

CXXIX.—*The "True" Ionisation Constants and the Hydration Constants of Piperidine, Ammonia, and Triethylamine.*

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IN three cases the data necessary for the application of the equations developed in the preceding paper have been published already, and it seemed to the author advisable to publish the results of the calculations in these cases without waiting for the results of further experimental investigation.

(1) *Piperidine*.—The partition coefficients of piperidine between water and benzene at temperatures from 5.5° to 50°, and values of the apparent ionisation constant over the same range of temperature, are given by Hantzsch and Sebaldt (*Zeitsch. physikal. Chem.*, 1899, 30, 259). Their results were plotted out, and the numbers used in the calculations (given in the first four columns of the following table) were read off from the smooth curves most nearly representing the results.

Temperature.	Percentage of piperidine in benzene layer.	Percentage of piperidine in aqueous layer.	$K \times 100.$	$s/r.$
5°	27.93	72.07	0.0973	1.121
10	31.44	68.56	0.1040	1.121
15	34.95	65.05	0.1100	1.122
20	38.43	61.57	0.1153	1.125
25	41.92	58.08	0.1200	1.129
30	45.42	54.58	0.1240	1.152
35	48.90	51.10	0.1250	

From these numbers the values of  $r$ ,  $s$ , and  $A$  are calculated, and the values of  $\frac{s}{r}$ \* are tabulated in the last column of the table; the constancy of the value of this ratio shows that we are justified in the assumption that  $l$ ,  $m$ , and  $n$  are constant over the range of experiment (see p. 1378).

The further calculation was carried out as follows. From equation (20) (p. 1377), by putting  $n = 1$  (for in all cases where the partition of a substance which has no peculiarity of ionisation has been investigated, it has been found that the partition coefficient varies only slightly with the temperature, that is,  $n$  is nearly unity), we get a value for  $\frac{m}{l}$ ; substituting this in equation (22) we get a simple equation in  $l$ , the value of which may then be calculated. Now there are two ways of testing the truth of the assumption that  $n = 1$ . The first by substituting  $n = 1$  and the value of  $l$  found as above in

\* The symbols have the same meaning as in the preceding paper.

## 1380 MOORE: THE "TRUE" IONISATION CONSTANTS AND THE

equation (19); if this equation is satisfied within the limits due to experimental error, the values of  $l$  and  $n$  used satisfy the three equations (19), (20), and (22), that is, are the values required. The second method is to put  $n=1$  in equation (19) and to solve the quadratic in  $l$  which results. Of the two roots obtained, the smaller always gave negative values for one of the concentrations, so that the larger root is the one required.

Range of temperature = $t_1 - t_3$ .	$l$ from equation (22).	$l$ from equation (19).	Result of substituting $n=1$ and values of $l$ from equation (22) in equation (19).
5—15	1.129	1.126	- 0.0008
10—20	1.111	1.108	- 0.0003
15—25	1.092	1.090	$\pm 0.0$
20—30	1.086	1.070	+ 0.012
25—35	(1.202)	(1.13)	(+ 0.079)
Mean.....	1.105		

The value of each side of equation (19) is about 1.2, so that the errors shown in the last column are surprisingly small. The assumption that  $n=1$  is justified in this case.

From these values of  $l$  and  $n$  the values of  $x$  and  $y$  may be calculated by equation (17) and (18), and  $y$  for any particular temperature may be calculated from two distinct equations. Thus  $y_{15}$  may be calculated from experiments at  $10^\circ$  and  $15^\circ$ , or from experiments at  $15^\circ$  and  $20^\circ$ . The mean of the two values thus obtained has been taken as the true value of  $y$  in each case, and has been used in the calculation of the other quantities given in the following table:

Tempera- ture to which values correspond.	Temperatures corresponding to equa- tions from which $y$ is found.	$y$ .	$y$ (mean).	$x$ .	$k_2 = y/x$ .	$k_1 \times 100$ .	Conc. of $C_5H_{10}NH$ in aqueous sol.	Conc. of $C_5H_{10}NH$ in benzene sol.
$5^\circ$	5— $10^\circ$	0.0157	0.0157	0.00258	6.09	0.1133		0.30
10	{ 5—10 10—15	{ 0.0143 0.0140	0.0141	0.00307	4.60	0.1266		0.31
15	{ 10—15 15—20	{ 0.0125 0.0125	0.0125	0.00361	3.47	0.1417		0.33
20	{ 15—20 20—25	{ 0.0111 0.0112	0.0111	0.00393	2.83	0.1560		0.33
25	{ 20—25 25—30	{ 0.0098 0.0101	0.0100	0.00406	2.46	0.1687		0.31
20	25—30	0.0088	0.0088	0.00424	2.08	0.1837		0.30

*Accuracy of Results for Piperidine.*—To find the effect of an error in the value of  $n$ , the equations for the range  $15-20^\circ$  were solved on the assumption that  $n=1.02$ , with the following results:

$l$ from equation (22).	$l$ from equation (19).	Result of substituting $\begin{cases} l=1.099. \\ n=1.02. \end{cases}$ in equation (19).
1.099	1.106	- 0.001
$y_{20} = 0.01105$ .		$y_{25} = 0.00976$ .

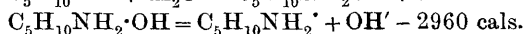
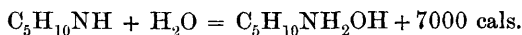
Thus an error of 2 per cent. on  $n$  cannot be detected by this method; but this is of little importance, since the error produced by such a change in  $l$  is little more than 1 per cent., and the error on  $y$  is less than 1 per cent.

The maximum difference in the two values of  $y$  given in the above table is 3 per cent. At  $15^\circ$  such an error would produce an error of 8 per cent. on  $x$ , 11 per cent. on  $k_2$ , 2.5 per cent. on  $k_1$ , and 8 per cent. on the partition coefficient given in the last column.

*Heat of Neutralisation of Piperidine.*—Taking  $l$  as 1.09 and  $\frac{m}{l}$  as 1.125, and using the ordinary formula

$$\log_e \frac{k''}{k'} = \frac{q}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right),$$

we find the heat changes involved in the hydration and ionisation of piperidine are:



The heat of neutralisation of a solution of piperidine is thus equal to  $13.7 + 7x - 2.96(x + y)$  larger calories, where  $x$  and  $y$  are the amounts of  $\text{C}_5\text{H}_{10}\text{NH}$  and  $\text{C}_5\text{H}_{10}\text{NH}_2\text{OH}$  respectively in the volume of solution containing 1 gram-molecule. (The heat changes due to incomplete ionisation of the acid and of the salt formed have been neglected.)

For a semi-normal solution this equation gives the value 12.7 larger calories. Colson (*Ann. Chim. Phys.*, 1890, [vi], 19, 408) found 13.02 at  $15^\circ$ ; Berthelot (*Thermochimie*, II, 646) found 13.32 at  $22^\circ$ .

(2) *Ammonia.*—Both Hantzsch and Sebaldt (*loc. cit.*) and Dawson and McCrae (*Trans.*, 1900, 77, 1239; 1901, 79, 1072; 1906, 89, 1666) have determined the partition coefficient of ammonia between water and chloroform at different temperatures. The results of the latter authors are the more accurate, and have been used in the calculations; but since experiments were carried out at three temperatures only,  $10^\circ$ ,  $20^\circ$ ,  $30^\circ$ , interpolation for  $15^\circ$  and  $25^\circ$  was impossible. These three temperatures were therefore taken as  $t_1$ ,  $t_2$ , and  $t_3$ .

Hantzsch and Sebaldt give also values of the apparent ionisation constant of ammonia at different temperatures, but, as is immediately apparent on plotting out the numbers, they are not sufficiently accurate to serve as a basis for calculation. The values of  $K$  used were obtained by combining the results of Kohlrausch (*Sitzungsber. k. Akad. Berlin*, 1900, 1002, and 1901, 1031) with the conductivity measurements of Kohlrausch, Bredig, and Hantzsch.

## 1382 MOORE: THE "TRUE" IONISATION CONSTANTS AND THE

Temperature.	$K \times 100.$	Concentration in chloroform layer.	$a.$	$s/r.$
10°	0·00169	0·01352	0·3917	1·045
20	0·00190	0·01588	0·3917	1·088
30	0·00203	0·01846	0·3917	

The condition that  $\frac{s}{r}$  should be constant is not so well fulfilled in this case as with piperidine. But, since ammonia is one of the most interesting cases, the calculation was carried out with the mean value of  $\frac{s}{r}$ ; the constants obtained must show at least the proper order of magnitude, and the striking agreement between the calculated and found heat effects (see below and p. 1383) indicates that the results are very near the truth.

Putting  $n = 1$ ,  $l$  from equation (22) = 1·52 }  
 $l$  „ „ (19) = 1·32 } Mean, 1·42.

Using the mean value of  $l$ , we get the following table :

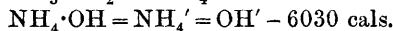
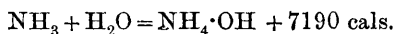
Temperature.	$y.$	$x.$	$y/x = k_2.$	$k_1 \times 100.$	Conc. of $\text{NH}_3$ in water.
					Conc. of $\text{NH}_3$ in chloroform.
10°	0·178	0·213	0·836	0·00368	15·8
20	0·141	0·251	0·560	0·00523	15·5
30	0·106	0·285	0·372	0·00743	15·4

Using the two values of  $l$ , 1·52 and 1·32, we find that at 20°

$$k_1 \text{ is between } 6\cdot5 \times 10^{-5} \text{ and } 4\cdot0 \times 10^{-5},$$

$$k_2 \quad \quad \quad 0\cdot42 \quad \quad \quad 0\cdot70.$$

*Heat of Neutralisation of Ammonia.*—Taking  $l$  as 1·42 and  $m$  as 1·52, we find :



from which the heat of neutralisation of a 0·278 *N*-solution of ammonia at 20° is found to be 12·3 larger calories. Thomsen (*Thermochemische Untersuchungen*) found 12·25 for a solution of this strength at 17·5°.

*Heat of Solution of Ammonia.*—Perman (Trans., 1903, 83, 1174) has determined the partial pressure of ammonia in the vapour of its solution at various temperatures and concentrations. The ratio between the partial pressure and the concentration of  $\text{NH}_3$  (as distinct from  $\text{NH}_4\cdot\text{OH}$  and its ions) in the solutions is the partition coefficient of ammonia between the two phases, and Perman's results might therefore be used to calculate the values of  $k_1$  and  $k_2$  by the above method. But  $n$  is not equal to unity in this case, since the act of solution is accompanied by considerable heat changes, and it is thus easier to show that the results already obtained for ammonia are

## HYDRATION CONSTANTS OF PIPERIDINE, AMMONIA, ETC. 1383

in agreement with Perman's results by calculation of the heat of solution, than by the direct application of the equations to the values of the vapour pressure.

Temperature.	$\alpha$ .	Partial pressure of $\text{NH}_3$ in mm. of Hg.	$x = \text{con-}$ centration of $\text{NH}_3$ .	$\frac{x}{\text{partial pressure}} = P.$	$\frac{Pt_1}{Pt_2} = n.$
10°	1.456	9.0	0.790	0.0879	1.46
20	1.453	15.5	0.930	0.0600	1.42
30	1.450	25.0	1.057	0.0430	
Mean ...					1.44

The first three columns are from Perman's tables;  $x$  is calculated from  $\alpha$  by means of the values of  $k_1$  and  $k_2$  (preceding page);  $P$  is the partition coefficient of  $\text{NH}_3$  between the two phases, and the last column gives the variation of  $P$  with temperature.

Applying van't Hoff's formula to this temperature coefficient, we find that the act of solution (apart from any hydration or ionisation) of one gram-molecule of ammonia in water is accompanied by an evolution of 6270 calories. Then the heat actually observed on solution of one gram-molecule is

$$6.27 + 7.19 (y + z) - 6.03 z \text{ large calories,}$$

where  $y$  and  $z$  are the quantities of  $\text{NH}_4\cdot\text{OH}$  and  $\text{NH}_4^+$  respectively in the resulting solution, and may be calculated from the values of  $k_1$  and  $k_2$  given above. For a solution approximately 0.3*N* at 20° this quantity is found to be 8.83 larger calories. Thomsen (*Thermochemische Untersuchungen*, II., 73) finds 8.44 for the same strength of solution and temperature; Berthelot (*Thermochimie*, II., 69) finds 8.82 at 10°.

(3) *Triethylamine*.—The partition coefficients are from the results of Hantzsch and Vagt (*Zeitsch. physikal. Chem.*, 1901, 38, 703). Hantzsch and Sebaldt give values for the apparent ionisation constant at different temperatures, but no curve can be drawn which represents them all. By neglecting the numbers for 10° and 40°, a fairly good curve was obtained from which the values used in the calculation were read off.

Temperature.	$c$ .	$\alpha$ .	100 <i>K</i> .	$s/r$ .
15°	0.0503	0.01224	0.0387	1.092
20	0.0516	0.01091	0.0414	1.088
25	0.0526	0.00987	0.0435	1.088
30	0.0535	0.00897	0.0453	1.079
35	0.0542	0.00828	0.0468	

The calculations were carried out exactly as in the case of piperidine, and  $n$  was found equal to unity within the limits of experimental error:

$$\text{Mean value of } l = 1.19.$$

$$,, \quad ,, \quad \frac{m}{l} = 1.09.$$

## 1384 IRVINE AND WEIR: THE APPLICATION OF BAEYER'S

Tem- per- ature.	Temperature of observa- tions used.	$y$ .	$y$ (mean).	$x$ .	$y/x = k_2$ .	$k_1 \times 100$ .	$\frac{x}{\text{Conc. in toluene}}$
15°	15—20°	0·00732	0·00732	0·00293	2·50	0·054	0·058
20	{ 15—20 20—25	{ 0·00597 0·00571	0·00584	0·00314	1·86	0·064	0·061
25	{ 20—25 25—30	{ 0·00466 0·00467	0·00467	0·00333	1·40	0·075	0·063
30	{ 25—30 30—35	{ 0·00381 0·00389	0·00385	0·00334	1·15	0·085	0·062
35	30—35	0·00318	0·00318	0·00335	0·95	0·096	0·062

At 20°:  $\text{N}(\text{C}_2\text{H}_5)_3 + \text{H}_2\text{O} = \text{N}(\text{C}_2\text{H}_5)_3\text{H}\cdot\text{OH} + 9000 \text{ cal.}$

$\text{N}(\text{C}_2\text{H}_5)_3\text{H}\cdot\text{OH} = \text{N}(\text{C}_2\text{H}_5)_3\text{H}^+ + \text{OH}^- - 6060 \text{ cal.}$

Heat of neutralisation of a semi-normal solution = 10·9 larger cal.

Berthelot (*Thermochimie*, I., 699) found = 9·6 „ „

The results communicated in this paper are neither sufficiently numerous nor based on sufficiently accurate data to warrant much discussion. One point is worthy of remark: for ammonia and triethylamine at 20° the values of  $k_1$  are  $5\cdot23 \times 10^{-5}$  and  $6\cdot4 \times 10^{-4}$ , so that the introduction of three ethyl groups into ammonia has increased the constant only twelve-fold. Now the introduction of a fourth ethyl group gives tetraethylammonium hydroxide, the degree of ionisation of which is comparable with that of sodium hydroxide. It is difficult to imagine that this large change of ionisation is produced solely by the introduction of the fourth ethyl group when the first three have produced a comparatively small effect. These results point rather to a difference in constitution between the quaternary ammonium hydroxides and the hydroxides of primary, secondary, and tertiary amines (compare Werner, *Ber.*, 1903, 36, 147; Hantzsch, *Ber.*, 1905, 38, 2161).

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