RATE OF ESCAPE OF AMMONIA FROM AQUEOUS SOLUTION.

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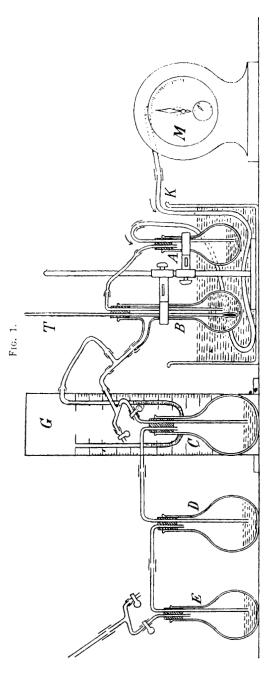
# LIV.—Rate of Escape of Ammonia from Aqueous Solution.

By Edgar Philip Perman, D.Sc.

In a recent paper on "Rate of Escape of Gases from Solutions of varying Concentration" (Trans., 1895, 67, pp. 868 and 983), the author has shown that, if a current of air is aspirated at a uniform rate through an aqueous solution of ammonia, the amount of ammonia in solution at any time t mins, from the beginning of aspiration is accurately represented by the equation  $\log q = a + bt$ , where q = amount of ammonia in solution; a and b are constants.

It was suggested by Mr. Vernon Harcourt that it would be better to measure the volume of air passing through the solution by means of a meter, instead of measuring the time of aspiration. A meter procured from Messrs. Alexander Wright and Co. was tested by aspirating measured volumes of air through it at varying rates, and also by forcing air through it. The results of these experiments proved the probable error of the meter to be less than 1 per cent.

Some experiments were then made to discover whether the formula  $\log q = a + bt$  could be replaced by  $\log q = a + bV$ , V = vol. of air (in litres) aspirated through the solution. The apparatus was similar to that used in the previous research, except in the following particulars; two sets of absorption flasks were used, so that the air-current could be passed through either set by means of two T-pieces and four clips, Fig. 1, p. 512. A thermometer, T, divided to 0.1°, was fixed into the aspiration flask B by means of a cement of litharge and glycerol. The air passed first through the meter M, then through a lead pipe K, coiled



in the dish of water, to the first flask A, which contained water so as to saturate the air with aqueous vapour, and to make up for loss of water by evaporation in B. B contained the ammonia solution; its capacity was a little more than 50 c.c., thus leaving very little spare space, 50 c.c. being the amount of the solution always used. C contained a measured quantity of standard sulphuric acid solution, and D and E contained distilled water. Nearly the whole of the ammonia drawn off was absorbed by the acid in C, only traces were found in D and E, and the total amount of ammonia was ascertained to be equal to that taken at the beginning of the experiment.

As it was found that the thermometer fell  $0.5^{\circ}$  or more in a few minutes after beginning the aspiration, the first portion of ammonia was not estimated; as soon, however, as the temperature became constant, the air current was directed through the other set of flasks, and the ammonia absorbed was afterwards estimated. In some of the experiments, a barrel was used as an aspirator, but the water pump and the regulator were always used with a quick air current. The following numbers were obtained with a current of air of 1.130 litres per min.

Temp. of solution 13.4°.

Vol. of air aspirated.*	$NH_3$ in solution $(q)$ .	$Log\ q\ (observed).$	$Log \ q \ (cal.).$
0 litre	$3.686~\mathrm{grams}$	0.5666	(0.5666)†
7	3.406	0.5322	0.5332
15	3.117	0.4937	0.4951
24	2.823	0.4507	0.4522
31	2.619	0.4181	0.4179
40	$2 \cdot 377$	0.3760	(0.3760)
	a = 0.5666, b = -	- 0.004765.	, ,

This was one of the quickest currents used, and the experiment was a difficult one, owing to the short time available for recharging the flasks with acid solution. The aspiration was continuous throughout the experiment; while the absorption of ammonia was going on in one set of flasks, the other set was being recharged.

These results show that the values of  $\log q$  are accurately given by the equation  $\log q = a + bV$  under the conditions of the experiment, or it may be written  $\log q = a - bV$ , when b becomes positive. The conditions were varied in several different ways in order to discover the relation between them and the rate of escape of the ammonia.

<sup>\*</sup> The volumes given are those read on the meter.

 $<sup>\</sup>dagger$  The numbers in brackets were taken as data for finding the value of b, and from this the other values of  $\log q$  were calculated.

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# Variation of Concentration.

In order to obtain the greatest possible variation in the concentration of the ammonia solution, 50 c.c. of strong solution were taken, and the ammonia drawn off until only about 1 gram remained; although it was found impossible to keep the temperature very constant, owing to the rapid loss of heat caused by the evaporation of the ammonia, it was maintained as nearly as possible at 20° by adding hot water when necessary. The results obtained are here given.

### Concentrated Ammonia Solution.

Temperature of solution, 19.9°. Bar., 766 m.m. Rate of air current, about 0.3 litre per minute. Temperature of air passing through the meter, 15°.

Vol. of air aspirated.	$NH_3$ in solution $(q)$	Log q.	$\Delta log \ q/\Delta V$
0 litres	14.207 grams	1.1525	0.0414
<b>2</b>	11.742	1.0697	0.0263
5.5	9.496	0.9775	0.0186
11.5	7.345	0.8660	0.0141
22	5.218	0.7175	0.01104
42	3.138	0.4966	0.00919
62	2.055	0.3128	0.00851
89	1.211	0.0831	0.00991

If the equation  $\log q = a - bV$  held for all concentrations of the solution, the values of  $\Delta \log q/\Delta V$  would be constant, but the value is seen to increase largely with the concentration. No simple formula has been found which will express the relation between q and V in the case of concentrated solutions. The experimental results are probably not very accurate, owing to the difficulty in keeping the temperature of the solution constant.

The ammonia solution used for further experiments contained about 70 grams of ammonia per litre at a temperature of  $15^{\circ}$ . No attempt was made to preserve the solution at exactly the same concentration, as small alterations make no difference in the value of b found from the experiments. It has already been shown that, with such a solution, more than 1 gram of ammonia may be removed without causing any discrepancy in the results calculated from the logarithmic formula, and this will be confirmed by many more results given later on.

# Variation in the Rate of Air-current.

The two following experiments were carried out at a temperature of  $13.4^{\circ}$  with very different rates of air-current. The numbers calculated

from the logarithmic formula are seen to express well the experimental results.

Rate of air-current, 0.637 litre per minute. Temperature of ammonia solution,  $13.4^{\circ}$ . Pressure in aspiration flask, 758 mm.

Vol. of air aspirated.	$NH_3$ in sol. $(q)$ .	$log \ q \ (observed)$ .	$log \ q \ (cal.).$
0 litres	$3.678~\mathrm{grams}$	0.5656	(0.5656)
6	<b>3·43</b> 9	0.5364	0.5368
12	3.217	0.5075	0.5081
18	3.010	0.4786	0.4793
24	<b>2</b> ·819	0.4501	0.4506
30	2.641	0.4218	(0.4218)

Rate of air-current, 0.20 litre per min. Temp. of ammonia solution, 13.4°. Pressure in aspiration flask, 750 mm.

Vol. of air aspirated.	$NH_3$ in sol. $(q)$ .	$log \ q \ (observed).$	log q (cal.).
0 litres	3.649  grams	0.5622	(0.5622)
6.05	3.413	0.5331	0.5325
$12 \cdot 10$	3.194	0.5043	0.5027
18.15	2.980	0.4742	0.4730
$24 \cdot 20$	2.781	0.4442	0.4433
30.25	2.591	0.4135	(0.4135)

The rate of escape of the ammonia, when any definite amount q grams of ammonia is in solution, is found by differentiation of the expression  $\log q = a - bV$  to be bq; that is, the amount of ammonia that would be removed by passing 1 litre of air through the solution, supposing the strength of the solution to remain constant, is bq grams; b is therefore a measure of the rate of escape of the gas from any solution as long as the logarithmic law holds good; it is, in fact, the amount of ammonia that would be drawn off by 1 litre of air, supposing the solution to always contain 1 gram of ammonia.

A number of experiments were carried out under conditions similar to those already described, and the process was simplified by making one continuous aspiration after the temperature of the solution had become constant; b was found at once from the expression  $b = (a - \log q) \div V$ , a being the logarithm of the amount of ammonia in the solution when the aspiration commences, and q the amount at the end. The pressure of the gases in the aspiration flask was read by means of a pressure-gauge G, Fig. 1, (p. 512), combined with the reading of the barometer. The volume of air passed through the solution was in every case reduced to the pressure in the aspiration flask and the temperature of the solution before calculating the value of b. The air was assumed to become saturated with aqueous vapour on passing through the meter; that this is the case was proved by testing the

meter with air passing in from a dry room, and again with air saturated with aqueous vapour by bubbling through three flasks containing water. The results show no difference in the two cases.

Barrel.	Metcr.
5 litres	4.97 litres, dry
5	4.99 ,, saturated
5	4·93 ,, dry
5	4.93 saturated

In calculating b, the volume read on the meter was corrected to the corresponding volume of dry air, and then reduced to the temperature and pressure of the solution. It may be said that the volume of air at its partial pressure in the aspiration flask should be reckoned; but the partial pressure is not constant, owing to the escape of the ammonia, and, moreover, if it could be calculated in that way, equal volumes read on the meter would not represent equal volumes in the aspiration flask, and the logarithmic equation would not hold at all. To take an example, the amount of ammonia drawn off by 20 litres of air in an experiment at 20° was 0.89 gram, which at the temperature of the solution would occupy as a gas a volume of 1.26 litres; this gives as the mean pressure of the ammonia present in the mixture of ammonia and air (neglecting the aqueous vapour) 1.26/20 = 0.063atmosphere; the actual pressure of the ammonia will, however, decrease as the ammonia is drawn off, and will be roughly proportional to the strength of the solution, as shown by the experiments of Roscoe and Dittmar on the solubility of ammonia at different pressures. strength of the ammonia solution varies about one-fourth; therefore, the pressure of the ammonia in the gaseous mixture will vary about 0.063/4 = 0.016 atmosphere, an amount which would affect the experimental results to a very appreciable extent. It would seem that the molecules of air only are effective in carrying off the ammonia. However this may be, the method of calculating the volumes adopted is the most convenient for obtaining comparable results under various conditions.

For the temperature,  $13.4^{\circ}$ , the following values of b were obtained; the experimental data are given in the Appendix (p. 526).

Rate of air current.	<i>b.</i>	Burometer.
1.271 litres per min.	0.00477	750 mm.
1.140	0.00480	-
0.918	0.00478	771
0.850	0.00484	742.5
0.653	0.00490	766
0.637	0.00490	758

Rate of air current.	b.	Barometer.
0.400 litres per min.	0.00470	761 mm.
0.394	0.00483	743
0.500	0.00499	752
0.180	0.00498	758
0.138	0.00475	761
Me	an 0:00484	

Individual results show considerable variation, but no connection can be traced between the values of b and the rates of air current, or between the values of b and barometic pressure.

In order to make certain of the latter point, a series of experiments was carried out with the ammonia solution under various pressures.

# Variation of Pressure.

In order to aspirate air at less than atmospheric pressure through the ammonia solution, another regulator containing mercury was substituted for the water regulator; it was made of a long, wide glass tube. A stopcock was placed between the flask A (Fig. 1) and the meter in order to regulate the air current, and at the same time the pressure in the aspiration flask. Otherwise, the arrangement of the apparatus was exactly as before. The air passing through was measured by the meter at atmospheric pressure. Great care was taken to avoid any leak between the aspiration flask and the meter. The following results were obtained by aspirating in stages.

# Pressure in aspiration flask, 623 mm.

Temperature of solution 19.9°. Rate of air-current, 0.62 litre at the reduced pressure.

Vol. of air aspirate	d,		
as read on meter.	$NH_3$ in solution $(q)$ .	log q.	Calculated.
0 litres	$3.224~\mathrm{grams}$	0.5084	(0.5084)
5	2.936	0.4678	0.4675
10	2.676	0.4275	0.4266
15	$2\ 433$	0.3861	0.3855
20	2.215	0.3454	0.3447
25	2.013	0.3038	(0.3038)

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# Pressure in aspiration flask, 429 mm.

Temperature of solution, 19.9°. Rate of air-current, 0.40 litre per min.

Vol. of air aspirate	d. $NH_3$ in solution $(q)$ .	log q.	log q (cal.).
0 litres	3.419  grams	0.5339	(0.5339)
3	3.131	0.4957	0.4960
6	2.874	0.4585	0.4582
9	2.641	0.4218	0.4203
12	2.417	0.3833	0.3825
15	2.211	0.3446	(0.3446)

The logarithmic law was thus proved to hold for large variations of pressure, and some further results were obtained by the short method.

# Temperature of the solution, 19.9°.

Pressure in aspiration flask.	b.	Rate of air-current.
941 mm.	0.00642	0.50 litre per min.
623	0.00666	0.62
591	0.00655	0.50
513	0.00666	0.40
435	0.00685	0.50
429	0.00702	0.40

The first result on the table, at a pressure higher than atmospheric, was obtained by forcing air through the solution by means of a waterair pump used as a condenser. The outlet of the pump was connected with a stoneware barrel, and the water was run out by a tube at the To keep the pressure constant, the excess of air was made to bubble through a tube dipping a certain depth under mercury. The meter was connected to the last flask in the series with a stopcock between them, so that the air was measured by the meter at atmospheric pressure. In calculating the values of b, the volumes of air read on the meter (at atmospheric pressure) were reduced to the pressure in the aspiration flask as given by the gauge and the barometer. These results show that a variation of 50 mm. in the pressure produces an inverse variation of about 1 per cent, in the value of b. The effect of variation of atmospheric pressure on the value of b may therefore be neglected.

# Variation of Temperature.

It has been already mentioned that the temperature of the solution was noted by means of a thermometer, divided into tenths of a degree, cemented into the aspiration flask. The thermometer, which was obtained from Messrs. C. E. Müller and Co., was carefully tested; the following readings were obtained.

Thermometer reading.	Rea	l temp.
100· <b>55</b> °	100·15°	(boiling water)
34.9	34.8	( ,, ether)
0.13	0.0	(melting ice)

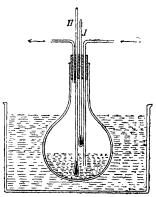
Some time after the experiments in which this thermometer was used had been completed, it was compared with a thermometer which had been directly compared with an air thermometer; the zero point was then  $0.3^{\circ}$ ; allowing for this alteration, the temperatures agreed to  $0.1^{\circ}$  up to  $50^{\circ}$ . The real temperatures were therefore taken as  $0.1^{\circ}$  lower than the thermometer reading, up to  $40^{\circ}$ ; above this temperature, another thermometer was used. The latter thermometer was compared with a simple form of constant-volume air-thermometer, and also with the boiling points of carbon bisulphide and water. The numbers obtained are as follow.

	Real temp.	Thermometer reading.
M. p. of ice	$0.0$ $\circ$	0·2°
Air thermometer	11.3	11.5
,,	16.6	16.9
**	16.4	16.6
,,	36.5	36.6
,,	28.6	28.8
B. p. of CS <sub>2</sub> at 750 mm.	45.85	46.1
,,	46.1	46.4
B. p. of H <sub>2</sub> O 744 ,,	99.4	99.95

If  $0.2^{\circ}$  is subtracted from the thermometer reading below  $30^{\circ}$ , and  $0.3^{\circ}$  between  $30^{\circ}$  and  $50^{\circ}$ , the remaining error is never more than  $0.1^{\circ}$ . At  $60^{\circ}$ , Fig. 2.

An experiment was made in order to determine whether the air and other gases leaving the solution are at the same temperature as the solution itself, the operation being conducted in a flask, Fig. 2, furnished with two thermometers, I and II, one to register the temperature of the solution and the other that of the gas. The results showed that the difference between the temperature of the solution and that of the gases leaving it was not more than 0.2°.

0.4° was subtracted.



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Various temperatures up to  $40^{\circ}$  were employed with the apparatus Fig. 1; the temperature was kept constant by the addition of hot water when necessary, the pan being surrounded by a flannel jacket for the higher temperatures. The temperature was allowed to fall  $0.2^{\circ}$ , and then hot water was added until it rose  $0.2^{\circ}$  above the stated temperature, then allowed to fall to  $0.2^{\circ}$  below this temperature, and so on. The logarithmic law was found to hold good up to  $46^{\circ}$ , as shown by the following experiments.

Temperature of ammonia solution, 39.9°. Rate of air-current, 0.4 litre per min. Pressure in aspiration flask, 737 mm.

Vol. of air aspirated.	$NH_3$ in solution $(q.)$	log q.	$log \ q \ (cal.).$
0 litres	3.273  grams	0.5149	(0.5149)
3	2.889	0.4607	0.4616
3	2.555	0.4074	0.4083
3	$2 \cdot 256$	0.3533	0.3550
3	2.004	0.3018	(0.3018)

Temperature of ammonia solution, 46·1°. Rate of air-current, 0·4 litres per min. Pressure in aspiration flask, 769 mm.

Vol. of air aspirated.	$NH_3$ in solution $(q_{\cdot})$	log q.	log q. (cal)
0 litres	1.1651 grams	0.0663	(0.0663)
3	0.8626	1.9358	$\bar{1}.9324$
3	0.6394	$\bar{1}.8058$	1.7985
3	0.4666	1.6689	1.6646
3	0.3393	$\bar{1}.5306$	$(\bar{1}.5306)$

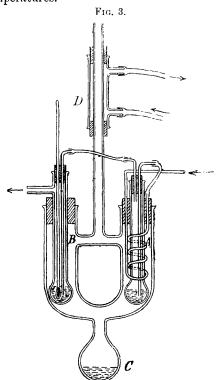
This last experiment was carried out with different apparatus from that previously used; the aspiration flask B. contained only about 25 c.c., and both it and the flask A containing water were jacketted by means of carbon bisulphide vapour, Fig. 3. The carbon bisulphide was boiled in the bulb C, and condensed at D. This arrangement did not give such accurate results as the other, for two reasons, namely (1), only half the amount of ammonia solution was used; (2), the temperature could not be maintained quite constant; it rose slowly during the experiment, owing to the decrease in the rate of evaporation of the ammonia; in the experiment of which the results are given above, the temperature rose  $0.4^{\circ}$ ; the mean temperature is given.

Similar experiments were made at a higher temperature, using chloroform instead of carbon bisulphide, but in that case the logarithmic law did not hold even with considerably more dilute solutions. This is proved by the following results.

Temperature of the solution, 60·1°. Rate of air-current, 0·05 litre per min. Pressure in aspiration flask, 758 mm.

Vol. of air aspirated.	$NH_3$ in solution $(q)$ .	log q.	△ log q.
0 litres	$1.645~\mathrm{grams}$	0.2162	0.0673
0.5	1.409	0.1489	0.0618
1.0	1.222	0.0871	0.0533
1.5	1.081	0.0338	0.0479
$2 \cdot 0$	0.968	$\overline{1}.9859$	0.0413

The values of  $\Delta \log q$  decrease rapidly, instead of remaining constant as at lower temperatures.



The following experiment was carried out with a much more dilute solution, but with a similar result.

Temperature of the solution, 60·2°. Rate of air-current, 0·1 litre per min. Pressure in aspiration flask, 759 mm.

Vol. of air aspirated.	$NH_3$ in solution $(q)$ .	log q.	$\triangle log q$ .
0 litres	$0.5998~\mathrm{gram}$	1.7780	0.0400
0.5	0.5442	$\bar{1}$ :7358	0.0422
1.0	0.4985	$\bar{1}$ :6977	0.0381
1.5	0.4588	Ĭ·6616	0.0361

Using a still more dilute solution,  $\Delta \log q$  became more regular, but there is evidently a large experimental error.

Temperature of the solution, 59.7°. Rate of air-current, 0.1 litre per min. Pressure in aspiration flask, 745 mm.

Vol. of air aspirated.	$NH_3$ in solution $(q)$ .	log q.	$\Delta \log q$ .	log q (cal.).
0 litres	0.3370 gram	$\overline{1}$ . $\overline{5276}$	0.0624	$(\bar{1}.\bar{5}276)$
1	0.2919	1.4652	0.0650	1.4580
2	0.2513	Ī·4002	0.0724	1.3884
$rac{3}{4}$	0.2127 $0.1803$	$ar{1} \cdot 3278 \ ar{1} \cdot 2560$	0.0718	$\frac{1.3188}{1.2492}$
5	0.1513	$\frac{1}{1} \cdot 1798$	0.0762	$(\bar{1}.1798)$

A dilute solution of ammonia, at a high temperature, behaves in a similar way to a concentrated solution at a lower temperature; the pressure of the ammonia becomes so great, that the air passing through the solution takes up far more ammonia than would be required by the logarithmic formula. This formula has been proved to hold, for solutions of moderate concentration, between  $0^{\circ}$  and  $46^{\circ}$ ; between these limits, therefore, the simplified method of finding the value of b, described on page 515, may be used; a large number of experiments were carried out in that way at different temperatures.

The following are the results obtained both by the full and the short methods (those at 13.4° have already been given).

### Temperature, 0°.

Rate of air-current per minute.	<i>b</i> .	Pressure in aspiration flask.
0.825 litre	0.00243	741 mm.
0.605	0.00258	753
0.370	0.00258	747
0.179	0.00270	745
Mean	0.00261.5	

Temperature, 13.4° (see page 516).

# Temperature, 19.9°.

Rate of air-current per minute.	b.	Pressure in aspiration flask.
0.879 litre	0.00643	760 mm.
0.616	0.00648	<b>7</b> 59
0.500	0.00650	770
0.421	0.00665	
0.400	0.00655	766
0.319	0.00645	760
0.520	0.00666	764
0.180	0.00660	748
Mean	ı 0·00654	

### Temperature, 29.9°.

Rate of air-current per minute.	b.	Pressure in aspiration flask.
0.860 litre	0.01023	761 mm.
0.433	0.01043	<b>7</b> 55
0.295	0.01034	<b>7</b> 58
Meas	a 0:01033	

# Temperature, 39.9°.

Rate of air-current per minute.	<i>b</i> .	Pressure in aspiration flask.
0.822 litre	0.01622	$754  \mathrm{mm}.$
0.460	0.01612	<b>7</b> 66
0.400	0.01670	740
0.292	0.01650	765
Mean	ı 0.01638	

### Temperature, about 46°.

i i	Rate of air-current		
Temperature.	per minute.	b.	Pressure.
45·9°	0·10 litre	0.02198	758 mm.
45.5	0.40	0.02227	767
46.0	0.40	0.02026	<b>769</b>
Mean 48.8	Mea	$n \ 0.02150$	

The values of b in the last series do not vary regularly with the temperature, and so the mean of the temperatures and the mean of the pressures have been taken, in order to obtain as accurate a result as possible. The mass of water present in the ammonia solution in the aspiration flask in these experiments was only half that in the experiments at lower temperatures. It has been shown that, if the mass of water remains constant, the rate of escape of the ammonia is proportional, within certain limits, to the amount of ammonia present. It may be inferred from this that, if the amount of water is altered, within certain limits, the rate of escape of the ammonia will be inversely proportional to the amount of water present, supposing the quantity of ammonia to remain constant. The following are the results of experiments made to prove this point.

	Vol. of solution		b $corrected$	b found when
$t^{\circ}$ .	taken (15°).	b.	to 50 c.c.	50 c.c.were used.
$19.9^{\circ}$	25 c.c.	0.01321	0.00660	0.00654
13.4	20	0.01245	0.00498	0.00485
13.4	20	0.01251	0.00500	0.00485

The agreement is very good with the 25 c.c. experiment, but not so good with the smaller volume when the experimental error was greater

The value of b obtained with the small flask in carbon bisulphide vapour was corrected in the same way, that is, it was halved.

At each temperature various rates of air-current were employed, but no certain connection has been traced between the rate of air-current and the value of b, although there appears to be a tendency for the latter to increase as the former decreases.

Attempts were made to discover some simple connection between the rate of escape of the ammonia, measured by b, and the temperature of the solution. After several trials, it was found that the relation is accurately represented by the equation  $\log b = a + \beta t$ , where a is a constant (namely,  $\log b$  at 0°),  $\beta$  a constant, and t the number of degrees in the temperature on the centigrade scale. The value of  $\beta$ , calculated between 0° and 39.9°, is 0.01997; the experiments at 46° are not so accurate, and are therefore not employed for this purpose. The results are given in the following table.

$t^{\circ}$ .	b.	log b.	$log \ b \ (cal.).$
$0_{\rm o}$	0.002615	$\bar{3}.4172$	(3.4175)
13.4	0.00485	$\bar{3} \cdot 6857$	$\bar{3}.6851$
19.9	0.00654	$\bar{3}$ ·8156	$\bar{3}.8149$
29.9	0.01033	2.0141	$\bar{2}$ ·0146
39.9	0.01638	$\bar{2}$ ·2143	$(\overline{2} \cdot 2143)$
<b>45</b> ·8	0.02150	$\mathbf{\bar{2} \cdot 3324}$	$\overline{2}$ ·3321

It will be seen that the agreement between the observed and calculated values is extremely close. There is no reason (except that of convenience) for reckoning the temperatures from zero; if absolute temperatures are taken, an exactly similar expression can be found.

It should be mentioned that no correction has been applied for the expansion of the ammonia solution on heating. The amount of expansion was, however, proved to be very small. The density of the solution made use of was found at different temperatures by weighing in a specific gravity bottle.

Temp.	Weight of $50 \ c.c.$	Vol. of 1 gram.
$0_{o}$	48.801 grams	1.025 c.c.
20.2	48.594	1.029
30.1	48.437	1.032
39.6	48.264	1.036

The total amount of expansion between 0° and 40° is thus only about 1 per cent., very little more than that of pure water. The mass of the water was the same in the experiments at different temperatures, and it is difficult to say what would be the nature of a correction for alteration in volume only. It appears, however, to be unnecessary.

It will be interesting to combine the two equations,  $\log q = a - bV$ , and  $\log b = a + \beta t$ . Let  $a = \log a'$ , and  $a = \log a'$ ,

thus  $q = a'(10)^{-bV}$ , and  $b = a'(10)^{\beta t}$ .

Therefore  $q = a' \cdot 10^{-\alpha' V \cdot 10\beta t}$ , or  $\log q = a - y$ , if  $\log y = a + \log V + \beta t$ . If a certain volume of air is aspirated through an aqueous ammonia

solution at a constant temperature (between 0° and 46°), the amount of ammonia left in solution can be at once calculated from the above expression.

q =amount of ammonia left in solution.

 $a = \log$  of amount of ammonia in the solution at the beginning of the aspiration.

 $a = \log \text{ of value of } b \text{ at } 0^{\circ}$ .

V = volume of air aspirated through the solution, reckoned as dry air at the temperature and pressure (by gauge) of the solution. passing into the solution, the air is saturated with moisture at the temperature of the solution.

 $\beta = a$  constant.

t =temperature of the solution in degrees centigrade.

In working out this expression, the mass of water has been assumed to be constant. If it varies, the equation  $\log q = a - bV$  will become  $\log q = a - Vb/m$  where m = mass of water present. It will only hold, however, within certain limits.

 $\log q = a - y$ ,  $_{
m final}$ equation then becomes where log  $y = a - \log m + \beta t + \log V$ .

If the ammonia solution were simply a mechanical mixture of water and ammonia molecules, the ammonia would be carried off according to the logarithmic equation,  $\log q = a - bV$ , just as if, for example, 10 c.c. of water were added to and mixed with a litre of ammonia solution, and then 10 c.c. of the solution were withdrawn, 10 c.c. more of water were added, another 10 c.c. of the solution withdrawn, and so on; then the amount q of ammonia present would be represented by the same expression,  $\log q = a - bV$ , V being the volume of water that had been added to (or withdrawn from) the solution. The ammonia is actually carried off by a current of air in this way from dilute solutions, but the rate of escape from a concentrated solution is far greater than required by this equation, probably owing to the less attraction (in proportion to the amount of ammonia present) between the water and the ammonia in concentrated solutions. The author is at present engaged in further experiments, the object of which is to discover the effect of the addition of various substances to the solution on the rate of escape of the ammonia. He is also investigating the vapourpressure of ammonia solution by a statical method. In conclusion, he

## PERMAN: RATE OF ESCAPE OF

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# Appendix.

# Temperature of solution, 0°.

Vol. of air in	Rate of $air$ -						
litres	current	<i>m</i>	Press. in		<b>.</b> .	* .	
read on	in	Temp.	aspiration		* $q_1$ in	$^*q_2\ in$	7
meter.	litres.	of $air$ .	flask.	Bar.	grams.	grams.	b.
27	0.825	$13^{\circ}$	$752 \mathrm{mm}$ .	752	3.643	3.153	0.00247
19	0.602	15	766	766	3.436	3.087	0.00262
20	0.370	15		-	3.666	3.275	0.00262
13.5	0.179	15	758	758	3.731	3.445	0.00275

# Temperature of solution, $13.4^{\circ}$ .

25	1.271	14	<b>75</b> 0	750	3.566	2.724	0.00477
40	1.140	12		_	3.686	$2 \cdot 377$	0.00480
34	0.918	11	771	771	3.707	2.549	0.00478
17	0.850	12	742.5	742.5	3.597	2.981	0.00484
19	0.653	16	766	766	3.537	2.870	0.00490
30	0.637	15	758	758	3.678	2.641	0.00490
21	0.400	15	761	761	3.492	2.788	0.00470
20.5	0.394	14	743	743	3.620	2.894	0.00483
30	0.200	14	752	760.5	3.649	2.591	0.00499
19	0.180	16	<b>7</b> 51	758	3.509	2.833	0.00498
12.8	0.138	15	761	761	3.648	3.175	0.00475

# Temperature of solution, $19.9^{\circ}$ .

<b>2</b> 5	0.879	17	760	760	3.558	2.465	0.00643
20	0.616	16	<b>75</b> 9	759	$3 \cdot 465$	2.576	0.00648
24	0.500	14	770	770	3.620	2.523	0.00650
17	0.421	17		-	3.614	2.792	0.00665
20	0.400	17	766	766	3.328	2.467	0.00655
20	0.319	21	<b>7</b> 60	760	3.319	2.484	0.00645
18	0.220	17	764	764	3.738	2.844	0.00666
18	0.180	17.5	748	755	3.323	2.529	0.00660

<sup>\*</sup>  $q_1$  and  $q_2$  are the quantities of ammonia in the aspiration flask at the beginning and end, respectively, of each experiment.

# Temperature of solution, 29.9°.

		10	meper wown	, 0, 00	200000000000000000000000000000000000000	•	
Vol. of air in	Rate of $air$ -						
litres	current		Press. in				
read on	in	Temp.	aspiration	<b>7</b> 1	$q_1$ in	$q_2 in$	7.
meter. $22$	litre. 0·860	of air. 18°	flask. 761 mm.	Bar. 761	$grams. \ 3 \cdot 241$	grams. 1.910	0.01023
	-						
$\frac{17.8}{21}$	0.433	19	755	755	3.450	2.235	0.01043
21	0.295	18	<b>7</b> 58	758	3.661	2.198	0.01034
		Tc	emperatur	e of so	lution, 39.9°		
12	0.822	16	754	754	2.562	1.591	0.01622
13	0.460	17	766	766	2.996	1.797	0.01612
12	0.400	19	740	740	3.273	2.004	0.01670
14	0.292	16	765	765	3.208	1.823	0.01650
	Small	asnirati	on flask.	Temr	perature of so	Jution.	45·9°.
	10 marc	aopurae	on jouisi.	1 onep	oralaro of sc	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	<i>b</i>
							2
4	0.10	16°	758 mm.	766	1.682	1.079	0.02198
		Tc	emperatur	e of so	lution, 45.5°		
4	0.40	13	767	772	1.613	1.025	0.02227
		T	'emperatur	e of so	olution, 46.0°	·.	
12	0.40	14	769	774	1.165	0.339	0.02026
14	0 10	1.1	100	117	1 100	0 000	0 02020
		Tc	emperatur	e of so	lution, 19.9°		
12	0.40	16	744	744	1.719	1.192	0.00660
		T	lemneratur	e of so	olution, 13·4	·	$\frac{2}{2}$
			1	,	ŕ		$\overline{5}b$
18	0.360	15			1.729	1.043	0.00498
18	0.314	18	758	758	1.760	1.067	0.00500
	Varia	tion of p	ressure.	Tempe	erature of soi	lution, 1	
26	0.50	18	941	769	3.349	2.457	0.00642
25	0.62	14.5	623	762	3.224	2.013	0.00666
18	0.50	16	591	763	3.339	2.356	0.00655
14	0.40	15	513	753	3.314	2.426	0.00666
11	0.50	13	435	760	3.336	2.457	0.00685
15	0.40	15	429	772	3.419	2.211	0.00702
10	0 10	10					0 00,02