

Citation:

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gous serum and is easily able to destroy a small quantity in a few days, even if the titre is very high.

To obtain an immunity for a longer time, a quantity of serum has to be injected, which the organism, even if it defends itself vigorously against the foreign serum, cannot destroy too soon. The disadvantage that is attached to the injection of a large quantity of serum, namely the developing of symptoms of serum disease, which are always temporary, is not of great importance when a perilous illness is to be prevented.

Relating to the passive immunization of the wounded against tetanus, which gave rise to our research, we came therefore to the conclusion that there is absolutely no cause to use for this purpose, as now commonly happens in our country, an antitetanus serum that contains in one c.c. 4 A.U.

The injection of 10 c.c. antitetanus serum with a titre of 2 A.U. deserves to be preferred, because in this way, an equal degree of immunity is produced as by injection of 5 c.c. antitetanus serum of 4 A.U., and the immunity lasts longer.

Moreover, the results of our experiments give an important indication concerning the immunization against diphtheria. Years ago, when in all countries diphtheria serum was used with a titre of about 100 A.U., it has been fixed empirically that the injection of 5 c.c. serum (= 500 A.U.) was sufficient to protect a child against diphtheria for about 3—4 weeks. Afterwards in some countries the titre of the diphtheria serum has been raised more and more. If now, — relying on the false supposition, that the duration of the immunity has nothing to do with the quantity of serum that is inoculated —, to prevent diphtheria, 1 c.c. diphtheria serum with a titre of 500 A.U. is injected into a child, expecting to get in this way the same result as formerly with the injection of 5 c.c. with a titre of 100 A.U., there is a great chance that the immunity, instead of 3 or 4 weeks, only lasts 1 week.

Chemistry. — “*On the Allotropy of the Ammonium Halides*”. III¹⁾.

By Dr. F. E. C. SCHEFFER. (Communicated by Prof. P. ZEEMAN.)

(Communicated in the meeting of Nov. 25, 1916).

§ 14. In § 1 I said that in the older literature statements occur which point to the occurrence of two different modifications of ammonium bromide and ammonium chloride, and that it has been demonstrated in a paper by WALLACE that ammonium bromide is

¹⁾ First paper. These Proc. XVIII p. 446. Second paper. These Proc. XVIII p. 1498.

enantiotropic. According to WALLACE's determinations the transition point lies at 109° . As it has, however, appeared to me when I repeated the experiments with ammonium chloride that the value that WALLACE gives, is considerably too low, I have determined the transition point of ammonium bromide in the same way as in the first paper. I already announced these experiments in my first paper in § 8, and I communicated the preliminary result that ammonium bromide possesses a transition point at 137° at the Natuur- en Geneeskundig Congres in April 1915¹⁾. I have, however, been obliged to postpone the full description of these experiments till now.

In 1916 there appeared two papers by SMITH and EASTLACK; in the former²⁾ they communicate that they discontinued the determination of the transition point of ammonium chloride at the publication of my first paper, but that they have continued the experiments with ammonium bromide. Their conclusion derived from determinations of the solubility in water is that the transition point lies at $137^{\circ}.3$. In the latter paper³⁾ it is stated that ammonium iodide does not possess a transition point between -19° and 136° .

In what follows I will briefly give the results of my investigation with ammonium bromide, which as appears from the above mentioned preliminary communication, agree with those of SMITH and EASTLACK, and those of ammonium iodide, which have yielded the transition point, which had not been found up to now.

The result obtained with ammonium iodide, has already been published by Mr. HOOGENBOOM in his Thesis for the Doctorate.⁴⁾

15. *Thermal determination of the transition point of ammonium bromide.*

The experiments described in §§ 15—18 have been carried out with ammonium bromide prepared from hydrogen bromide and ammonia. Hydrogen bromide was obtained by leading purified bromine (method MEERUM TERWOGT⁵⁾) with hydrogen over heated platinum; ammonia was obtained by fractionating liquid ammonia obtained from ammonia liquida and leading it into water.

When we try to determine the transition point of ammonium bromide in the well-known way through curves of heating and cooling, it appears that the conversion of the two modifications into

¹⁾ Handelingen van het 15e Ned. Nat. en Gen. Congr. (April 1915) p. 242 e.seq.

²⁾ Journ. Amer. Chem. Soc. **38**, 1261, (1916).

³⁾ Journ. Amer. Chem. Soc. **38**, 1500, (1916).

⁴⁾ Dissertatie Amsterdam (July 1916), p. 64 and 65.

⁵⁾ Dissertatie Amsterdam (Nov. 1904), p. 6 et seq.

each other goes so slowly that the temperature which remains constant is found much higher for heating than for cooling.

The limits found in this way for the transition point, are $\pm 124^\circ$ and 147° . The distance between them is, therefore, still greater than for ammonium chloride. (Cf. § 3).

The velocity of conversion can, however, just as for ammonium chloride, be increased by the addition of glycerine. (Cf. § 6). The limits between which the transition point must lie, are reduced in this case to $137^\circ.3$ and $139^\circ.5$. Hence also with the catalyzer the distance remains greater than for ammonium chloride. Experiments with glycol as catalyzer yielded $137^\circ.3$ and $140^\circ.1$.

16. Vapour pressure measurements.

I have determined the vapour tensions of the saturated solutions in an apparatus of the form as described by LEOPOLD¹⁾. No more than for NH_4Cl does the transition point express itself in the vapour

T A B L E 11.

t	p	$10^3 T^{-1}$	$\log p$	t (calc.)	Error	Series
98.1	43.1	2.6947	1.6345	98.0	+ 0.1	I
110.3 ⁵	63.6	2.6086	1.8035	110.5	- 0.1 ⁵	I
116.7 ⁵	76.6 ⁵	2.5657	1.8845	116.7 ⁵	0	I
126.0	99.8	2.5063	1.9991	126.0	0	I
128.8	107.9	2.4888	2.0330	128.8	0	II
129.3	109.1	2.4857	2.0378	129.2	+ 0.1	III
134.7	125.8	2.4528	2.0997	134.5	+ 0.2	II
136.3	131.8	2.4432	2.1199	136.2 ⁵	+ 0.0 ⁵	I
141.0	149.5	2.4155	2.1746	141.0 ⁵	- 0.0 ⁵	I
144.0	161.2	2.3981	2.2074	144.0	0	III
147.2	174.9	2.3798	2.2428	147.2	0	II
147.4 ⁵	175.8	2.3784	2.2450	147.4	+ 0.0 ⁵	I
147.8	176.8	2.3764	2.2475	147.6	+ 0.2	II
153.4	204.0	2.3452	2.3096	153.4	0	I
153.9	206.4	2.3424	2.3147	153.9	0	III
154.8	210.3	2.3375	2.3228	154.6 ⁵	+ 0.1 ⁵	II
157.5	225.2	2.3229	2.3526	157.5	0	I

¹⁾ Dissertatie Amsterdam (Sept. 1906), p. 64 et seq.

tension curves, though the pressure measurement could take place here with greater accuracy. The values which were found for the vapour tensions (in cm. of mercury) with three different fillings, and which were used for the calculations of § 17, have been combined in table 11 (p. 800). If in a graphical representation we draw $\log p$ as function of T^{-1} , one straight line can be drawn through the found points. A break is not to be found, though the pressure in the neighbourhood of the transition point has been determined with an accuracy of 1 or 2 ‰. As appears from table 11 the vapour tension line can be represented by the formula:

$$\log p = -\frac{1927.6}{T} + 6.8302.$$

17. *Determinations of the solubility of ammonium bromide in water for temperatures between 95° and 158°.*

The experiments were executed in the way described in § 5. The data are combined in table 12 (p. 802); x represents the number of molecules of NH_4Br , present in one molecule of the mixture, and is therefore determined by:

$$x = \frac{\frac{g}{M_{\text{NH}_4\text{Br}}}}{\frac{g}{M_{\text{NH}_4\text{Br}}} + \frac{100}{M_{\text{H}_2\text{O}}}} = \frac{g}{g + 543.7}$$

In fig. 7. the values are drawn of $\log x$ and T^{-1} . The values below the transition point appear to lie on a smooth curve with a faint curvature; the curve is convex seen from below; through the points in the neighbourhood of the transition point, however, the straight line can be drawn given by the equation:

$$\log x = -\frac{372.7}{T} + 0.31978.$$

The points above the transition point lie on the line:

$$\log x = -\frac{293.7}{T} + 0.12727.$$

The concordance between the values calculated from these lines and the observations is satisfactory as appears from table 13. (Error 1 ‰ or smaller.)

The two straight lines indicated above yield for the point of intersection:

$$t = 137.4^\circ.$$

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T A B L E 12.
Melting points of the solid substance in $\text{NH}_4\text{Br}-\text{H}_2\text{O}$ mixtures.
 $M_{\text{NH}_4\text{Br}} = 97.96$; $M_{\text{H}_2\text{O}} = 18.016$.

No.	Weight		t	Weight water in vapour	Weight water (corr.)	Grammes NH_4Br in 100 Grs H_2O (g)	$-\log x$	$10^3 T^{-1}$
	NH_4Br	H_2O						
1	2505.0	1791.6	94.95	0.2	1791.4	139.84	0.68913	2.7178
2	3091.5	2038.6	106.25	0.2	2038.4	151.66	0.66134	2.6368
3	3155.6	2019.5	110.4	0.5	2019.0	156.29	0.65116	2.6083
4	3195.0	1886.2	121.8	0.4	1885.8	169.42	0.62420	2.5329
5	3275.7	1852.3	128.0	0.7	1851.6	176.91	0.60995	2.4938
6	3346.3	1850.0	131.1	0.9	1849.1	180.97	0.60255	2.4746
7	3647.4	1967.2	134.6	0.6	1966.6	185.46	0.59457	2.4534
8	3410.5	1800.7	137.65	1.0	1799.7	189.50	0.58761	2.4352
9	4342.9	2241.4	142.05	0.4	2241.0	193.79	0.58043	2.4094
10	4220.7	2147.5	144.75	1.0	2146.5	196.63	0.57578	2.3938
11	3318.4	1665.1	147.65	1.2	1663.9	199.43	0.57127	2.3773
12	3802.8	1885.8	149.7	1.3	1884.5	201.79	0.56754	2.3658
13	4342.4	2121.7	152.6	1.0	2120.7	204.76	0.56292	2.3496
14	3746.0	1779.6	157.95	1.4	1778.2	210.66	0.55401	2.3204

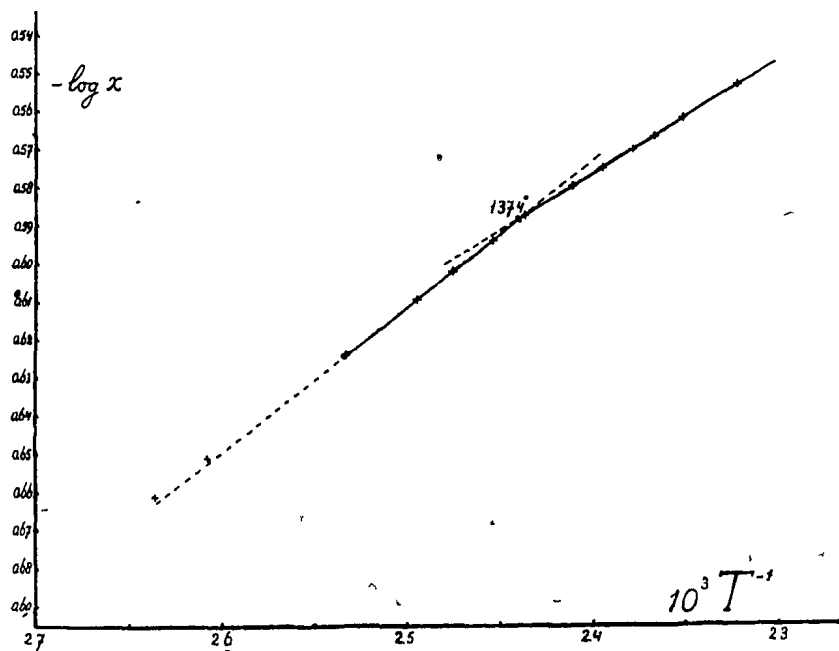


Fig. 7.

T A B L E 13.

N ^o	<i>t</i>	Number of grammes NH ₄ Br to 100 Grammes of H ₂ O		error
		calculated	found	
4	121.8	169.4 ^o	169.4 ^o	+ 0.0 ²
5	128.0	177.0 ⁶	176.9 ¹	- 0.1 ⁵
6	131.1	180.9 ⁸	180.9 ⁷	- 0.0 ¹
7	134.6	185.4 ⁴	185.4 ⁶	+ 0.0 ²
8	137.6 ⁵	189.3 ⁹	189.5 ⁰	+ 0.1 ¹
8	137.6 ⁵	189.3 ¹	189.5 ⁰	+ 0.1 ⁹
9	142.0 ⁵	193.8 ³	193.7 ⁹	- 0.0 ⁴
10	144.7 ⁵	196.6 ³	196.6 ³	0
11	147.6 ⁵	199.6 ⁵	199.4 ³	- 0.2 ²
12	149.7	201.7 ⁹	201.7 ⁹	0
13	152.6	204.8 ³	204.7 ⁶	- 0.0 ⁷
14	157.9 ⁵	210.4 ⁹	210.6 ⁶	+ 0.1 ⁷

This value for the transition point can, in my opinion, only deviate a few tenths of degrees from the real value.

18. It can be derived from the results of §§ 15 and 17 that the transition point of ammonium bromide lies at **137.4°**, a value which within the errors of observation agrees with the value found by SMITH and EASTLACK. In the thermal determinations the retardation on cooling appears to have been destroyed by the catalyzers glycerine and glycol, in case of rising temperature some retardation continues to exist in spite of the catalyzer.

19. *Thermal determination of the transition point of ammonium iodide.*

I have succeeded in demonstrating the existence of a transition point of ammonium iodide unknown up to now by thermal experiments.

In these experiments the same difficulty presents itself as for NH₄Cl and NH₄Br. On cooling a value is again found that lies lower than that which is found from the curves of heating. For my experiments I used a preparation of SCHLIERING, which as appears from the analysis (expulsion of iodine by NaNO₂ and H₂SO₄)

contained only 0.1 or 0.2 % NH_4Cl or NH_4Br . Thermal experiments yielded the limits -20° and -14° for the transition point. To bring these limits closer together I have examined whether a small quantity of water is a suitable catalyzer. I have succeeded in reducing the limits to -17.2 and -15.6 . From these experiments I have, therefore, to conclude to a transition point at -16° , a value, which can depart a degree from the accurate one. The eutectic point $\text{NH}_4\text{I}-\text{H}_2\text{O}$ lies at -28° ; I have been able to observe both the occurrence of the eutectic point and of the transition point in one curve of cooling.

I have not yet had an opportunity to determine the transition point more accurately. In the cited paper by SMITH and EASTLACK there have been recorded determinations of the solubility of ammonium iodide; the lowest temperature already lies below the transition point. When these determinations of the solubility are continued towards lower temperatures the break will undoubtedly be clearly perceptible and the value can be determined with greater accuracy than has taken place above by the aid of thermal experiments.

20. *Summary of the results.*

The ammonium halides NH_4Cl , NH_4Br , and NH_4I can all occur in two modifications. The transition points of the two first lie *above*, that of the third *below* the ordinary temperature of the room. At the ordinary temperature $\alpha\text{-NH}_4\text{Cl}$ and $\alpha\text{-NH}_4\text{Br}$ are isomorphous; $\beta\text{-NH}_4\text{I}$ is, however, not continuously miscible with the two others. By the α -form the form is indicated that is stable *below*, by the β -form the form that is stable *above* the transition point. The supposition suggests itself that the α -forms are continuously miscible inter se, and likewise the β -forms, but that between α - and β -forms incomplete mixing always takes place. The succession of the transition points NH_4Cl 184.5° , NH_4Br 137.4° and NH_4I -16° is that which would be expected according to the periodic system.

Postscript during the correction: In Proc. Amer. Acad. of Arts and Sciences 52 91 et seq. (1916) BRIDGMAN calculates from observations at high pressure that the transition points of NH_4Cl , NH_4Br and NH_4I at ordinary pressure must lie at 184.3° , 137.8° , and -17.6° . The first two deviate but little from my determinations; the third value may point to this that the transition point lies at the lower limit of my thermal determinations.