoxide in small amounts poisoned the surface of the copper; the first amount had the greatest inhibiting effect.

Some objections to the use of heats of adsorption in calculating true heats of activation of heterogeneous reactions have been pointed out. Measurements on rates of adsorption of gases by copper are in progress.

PRINCETON, NEW JERSEY