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I.—*The Thermal Decomposition of Ammonia, with Particular Reference to the Existence of Active and Inactive Phases of Ammonia.*

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The work now described was undertaken in order to test the conclusion of Baly and Duncan (J., 1922, **121**, 1008) that ammonia gas formed by very rapid evaporation of the liquid is decomposed less rapidly by a hot platinum wire than that obtained by slow evaporation, but their results could not be confirmed.

The method used was based upon that of Baly and Duncan, so far as the information given in their paper allowed.

Sources of Ammonia.—Two cylinders of liquid ammonia were used, one of synthetic ammonia, which was connected directly to the apparatus, and the other of gas-works origin, from which liquid was drawn off into a vessel, suitably protected from the atmosphere, which could then be attached to the apparatus.

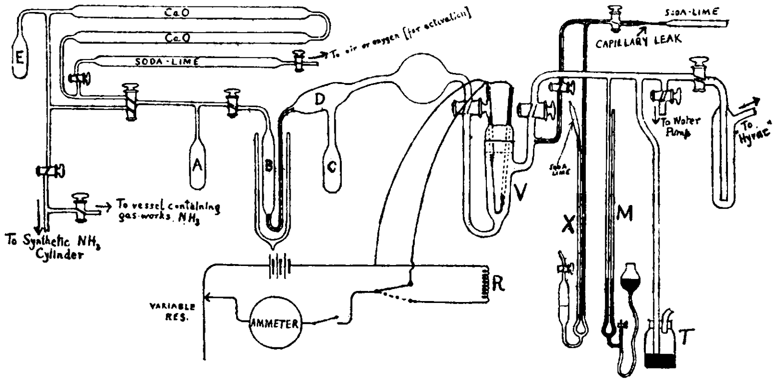
Variation of Rate of Evaporation.—Ammonia gas from the cylinder or other source was condensed, after passing very slowly through two drying tubes, each 70 cm. long and containing quicklime, or through an alternative direct connexion, in one or other of the three vessels, A, B, or C (Fig. 1). Vessel A was used for slow isothermal evaporation; the actual rate of gas formation therefrom was about 15 c.c. per minute. From B the liquid could be evaporated very quickly, by allowing it to be forced up the capillary to the bulb D by the pressure of its own vapour. Vessel C could be used for rapid boiling by direct heating. From either B or C evaporation readily occurred at the rate of 10,000 c.c. of gas per minute, and this rate was often exceeded. These alternative methods of rapid evaporation gave identical results in the decomposition experiments.

Reaction Vessel.—This vessel, V, which was kept in a thermostat maintained at 20°, was provided with inlet and outlet tubes of 7 mm. bore, to cope with the rapid flow of gas. The platinum wire, about 9 cm. long and of 40 gauge, was welded to stout platinum wires sealed into tubes passing through a "slip-joint" top to the vessel, so that the wire could be easily removed and replaced. The reaction vessel was connected by a ½-mm. capillary tube over 1 m. long to a manometer, X, containing xylene, which was chosen because it had been used by Baly and Duncan.

Temperature Control.—The wire was heated by means of a battery of accumulators. The time during which current passed was recorded on a 1/5-second stop-watch, arranged so that the actual "make" and "break" movements started and stopped it.

Current was measured on an open-scale Weston ammeter reading direct to 0·02 amp. and allowing easy estimation to 0·002 amp. Measurements of *E.M.F.* also were made in preliminary work, but were discontinued, since actual measurements of the wire temperature were not desired. Reproducibility of temperature was secured by the use of an auxiliary resistance, R, kept at constant temperature in the thermostat, and roughly equal to the resistance of the reaction wire, which could be made to form an alternative path for the current by means of the three-way switch. This alternative resistance was used suitably to adjust the value of the current before making connexion *via* the reaction wire, and again to check it after breaking this connexion. If, in successive experiments, a given current through R corresponds to identical values of current through the reaction wire, then, since the *P.D.* across the latter is the same in each case, its resistance and hence the energy input must be the same in each experiment. This disposes of the possibility that the same current might cause different heating effects, due to variation of the resistance.

FIG. 1.



Owing to the extra cooling effect caused by the hydrogen formed, the resistance of the platinum wire must alter slightly during the course of an experiment. The " drift " in the current due to this was found to be very small—of the order of 0·002 amp.—during the 20-second periods used. No attempt was made, therefore, to keep the current constant by continuous adjustment of resistance, but in order to ensure more comparable results, its value was always read 5 seconds after the reaction started.

Filling of Reaction Vessel.—The vessel was exhausted fairly thoroughly by a " Hyvac " pump, after the bulk of any ammonia present had first been removed by a water-pump. Sufficient ammonia was then allowed to evaporate through it to fill it about five times over, the excess escaping *via* a mercury trap, T.

Care was usually taken that only a part of the liquid in the evaporation vessel was used, about one-third being left behind; for, if the effect observed by Baly and Duncan were due to partial separation of the constituents of an impure ammonia, the effect might be annulled if the residuary portion evaporated. In certain instances, indicated in the table below, this precaution was not observed. The gas filling the reaction vessel was, prior to decomposition, brought to exactly 760 mm. pressure by means of a capillary leak, L, and manometer adjustment, M. The reaction vessel was in every case heated for a period of 20 seconds, as in Baly and Duncan's experiments. After thermal equilibrium had been restored, connexion was made to the xylene manometer and the increase in pressure at constant volume recorded.

Preliminary Experiments.—In a series of decompositions carried out with gas direct from the cylinder, without intermediate condensation, somewhat discordant results were obtained. The decomposition rate was found to vary considerably, depending upon the history of the platinum wire between successive experiments, *e.g.*, on the time during which vacuum was maintained, and on intervals elapsing between operations. By adopting a uniform practice in these details the difficulty was largely overcome, but variations were always liable to occur after any interruption, and results could only be taken as truly comparable when the " rapid " and " slow " methods were used alternately, in quick succession.

" Rapid " and " slow " experiments with the unactivated wire, in which the ammonia used was (1) synthetic, (2) gas-works, (3) quicklime-dried, and (4) undried, gave substantially identical results for the rate of decomposition.

Activation of the Wire.—Attempts were then made to activate the wire by the methods described by Baly and Duncan.

The first method, in which the wire was alternately heated and cooled to about 500° for some hours, failed to produce the results claimed. Baly and Duncan do not refer to any actual measurements of wire temperature, but in the present work temperatures were roughly estimated by the brightness of glow, and, both in activation and decomposition experiments, a range of temperatures was employed (*e.g.*, 600—1100° for decomposition) which must certainly have included such values as were used by those authors. This first activation process was carried out both in air, at atmospheric pressure, and in a vacuum (Baly and Duncan do not state the medium).

The second method, that of heating the wire to bright redness in a stream of air and ammonia until its temperature begins to rise and it continues to glow when the current is switched off, was also tried. In carrying out this process, difficulties arose from the fact that traces of ammonium nitrate, formed during the initial stages of the ammonia oxidation, condensed on the walls of the vessel. This caused a negative pressure drift after admission of ammonia for the decomposition experiments, owing to the solubility of ammonia in the nitrate, and a positive drift after the decomposition, due to the release of ammonia from the solution when its partial pressure in the gas phase was reduced. This could be allowed for to some extent, but the most satisfactory, though time-consuming, method was to remove the wire after activation and clean the vessel, taking care not to expose the wire to treatment likely to impair its activity, and then to replace it. That this cleaning did not affect the activity was shown by the fact that, after it had been carried out, the wire was capable of showing the " after-glow " effect on being heated for a few seconds in an air–ammonia mixture.

So far, no success has attended repeated attempts to activate a wire so that it behaves differently towards the rapidly and the slowly formed gas. Several wires have been tried, the temperatures during activation have been varied, various proportions of air and ammonia have been used, and ammonia–oxygen mixtures have also been employed. The time of activation by this second method has been prolonged up to 3½ hours after the first appearance of the after-glow.

Experiments have been made in which the ammonia has been distilled backwards and forwards slowly up to eight times through the lime tubes (between bulb A and bulb E), in case it might otherwise retain sufficient moisture to annul the effect under investigation, for, according to Baly and Duncan, water vapour can render inactive ammonia active. No difference in decomposition rate resulted.

The wire used was of ordinary commercial platinum; and since this showed the usual signs of being susceptible to such activation as rendered it suitable for ammonia oxidation, it does not appear likely that it contained any impurity that would unfit it for demonstrating the effect noted by Baly and Duncan.

Results.

Data obtained with five different wires are given below. The first column of each table contains observed values (C) of the current in amps.; cols. 2 and 3 show the pressure increases (in cm. of xylene) P_S and P_R for slow and rapid evaporation, respectively; cols. 4 and 5 give the corresponding calculated percentage decompositions, x_S and x_R (corrected, see below); and in the last column is given E, the percentage difference (to the nearest 0·1 unit) between the values of x_S and x_R, this difference being reckoned positive when the decomposition value is greater for slowly evaporated ammonia, *i.e.*, when it is such as to tend to confirm Baly and Duncan's observation.

Since it was impossible always to get a pair of identical values for C for the corresponding slow and rapid experiments, in all cases where these differed the values of x_R given in col. 5 have been calculated so as to correspond to a current value equal to that in the slow evaporation. The necessary corrections were obtained graphically from the values of dx/dC at various values of C. Whenever the observed values of the current in corresponding "slow" and "rapid" experiments differed by more than 0·002 amp., the observations were rejected. In 41 out of the 86 observations herein recorded, the C_{rapid} and C_{slow} values were actually identical, and the correction necessary in the other cases was in only one case greater than 2% of the value of x_R.

(*a*) Wire No. 1, activated by alternate heating and cooling to about 500° for 4 hours.

C.	P_S.	P_R.	x_S.	x_R.	E.
		(1)			
1·872	16·44	16·03	2·16	2·13	+1·5
1·896	18·14	18·78	2·39	2·47	−3·3
1·942	22·69	22·61	2·99	2·94	+1·6
1·984	29·38	29·14	3·87	3·75	+3·1
1·990	30·96	31·33	4·07	4·06	+0·2
		(2)			
1·882	17·00	17·09	2·24	2·26	−0·9
1·952	23·76	23·60	3·13	3·10	+1·0
1·968	26·65	26·50	3·51	3·47	+1·1
1·992	32·26	32·99	4·24	4·34	−2·4
		(3)			
1·870	16·02	16·21	2·11	2·13	−1·0
1·922	20·40	20·08	2·68	2·62	+2·3
1·972	26·55	26·86	3·49	3·56	−2·0
1·994	31·34	31·49	4·12	4·14	−0·5
		(4)			
1·858	15·12	15·01	1·99	2·00	−0·5
1·894	18·10	18·66	2·38	2·44	−2·5
1·932	21·36	21·11	2·81	2·78	+0·7
1·972	27·68	27·39	3·64	3·62	+0·6
1·996	35·74	35·66	4·70	4·69	+0·2

(*b*) Wire No. 2, after 2 hours' activation by "ammonia oxidation" method.

C.	P_S.	P_R.	x_S.	x_R.	E.
		(1)			
1·874	15·06	15·82	1·98	2·06	−4·0
1·894	16·47	16·30	2·17	2·16	+0·5
1·954	22·31	22·79	2·94	3·00	−2·0
1·998	32·60	33·48	4·30	4·28	+0·5
		(2)			
1·916	18·34	18·22	2·41	2·39	+0·8
1·954	22·67	22·00	2·98	2·92	+2·0
1·998	32·07	31·95	4·22	4·30	−1·9
		(3)			
1·888	15·92	15·64	2·09	2·08	+0·5
1·944	20·97	20·82	2·76	2·75	+0·4
1·998	32·51	33·34	4·28	4·27	+0·2
		(4)			
1·936	20·35	20·87	2·68	2·72	−1·5
1·954	22·68	22·36	2·98	2·94	+1·3
1·972	24·95	24·57	3·28	3·28	±0·0
1·988	27·50	27·61	3·62	3·70	−2·2
2·006	35·93	35·79	4·73	4·71	+0·4

(*c*) Wire No. 3, activated by heating and cooling, followed by 2 hours' ammonia-oxidation treatment.

C.	p_S.	p_R.	x_S.	x_R.	*E*.
		(1)			
1·936*	20·92	20·60	2·75	2·74	+0·4
1·940*	21·44	21·65	2·82	2·85	−1·0
1·946	22·73	22·50	2·99	2·92	+2·3
1·984	29·09	28·67	3·83	3·73	+2·6
1·988	30·10	30·24	3·96	4·03	−1·7
1·994*	31·78	31·42	4·18	4·13	+1·2
		(2)			
1·938	21·02	20·77	2·76	2·73	+1·2
1·942	21·74	21·89	2·86	2·88	−0·7
1·982	27·85	28·19	3·66	3·75	−2·4
1·996	32·16	31·66	4·23	4·22	+0·2
		(3)			
1·894*	17·24	17·20	2·27	2·23	+1·7
1·920*	19·95	19·57	2·63	2·64	−0·4
1·954*	23·56	23·50	3·10	3·09	+0·3
1·970	25·75	25·98	3·39	3·39	±0·0
1·984	28·74	29·31	3·78	3·86	−2·1
		(4)			
1·890	17·27	17·14	2·27	2·29	−0·9
1·916	19·29	19·48	2·54	2·60	−2·2
1·950	23·80	23·04	3·13	3·07	+2·3
1·974	26·42	26·31	3·48	3·46	+0·6
1·984	29·86	30·24	3·93	3·98	−1·2

(*d*) Wire No. 4, activated by oxidation method for about 2 hours in air–ammonia mixture, and later for 1 hour in oxygen–ammonia mixture.

C.	p_S.	p_R.	x_S.	x_R.	*E*.
		(1)			
1·870	16·08	16·27	2·12	2·14	−0·9
1·948	23·46	24·01	3·09	3·16	−2·3
2·006	37·38	37·12	4·92	4·88	+0·8
		(2)			
1·860	15·51	15·78	2·04	2·05	−0·5
1·904	19·32	19·39	2·54	2·55	−0·4
1·986	30·34	30·30	3·99	4·01	−1·7
1·986	30·42	30·06	4·00	3·95	+1·2
		(3)			
1·880*	17·24	16·69	2·27	2·22	+2·2
1·894*	18·32	18·39	2·41	2·44	−1·3
1·936	22·20	22·68	2·92	2·96	−2·0
1·966	25·24	25·03	3·32	3·33	−0·3
		(4)			
1·862	16·92	16·20	2·23	2·15	+3·6
1·910	20·02	20·52	2·63	2·69	−2·2
1·972	27·20	27·38	3·58	3·55	+0·8
1·990	34·25	34·16	4·51	4·49	+0·4
2·002	36·36	36·60	4·78	4·80	−0·4

(*e*) Wire No. 5, activated for 3½ hours by oxidation method.

		(1)			
1·922	14·77	15·14	1·94	1·99	−2·5
1·956*	15·26	15·31	2·01	2·01	±0·0
1·988	15·74	15·95	2·07	2·10	−1·4
2·046*	17·20	17·33	2·26	2·27	−0·5
2·070	17·64	17·49	2·32	2·29	+1·3
		(2)			
1·926	14·92	14·81	1·96	1·95	+0·5
1·944†	15·10	15·42	1·99	2·03	−2·0
1·970†	15·53	15·48	2·04	2·04	±0·0
2·024	16·57	16·79	2·18	2·20	−1·4
2·056	17·16	17·02	2·26	2·24	+0·9
2·148	20·53	20·13	2·70	2·66	+1·5
		(3)			
1·950	15·22	15·24	2·00	2·00	±0·0
1·984*	15·73	15·40	2·07	2·03	+1·9
2·058*	17·28	17·45	2·27	2·28	−0·5
2·094	18·11	18·30	2·38	2·42	−1·7
2·134*	19·65	19·32	2·59	2·54	+1·9
		(4)			
1·934†	14·90	15·23	1·96	2·00	−2·0
1·990†	15·96	15·74	2·10	2·08	+0·9
2·032	16·80	16·85	2·21	2·21	−0·4
2·088	17·81	18·04	2·34	2·37	−1·3
2·110†	18·64	18·90	2·45	2·48	−2·8
2·168	21·58	21·30	2·84	2·80	+1·4

* In these experiments the contents of the evaporation vessel were allowed to evaporate completely.

† In experiments marked thus, the ammonia was distilled several times through the drying tubes (see p. 4).

In the tables, the experiments are classified according as the ammonia was (1) synthetic, direct from cylinder; (2) synthetic, dried by passing once over lime (except those marked †); (3) gas-works, direct from cylinder; (4) gas-works, dried as in (2).

Summary of Results.

Kind of ammonia used.	Total no. of expts.	No. of expts. giving *positive* effect, and average value of effect.	No. of expts. giving *negative* effect, and average value of effect.
Synthetic (undried)	22	12, +1·3%	10, −1·9%
Synthetic (dried)	20	10, +1·0%	10, −1·4%
Gas-works (undried)	19	9, +1·3%	10, −1·2%
Gas-works (dried)	25	12, +1·1%	13, −1·5%

Discussion and Conclusions.

According to Baly and Duncan, rapidly evaporated ammonia showed a decrease in reactivity, compared with slowly evaporated, of from 25% to 50%, the higher value being obtained for low temperatures of the reaction wire. The above data do not in any way confirm their results : if anything, they establish a very small negative effect, but this may be ascribed to some systematic error in the method. In the present work, the " rapid " experiments were in nearly every case made directly after the " slow," whilst short intervals separated the latter from the succeeding " rapid " ones.

Baly and Duncan state that " the addition of water vapour *very greatly* increases the amount of decomposition by a definite amount of energy." The present results do not confirm this observation. It should be pointed out, however, that Baly and Duncan do not specify the degree of wetness or dryness necessary to establish this difference, and the variation in moisture content may have been greater in their samples. They attribute the effect which they observed to the existence of two molecular species in equilibrium in liquid ammonia, one of less energy content than the other, and they consider that, whereas in slow evaporation all molecules assume the more active form on evaporation, in the case of rapid ebullition the balance between active and inactive phases to some extent persists in the gaseous state.

The maintenance of this kind of metastable equilibrium in a gas phase seems somewhat doubtful. The fact that a heterogeneous decomposition was involved in testing the " reactivity " of the gas suggests at once that the effect was due to some variation of the catalyst surface. Briscoe (*Ann. Report*, 1922, **19**, 37) points out that ammonia dried over quicklime may retain a relatively large amount of moisture, and in view of Mulliken's statement (*J. Amer. Chem. Soc.*, 1922, **44**, 2389), that rapid irreversible distillation may effect partial separation even of the constituents of a constant-boiling mixture, he suggests that the ammonia gas formed by very rapid evaporation may have been appreciably the drier. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 268) favours this explanation, but the negative results of the present investigation do not support it.

Baly and Duncan refer to a streaming method of filling their vessel, and do not mention prior exhaustion of the latter. If air, or products of a previous decomposition, were present before the ammonia was admitted, it appears possible that, owing to eddies set up, very rapid streaming might result in their not being so completely displaced as by the slow passage of the same quantity of ammonia, and that the presence of adsorbed residuary gases on the wire might inhibit the reaction. It is noteworthy that Baly and Duncan found the greatest effect for low wire temperatures, at which adsorbed gas would be more firmly held.

It is concluded from the results of the present investigation that the effect observed by Baly and Duncan was dependent upon factors not explicitly defined in their paper, and did not result from the existence of different phases of gaseous ammonia.

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