CLXXXIII.—*The Dilution and Neutral-salt Errors of Buffer Mixtures.*

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OWING to the wide distribution of neutral salts in tissues and body-fluids, the well-known fact that the apparent hydrogen-ion concentration of buffer mixtures is increased on the addition of neutral salts is of especial importance in biochemical investigations. In the case of polybasic buffers, such as the phosphate mixtures, neglect of neutral-salt effects may lead to appreciable error. The problem has been examined, so far as the phosphate mixtures are concerned, by Michaelis and Krüger (*Biochem. Z.*, 1921, **119**, 307), and by Cohn (*J. Amer. Chem. Soc.*, 1927, **49**, 173), but no systematic investigation of the dilution and salt errors of buffer mixtures in general appears to have been undertaken.

The properties of the following mixtures have now been studied: (1) Half-neutralised solutions of acetic and cacodylic acids; (2) one-fourth-neutralised solutions of aspartic acid and of arginine; (3) three-fourths-neutralised solutions of *o*-phthalic and α-mono-glycerylphosphoric acids; (4) mixtures of sodium pyrophosphate and hydrochloric acid in the molecular proportions (*a*) 2 : 3, (*b*) 2 : 1. For such mixtures we have, respectively, (1) $p_{\mathrm{H}} = p_{\mathrm{K}}$, (2) $p_{\mathrm{H}} = p_{K_1}$, (3) $p_{\mathrm{H}} = p_{K_2}$, (4*a*) $p_{\mathrm{H}} = p_{K_3}$. (4*b*) $p_{\mathrm{H}} = p_{K_4}$, where $K = 10^{-p_K}$ is the apparent dissociation constant of the buffer electrolyte. To these solutions various amounts of N-potassium chloride, N-sodium chloride, $M/3$-potassium sulphate, $M/3$-barium chloride, and $M/4$-magnesium sulphate were added, and the p_H (or p_K) change produced by each addition was noted. The effect of dilution was also studied.

The experimental results are in Tables I–IX. In all cases p_K decreases on the addition of neutral salts, but increases on dilution. Both effects become more strongly marked as the valency of the buffer acid increases. When the concentration of added salt is small, the p_H change is independent of the specific nature of the salt, depending only on the valency type; with larger additions a specific salt action is exhibited. As regards the importance of their effects in inducing p_H change in acid buffer mixtures, the influence of neutral salts is in the order $BaCl_2 > MgSO_4 > NaCl > KCl > K_2SO_4$, whatever the nature of the buffer acid. For basic buffers the order is reversed : $K_2SO_4 > KCl > NaCl$.

In dilute solution, when free acid and salt were present in equivalent concentration, the p_K or p_H changes brought about by further dilution, or by the addition of small quantities of neutral salts, were satisfactorily described by the equation

$$p_k = p_H + A\sqrt{\mu} = p_K + A\sqrt{\mu} \quad . \quad . \quad . \quad . \quad (1)$$

where μ is the ionic strength as defined by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1112), and p_k and A are true constants. When acid and salt are not present in equivalent concentration, the equation

$$p_k = p_H + \log\,[\text{acid}]/[\text{salt}] + A\sqrt{\mu} \quad . \quad . \quad . \quad (2)$$

applies within the limits of validity of Henderson's equation (*i.e.*, within the p_H limits 4—10). The numerical value of A is 0·5 for monobasic acids, of the order of 1·5 for dibasic acids, 2·5 for tribasic acids, and, in general, roughly equal to $(n - 0{\cdot}5)$ for an n-valent acid.

In solutions of higher ionic strength, the hydrogen-ion relationships are defined by the expression

$$p_k = p_K + A\sqrt{\mu} - B\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$p_k = p_H + \log\,[\text{acid}]/[\text{salt}] + A\sqrt{\mu} - B\mu \quad . \quad . \quad (4)$$

The constants A and p_k have the same significance and numerical values as before, and B is a coefficient expressing the specific action of the ions. Let the values of p_K in three buffer solutions containing identical ions, but of different ionic strengths μ', μ'', μ''', be $p_{K'}$, $p_{K''}$, and $p_{K'''}$, respectively. Then $p_k = p_{K'} + A\sqrt{\mu'} - B\mu' = p_{K''} + A\sqrt{\mu''} - B\mu'' = p_{K'''} + A\sqrt{\mu'''} - B\mu'''$

whence

$$A = \frac{ac_1 - a_1c}{bc_1 - b_1c} \text{ and } B = \frac{ab_1 - a_1b}{bc_1 - b_1c} \quad . \quad . \quad . \quad (5)$$

where $a = p_{K''} - p_{K'}$, $b = \sqrt{\mu'} - \sqrt{\mu''}$, $c = \mu' - \mu''$.
$a_1 = p_{K'''} - p_{K'}$, $b_1 = \sqrt{\mu'} - \sqrt{\mu'''}$, $c_1 = \mu' - \mu'''$.

By means of (5) the values of A and B may be obtained independently of one another, and by substitution in equation (3) p_k is obtained.

By the use of this method, the values of A, B, and p_k given in Tables II—IX were obtained. The constancy of k throughout ranges of dilution and salt concentration varying from $N/2$ to $N/1000$ is in general good, and appears to justify the use of the above method of formulation. The mean values of p_k and the salt coefficient B for the salts and mixtures studied were as follows (C is the molar concentration of the free acid and of the salt):

Buffer electrolyte.		C.	p_k.	Values of B for				
				K_2SO_4.	KCl.	NaCl.	$MgSO_4$.	$BaCl_2$.
Aspartic acid	K	0·02	3·895	0·485	0·402	0·252	0·209	0·057
Acetic acid	K	0·01	4·735	0·411	0·348	0·295	0·160	0·148
Cacodylic acid	K	0·04	6·247	0·352	—	0·259	0·119	0·153
Phthalic acid	K_2	0·01	5·333	0·961	0·845	0·759	0·466	0·435
α-Glycerylphosphoric acid	K_2	0·01	6·744	0·965	0·837	0·629	0·288	0·256
Pyrophosphoric acid...	K_3	0·02	6·704	1·48	1·29	0·983		
Pyrophosphoric acid...	K_4	0·02	9·880	1·74	1·33	0·687		
Arginine	K_{B_1}	0·005	5·178	0·371	0·408	0·466		

It is clear that the value of B depends on the specific nature of the salt, and to a less extent on the strength and valency of the buffer acid, decreasing slightly with decreasing strength of the acid and increasing with the valency of the acid.

The Quantitative Expression of Buffer Capacity.

Van Slyke (*J. Biol. Chem.*, 1922, **52**, 525) has suggested as a unit of buffer capacity the differential ratio $\beta = dB/dp_H$, expressing the relationship between the increment dB of strong base and the resulting p_H change. The practical value of a buffer solution depends on the degree of resistance offered to changes in hydrogen-ion concentration occasioned (1) by the presence of acid or basic impurities, (2) by errors of dilution, or by the presence of foreign salts. If trustworthy conclusions as to the reproducibility of a given solution are to be drawn, the magnitude of the errors due to both sources must be known. This point may be illustrated by a comparison of the effects of strong bases and of dilution on the hydrogen-ion concentration of (*a*) 0·1N-sulphuric acid, (*b*) 0·1N-glycine, (*c*) 0·1N-standard acetate.

	(*a*).	(*b*).	(*c*).
p_H change on adding 0·005 equiv. of strong base	0·026	2·48	0·043
p_H change on ten-fold dilution	0·88	0·059	0·061
$\beta = \Delta B/\Delta p_H$	0·19	0·002	0·12
$\pi' = \Delta p_H/\Delta C$	−9·8	−0·66	−0·68

The dilution error (provisionally formulated as $\pi' = \Delta p_H/\Delta C$) involved in the preparation of 0·1N-sulphuric acid is 14 times as great as that of standard acetate; this accounts for the experimental observation that, whereas the former solution has the higher β value, the latter is the more readily reproduced. On the other hand, although 0·1N-glycine and 0·1N-standard acetate have approximately the same dilution errors, the alkali-resisting capacity of standard acetate is 60 times as great as that of the glycine. Of the three solutions, only standard acetate fulfils the requirements of an ideal buffer solution, combining a high β value with a low π' or dilution error.

It appears desirable to supplement the β value of van Slyke by a second unit which will serve as a criterion of the probable dilution or salt error. It has been shown above that in the case of typical buffer mixtures, *i.e.*, mixtures prepared from acids or bases the dissociation constants of which lie between the limits 10^{-4} and 10^{-10}, the dilution and salt errors are functions of the ionic strength rather than of concentration. The proposed unit will be defined, therefore, as the differential ratio $\pi = dp_H/d\sqrt{\mu}$. When both the β and π values of a solution are stated, the buffer efficiency is completely defined : the higher the β value, and the lower the π value, the greater the efficiency.

For a typical buffer mixture within the range of validity of Henderson's equation, we have, from (4),

$$\pi = dp_H/d\sqrt{\mu} = 2B\sqrt{\mu} - A \quad . \quad . \quad . \quad . \quad (6)$$

since the values of p_k and the ratio of acid to salt are inappreciably affected by dilution or by the addition of neutral salts.

In solutions of low ionic strength ($\mu < 0·01$), *e.g.*, in dilute buffer solutions, (6) reduces to

$$\pi = -A = 0·5 - n \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From equations (6) and (7) it can be deduced that :

(1) The dilution error, unlike the β value, is independent of the strength of the buffer electrolyte.

(2) The limiting dilution error is the same for all mixtures of the same salt and acid, *e.g.*, all the phosphate mixtures of Clark and Lubs have the same limiting dilution error.

(3) All buffer mixtures prepared from monobasic acids or monoacid bases have the same limiting dilution error, *viz.*, —0·5.

(4) The limiting dilution error rapidly increases with the valency of the buffer acid or base. For dibasic acids, *e.g.*, the phthalate and phosphate mixtures, the error is 3 times as great as for monobasic acid mixtures. Hence, *ceteris paribus*, monobasic buffer mixtures are preferable to polybasic mixtures.

TABLE I.

Buffer electrolyte.		*A.*	*C.*	$\sqrt{\mu}$.*	*E.M.F.*	p_H.	*K.*	*k.*
Aspartic acid †	K_1	0·5	0·02	0·142	0·4721	3·832	$1·5 \times 10^{-4}$	$1·27 \times 10^{-4}$
			0·01	0·101	0·4748	3·878	1·4	1·21
			0·005	0·072	0·4757	3·892	1·3	1·24
			0·0025	0·051	0·4782	3·933	1·3	1·26
			0·00125	0·037	0·4793	3·952	1·3	1·28
Cacodylic acid	K	0·5	0·04	0·200	0·6116	6·153	$7·0 \times 10^{-7}$	$5·6 \times 10^{-7}$
			0·02	0·141	0·6123	6·165	6·8	5·8
			0·01	0·100	0·6135	6·184	6·5	5·8
			0·005	0·0707	0·6144	6·198	6·3	5·8
			0·0025	0·050	0·6145	6·200	6·3	5·9
			0·00125	0·035	0·6150	6·209	6·2	5·9
Phthalic acid	K_2	1·5	0·010	0·200	0·5476	5·055	$8·8 \times 10^{-6}$	$4·4 \times 10^{-6}$
			0·005	0·141	0·5502	5·098	8·0	4·9
			0·0025	0·100	0·5535	5·153	7·0	5·0
			0·00125	0·071	0·5543	5·166	6·8	5·3
			0·000625	0·050	0·5584	5·235	5·8	4·9
Glycerylphosphoric acid	K_2	1·5	0·01	0·200	0·6296	6·452	$3·5 \times 10^{-7}$	$1·8 \times 10^{-7}$
			0·005	0·141	0·6330	6·509	3·1	1·9
			0·0025	0·100	0·6348	6·539	3·9	2·0
			0·00125	0·0707	0·6385	6·601	2·5	2·0
Pyrophosphoric acid (i)	K_3	2·5	0·02	0·490	0·5922	5·797	$16·0 \times 10^{-7}$	$0·95 \times 10^{-7}$
			0·01	0·346	0·6012	5·947	11·3	1·5
			0·005	0·245	0·6066	6·037	9·2	2·2
			0·0025	0·173	0·6148	6·173	6·7	2·5
			0·00125	0·123	0·6198	6·256	5·5	2·7
Pyrophosphoric acid (ii)	K_4	3·5	0·02	0·583	0·7410	8·307	49×10^{-10}	$0·45 \times 10^{-10}$
			0·01	0·412	0·7520	8·489	32	1·2
			0·005	0·292	0·7626	8·664	22	2·1
			0·0025	0·206	0·7673	8·744	18	3·4
			0·00125	0·146	0·7723	8·826	15	4·6

* From the definition of Lewis and Randall, it follows that the ionic strengths of solutions of uni-bivalent, uni-tervalent, and uni-quadrivalent electrolytes are respectively equal to three, six, and ten times the molar concentrations, and that of a uni-univalent electrolyte is equal to the normality. The ionic strengths of the various mixtures were therefore derived as follows:

Arginine and aspartic, acetic, and cacodylic acid mixtures: $\mu = [\text{salt}] = C$.

Phthalic and glycerylphosphoric mixtures: $\mu = [HA'] + 3[A''] = 4C$, where $C = [HA'] = [A'']$.

Pyrophosphoric mixture (i): $\mu = 6[HP_2O_7'''] + 3[H_2P_2O_7''] + [Cl'] = 12C$, where $C = [HP_2O_7'''] = [H_2P_2O_7''] = \frac{1}{3}[Cl']$.

Pyrophosphoric mixture (ii): $\mu = 10[P_2O_7''''] + 6[HP_2O_7'''] + [Cl'] = 17C$, where $C = [P_2O_7''''] = [HP_2O_7'''] = [Cl']$.

† In computing K_1, the expression $p_{K_1} = p_H + \log([\text{salt}] - [H^\cdot])/([\text{salt}] + [H^\cdot])$ was used, the Henderson equation being inexact when $[H^\cdot] > 10^{-4}$.

(5) When $\sqrt{\mu} < A/2B$, $dp_H/d\sqrt{\mu}$ has a negative value, the p_H value of the solution decreasing with increasing ionic strength. When $\sqrt{\mu} = A/2B$, $dp_H/d\sqrt{\mu} = 0$, and, from (4), the corresponding value of the hydrogen-ion concentration, the lowest which can be obtained with a given buffer mixture, is given by $p_H = p_k - \log [\text{acid}]/[\text{salt}] - A^2/4B$. When $\sqrt{\mu} > A/2B$, the p_H value of the mixture increases with increasing ionic strength.

(6) The π–$\sqrt{\mu}$ graph is a straight line, the slope of which is equal to $2B$.

The Thermodynamical Significance of the Dilution and Salt Errors.

Henderson's equation is derived on the assumptions that (1) the concentrations of hydrogen and hydroxyl ions are negligibly small compared with those of the total acid and base; (2) the salt is completely dissociated; (3) the law of mass action, as ordinarily defined in concentration terms, is obeyed. Between the p_H limits

TABLE II.

Aspartic acid mixture.

$[H_2A] = [HA'] = 0{\cdot}02$.

Salt.	*A.*	*B.*	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·020	0·0485	0·0667	0·1091	0·1478	0·1834	0·2462
N-KCl	0·497	0·402	*E.M.F.*	0·4721	0·4712	0·4707	0·4698	0·4690	0·4686	0·4680
			p_H	3·832	3·818	3·809	3·794	3·781	3·774	3·764
			$K \times 10^4$	1·47	1·52	1·55	1·61	1·66	1·68	1·72
			$k \times 10^4$	1·28	1·24	1·22	1·22	1·22	1·22	1·22
N-NaCl	0·495	0·252	*E.M.F.*	0·4721	0·4701	0·4699	0·4685	0·4675	0·4667	0·4656
			p_H	3·832	3·799	3·796	3·772	3·756	3·743	3·724
			$K \times 10^4$	1·47	1·59	1·60	1·69	1·75	1·81	1·89
			$k \times 10^4$	1·27	1·27	1·24	1·24	1·23	1·23	1·24
M/3-K_2SO_4	0·499	0·485	*E.M.F.*	0·4721	0·4718	0·4715	0·4712	0·4710	0·4705	0·4704
			p_H	3·832	3·827	3·822	3·818	3·815	3·806	3·805
			$K \times 10^4$	1·47	1·49	1·51	1·52	1·53	1·56	1·57
			$k \times 10^4$	1·28	1·22	1·21	1·18	1·16	1·17	1·16
M/3-$BaCl_2$	0·498	0·057	*E.M.F.*	0·4721	0·4695	0·4685	0·4661	0·4646	0·4634	0·4614
			p_H	3·832	3·788	3·772	3·733	3·708	3·688	3·655
			$K \times 10^4$	1·47	1·63	1·69	1·85	1·96	2·05	2·21
			$k \times 10^4$	1·26	1·27	1·37	1·28	1·28	1·29	1·29
M/4-$MgSO_4$	0·500	0·209	*E.M.F.*	0·4721	0·4710	0·4700	0·4682	0·4670	0·4663	0·4652
			p_H	3·832	3·815	3·797	3·768	3·748	3·736	3·718
			$K \times 10^4$	1·47	1·53	1·60	1·71	1·79	1·84	1·91
			$k \times 10^4$	1·26	1·22	1·22	1·23	1·23	1·23	1·22
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·3000	0·3467	0·3875	0·4235	0·4556	0·4842	0·5100
N-KCl	0·497	0·402	*E.M.F.*	0·4678	0·4677	0·4675	0·4674	0·4674	0·4673	0·4672
			p_H	3·761	3·759	3·756	3·755	3·755	3·753	3·752
			$K \times 10^4$	1·73	1·74	1·75	1·76	1·76	1·77	1·77
			$k \times 10^4$	1·22	1·22	1·23	1·23	1·23	1·25	1·25
N NaCl	0·495	0·252	*E.M.F.*	0·4647	0·4642	0·4639	0·4636	0·4633	0·4630	0·4627
			p_H	3·710	3·701	3·697	3·691	3·686	3·681	3·676
			$K \times 10^4$	1·95	1·99	2·01	2·04	2·06	2·08	2·11
			$k \times 10^4$	1·24	1·24	1·24	1·24	1·24	1·25	1·26
M/3 K_2SO_4	0·499	0·485	*E.M.F.*	0·4704	0·4703	0·4703	0·4704	0·4703	0·4702	0·4701
			p_H	3·805	3·803	3·803	3·805	3·803	3·801	3·799
			$K \times 10^4$	1·57	1·57	1·57	1·57	1·57	1·58	1·59
			$k \times 10^4$	1·16	1·18	1·19	1·19	1·21	1·22	1·23
M/3-$BaCl_2$	0·498	0·057	*E.M.F.*	0·4603	0·4592	0·4585	0·4577	0·4568	0·4567	0·4563
			p_H	3·637	3·618	3·607	3·593	3·578	3·576	3·570
			$K \times 10^4$	2·31	2·41	2·47	2·55	2·64	2·66	2·69
			$k \times 10^4$	1·28	1·28	1·27	1·28	1·29	1·27	1·27
M/4-$MgSO_4$	0·500	0·209	*E.M.F.*		0·4639	0·4632	0·4626	0·4623	0·4618	0·4617
			p_H		3·697	3·684	3·674	3·669	3·661	3·659
			$K \times 10^4$		2·01	2·07	2·12	2·14	2·18	2·19
			$k \times 10^4$		1·21	1·22	1·23	1·23	1·24	1·23

Mean value of $k_A = 1{\cdot}27 \times 10^{-4}$.

4—10 the first assumption is obviously justified at ordinary concentrations. If the second and third assumptions were both valid, therefore, dilution and neutral salt errors would be non-existent. The fact that both errors are functions of the ionic strength rather than of concentration suggests that it is the third assumption which is at fault, and that the activity concept may offer a solution. The introduction of the activity correction into the Henderson equation leads to the expression

$$p_k = p_H + \log [\text{acid}]/[\text{salt}] + \log f_a/f_s \quad . \quad . \quad . \quad (8)$$

in which f_a and f_s are the activity coefficients of the undissociated acid and of the salt anions, or of the acid anions of lower and higher valency, respectively, and $k = 10^{-p_k}$ is a true constant, the thermodynamic dissociation constant. Brønsted (*Trans. Faraday Soc.*,

Table III.

Acetic acid mixture.

[HA] = [A′] = 0·01.

Salt.	A.	B.	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·010	0·0388	0·0571	0·100	0·1391	0·1750	0·2385
M/3-$BaCl_2$	0·5	0·148	*E.M.F.*	0·5233	0·5204	0·5197	0·5177	0·5163	0·5153	0·5138
			p_H	4·684	4·635	4·624	4·591	4·567	4·551	4·527
			$K \times 10^5$	2·07	2·32	2·38	2·56	2·71	2·81	2·97
			$k \times 10^5$	1·85	1·87	1·84	1·85	1·85	1·85	1·83
N-NaCl	0·5	0·295	*E.M.F.*	0·5233	0·5200	0·5190	0·5179	0·5170	0·5164	0·5154
			p_H	4·684	4·629	4·613	4·594	4·580	4·569	4·553
			$K \times 10^5$	2·07	2·35	2·44	2·55	2·63	2·70	2·80
			$k \times 10^5$	1·86	1·92	1·92	1·90	1·88	1·88	1·87
M/3-K_2SO_4	0·5	0·411	*E.M.F.*	0·5233	0·5213	0·5210	0·5200	0·5192	0·5187	0·5183
			p_H	4·684	4·650	4·646	4·629	4·616	4·608	4·601
			$K \times 10^5$	2·07	2·24	2·26	2·35	2·42	2·47	2·51
			$k \times 10^5$	1·86	1·85	1·81	1·80	1·80	1·80	1·79
N-KCl	0·5	0·348	*E.M.F.*	0·5233	0·5210	0·5205	0·5194	0·5188	0·5182	0·5176
			p_H	4·684	4·646	4·637	4·619	4·610	4·599	4·588
			$K \times 10^5$	2·07	2·26	2·31	2·40	2·46	2·52	2·58
			$k \times 10^5$	1·86	1·86	1·83	1·81	1·78	1·79	1·78
M/4-$MgSO_4$	0·5	0·160	*E.M.F.*	0·5233	0·5200	0·5192	0·5179	0·5170	0·5160	0·5145
			p_H	4·684	4·629	4·616	4·594	4·580	4·563	4·538
			$K \times 10^5$	2·07	2·35	2·42	2·55	2·63	2·74	2·90
			$k \times 10^5$	1·85	1·90	1·88	1·84	1·80	1·80	1·80

Salt.	A.	B.	C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·2928	0·3401	0·3813	0·4176	0·4501	0·4790	0·5050
M/3-$BaCl_2$	0·5	0·148	*E.M.F.*	0·5127	0·5119	0·5110	0·5105	0·5100	0·5097	0·5093
			p_H	4·508	4·494	4·480	4·471	4·463	4·458	4·451
			$K \times 10^5$	3·11	3·21	3·31	3·38	3·44	3·48	3·54
			$k \times 10^5$	1·84	1·84	1·85	1·85	1·85	1·85	1·85
N-NaCl	0·5	0·295	*E.M.F.*	0·5148	0·5142	0·5138	0·5135	0·5130		
			p_H	4·543	4·533	4·527	4·522	4·513		
			$K \times 10^5$	2·86	2·93	2·97	3·01	3·07		
			$k \times 10^5$	1·87	1·88	1·89	1·89	1·92		
M/3-K_2SO_4	0·5	0·411	*E.M.F.*	0·5180	0·5179	0·5178	0·5176	0·5176	0·5175	0·5175
			p_H	4·596	4·594	4·593	4·588	4·588	4·587	4·587
			$K \times 10^5$	2·54	2·55	2·55	2·58	2·58	2·59	2·59
			$k \times 10^5$	1·79	1·80	1·80	1·80	1·82	1·84	1·84
N-KCl	0·5	0·348	*E.M.F.*	0·5172	0·5170	0·5168	0·5156	0·5155	0·5153	0·5153
			p_H	4·582	4·580	4·576	4·556	4·555	4·551	4·551
			$K \times 10^5$	2·62	2·63	2·66	2·78	2·79	2·81	2·81
			$k \times 10^5$	1·77	1·76	1·77	1·84	1·85	1·86	1·86
M/4-$MgSO_4$	0·5	0·160	*E.M.F.*	0·5134	0·5125	0·5118	0·5110	0·5104	0·5098	0·5093
			p_H	4·520	4·505	4·493	4·480	4·469	4·460	4·451
			$K \times 10^5$	3·02	3·13	3·21	3·31	3·40	3·47	3·54
			$k \times 10^5$	1·80	1·81	1·82	1·83	1·85	1·87	1·88

Mean value of $k = 1{\cdot}84 \times 10^{-5}$.

1927, **23**, 418) puts the Debye–Hückel (*Physikal. Z.*, 1923, **24**, 185) equation for the activity coefficient f of an ion of valency z in the form $-\log f = 0{\cdot}5z^2\sqrt{\mu} + b\mu$. For the n-th stage in the dissociation of a weak acid this gives $-\log f_a = 0{\cdot}5(n-1)^2\sqrt{\mu} + b'\mu$ and $-\log f_s = 0{\cdot}5n^2\sqrt{\mu} + b''\mu$, or $\log f_a/f_s = (n - 0{\cdot}5)\sqrt{\mu} - B\mu$, where $B = b' - b''$.

Equations (8) and (4), therefore, are identical and the data of Tables I—IX constitute an experimental verification of the Debye–Hückel theory.

For mono- and di-basic acids, the numerical values of the proportionality constant A are in excellent agreement with those derived thermodynamically from the Debye–Hückel theory, *viz.*, 0·5 and 1·5, respectively, but for acids of higher valency there is

TABLE IV.

Cacodylic acid mixture.

[HA] = [A'] = 0·04.

Salt.	A.	B.								
			C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·0400	0·068	0·0857	0·1273	0·1652	0·200	0·2616
N-NaCl	0·5	0·259	*E.M.F.*	0·6116	0·6100	0·6095	0·6089	0·6080	0·6073	0·6065
			p_H	6·153	6·127	6·119	6·108	6·094	6·081	6·068
			$K \times 10^7$	7·0	7·5	7·6	7·8	8·1	8·3	8·6
			$k \times 10^7$	5·7	5·7	5·7	5·6	5·6	5·6	5·6
$M/3$-K_2SO_4	0·5	0·352	*E.M.F.*	0·6116	0·6103	0·6100	0·6094	0·6092	0·6083	0·6079
			p_H	6·153	6·131	6·127	6·116	6·113	6·098	6·091
			$K \times 10^7$	7·0	7·4	7·5	7·7	7·7	8·0	8·1
			$k \times 10^7$	5·8	5·8	5·7	5·6	5·5	5·6	5·6
$M/3$-$BaCl_2$	0·5	0·153	*E.M.F.*	0·6116	0·6101	0·6094	0·6079	0·6068	0·6061	0·6047
			p_H	6·153	6·128	6·116	6·091	6·073	6·061	6·039
			$K \times 10^7$	7·0	7·4	7·7	8·1	8·5	8·7	9·1
			$k \times 10^7$	5·7	5·6	5·6	5·6	5·6	5·6	5·6
$M/4$-$MgSO_4$	0·5	0·119	*E.M.F.*	0·6116	0·6090	0·6082	0·6067	0·6059	0·6050	0·6033
			p_H	6·153	6·110	6·096	6·071	6·057	6·043	6·015
			$K \times 10^7$	7·0	7·8	8·0	8·5	8·8	9·1	9·7
			$k \times 10^7$	5·6	5·8	5·8	5·8	5·8	5·7	5·8
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·3143	0·3601	0·400	0·4352	0·4667	0·4948	0·5200
N-NaCl	0·5	0·259	*E.M.F.*	0·6055	0·6050	0·6048	0·6043	0·6040	0·6038	0·6036
			p_H	6·052	6·043	6·039	6·032	6·027	6·023	6·020
			$K \times 10^7$	8·9	9·1	9·1	9·3	9·4	9·5	9·6
			$k \times 10^7$	5·6	5·6	5·6	5·6	5·7	5·7	5·7
$M/3$-K_2SO_4	0·5	0·352	*E.M.F.*	0·6079	0·6078	0·6070	0·6063	0·6062	0·6061	0·6060
			p_H	6·091	6·089	6·077	6·064	6·063	6·061	6·060
			$K \times 10^7$	8·1	8·1	8·4	8·6	8·7	8·7	8·7
			$k \times 10^7$	5·5	5·5	5·6	5·7	5·7	5·8	5·8
$M/3$-$BaCl_2$	0·5	0·153	*E.M.F.*	0·6037	0·6028	0·6022	0·6015	0·6012	0·6009	0·6004
			p_H	6·022	6·006	5·996	5·985	5·980	5·974	5·968
			$K \times 10^7$	9·5	9·9	10·1	10·4	10·5	10·6	10·8
			$k \times 10^7$	5·6	5·6	5·6	5·6	5·6	5·6	5·6
$M/4$-$MgSO_4$	0·5	0·119	*E.M.F.*	0·6025	0·6011	0·6008	0·6002	0·5995	0·5988	0·5986
			p_H	6·002	5·978	5·973	5·964	5·953	5·940	5·936
			$K \times 10^7$	10·0	10·5	10·6	10·9	11·1	11·5	11·6
			$k \times 10^7$	5·7	5·8	5·7	5·7	5·8	5·8	5·8

Mean value of $k = 5{\cdot}66 \times 10^{-7}$.

only rough correspondence between the two values. Moreover, the above considerations apply only to weak electrolytes, the dissociation constants of which lie within the limits 10^{-4} and 10^{-9} or 10^{-10}. In any attempt to formulate the dilution errors of strong electrolytes, or of the strongly hydrolysed salts of very weak electrolytes, the effects of changing concentration, as well as of changing ionic strength, must be taken into account. For such electrolytes, the dilution error may be provisionally formulated as $\pi' = \Delta p_H/\Delta C$, and determined experimentally.

EXPERIMENTAL.

The hydrogen electrode was used in conjunction with a saturated calomel half-cell, and with saturated potassium chloride solution as the junction liquid. The temperature was maintained at 30° by circulating water from an electrically controlled thermostat, by means of an " Albany " pump, through jackets surrounding the two electrode vessels.

TABLE V.

Arginine mixture.

[BOH] = [B˙] = 0·00545.

Salt.	*A.*	*B.*	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·00545	0·0344	0·0528	0·0959	0·1351	0·1712	0·2350
N-KCl	0·5	0·408	*E.M.F.*	0·7629	0·7672	0·7681	0·7690	0·7695	0·7698	0·7705
			p_H	8·569	8·640	8·654	8·670	8·678	8·684	8·696
			$K \times 10^6$	7·0	8·2	8·5	8·8	9·0	9·1	9·4
			$k \times 10^6$	6·4	6·9	6·9	6·8	6·7	6·6	6·7
M/3-K_2SO_4	0·5	0·371	*E.M.F.*	0·7629	0·7683	0·7693	0·7707	0·7717	0·7726	0·7730
			p_H	8·569	8·658	8·674	8·698	8·714	8·730	8·738
			$K \times 10^6$	7·0	8·6	8·9	9·4	9·8	10·1	10·3
			$k \times 10^6$	6·4	7·1	7·1	7·1	7·2	7·3	7·2
N-NaCl	0·5	0·466	*E.M.F.*	0·7629	0·7646	0·7656	0·7660	0·7667	0·7670	0·7674
			p_H	8·569	8·596	8·614	8·620	8·632	8·638	8·644
			$K \times 10^6$	7·0	7·4	7·8	7·9	8·1	8·2	8·3
			$k \times 10^6$	6·5	6·2	6·3	6·1	6·1	6·1	6·1
M/4-$MgSO_4$			*E.M.F.*	0·7629	0·7641	0·7643	0·7638	0·7626	0·7615	0·7593
			p_H	8·569	8·588	8·590	8·582	8·565	8·545	8·507
M/3-$BaCl_2$			*E.M.F.*	0·7629	0·7631	0·7634	0·7633	0·7628	0·7619	0·7597
			p_H	8·569	8·572	8·576	8·574	8·567	8·553	8·515

Salt.	*A.*	*B.*	C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·2896	0·3370	0·3784	0·4149	0·4475	0·4766	0·5027
N-KCl	0·5	0·408	*E.M.F.*	0·7708	0·7708	0·7710	0·7710	0·7710	0·7710	0·7710
			p_H	8·700	8·700	8·704	8·704	8·704	8·704	8·704
			$K \times 10^6$	9·4	9·4	9·5	9·5	9·5	9·5	9·5
			$k \times 10^6$	6·7	6·6	6·7	6·7	6·7	6·7	6·7
M/3-K_2SO_4	0·5	0·371	*E.M.F.*	0·7735	0·7736	0·7734	0·7730	0·7730	0·7729	0·7731
			p_H	8·746	8·748	8·744	8·738	8·738	8·736	8·738
			$K \times 10^6$	10·5	10·5	10·5	10·3	10·3	10·3	10·3
			$k \times 10^6$	7·2	7·2	7·1	7·0	7·0	7·0	7·0
N-NaCl	0·5	0·466	*E.M.F.*	0·7672	0·7678	0·7682	0·7675	0·7677	0·7672	0·7672
			p_H	8·640	8·650	8·656	8·646	8·650	8·640	8·640
			$K \times 10^6$	8·2	8·4	8·5	8·3	8·4	8·2	8·2
			$k \times 10^6$	6·0	6·2	6·3	6·2	6·3	6·2	6·2
M/4 $MgSO_4$			*E.M.F.*	0·7572		0·7538	0·7520	0·7503	0·7485	0·7468
			p_H	8·472		8·418	8·387	8·358	8·318	8·301
M/3-$BaCl_2$			*E.M.F.*	0·7566	0·7535	0·7521	0·7510	0·7502	0·7496	0·7495
			p_H	8·465	8·412	8·389	8·371	8·356	8·347	8·345

Mean value of $k_{B_1} = 6{\cdot}64 \times 10^{-6}$.

(1) *Dilution Experiments.*

In these experiments (Table I) each solution was prepared by mixing 50 c.c. of the previous dilution with an equal volume of water, the same pipette being used.

The values of k, the thermodynamic dissociation constant, given in the last column of Table I, are those deduced from the limiting equation (1). At the highest dilutions studied (about *M*/1,000), the experimental error is necessarily somewhat large; it may be claimed, nevertheless, that the Debye–Hückel theory satisfactorily describes the hydrogen-ion relationships of mono- and di-basic mixtures over a wide range of concentration. For mixtures prepared from acids of higher valency, such as the pyrophosphate mixtures, the lack of constancy of k indicates that the use of the Debye–Hückel equation is justifiable only as a first approximation.

(2) *Neutral-salt Experiments.*

To 10 c.c. of the mixture under examination, successive small increments of *N*-potassium chloride, *N*-sodium chloride, *M*/3-

TABLE VI.

Phthalic acid mixture.

[HA′] = [A″] = 0·01.

Salt.	A.	B.	C.c. added	0·5	1·0	1·5	2·0	3·0	4·0
			μ	0·0857	0·1273	0·1652	0·2000	0·2616	0·3143
N-NaCl	1·5	0·759	*E.M.F.*	0·5414	0·5380	0·5353	0·5331	0·5302	0·5280
			p_H	4·952	4·895	4·851	4·814	4·766	4·730
			$K_2 \times 10^6$	11·2	12·7	14·1	15·4	17·1	18·6
			$k_2 \times 10^6$	4·7	4·7	4·6	4·6	4·6	4·7
M/3-K_2SO_4	1·5	0·961	*E.M.F.*	0·5426	0·5400	0·5378	0·5363	0·5345	0·5330
			p_H	4·972	4·928	4·891	4·867	4·838	4·818
			$K_2 \times 10^6$	10·7	11·8	12·9	13·6	14·5	15·4
			$k_2 \times 10^6$	4·7	4·6	4·6	4·5	4·4	4·4
M-$BaCl_2$	1·5	0·435	*E.M.F.*	0·5337	0·5248	0·5201	0·5162	0·5116	0·5086
			p_H	4·823	4·677	4·597	4·533	4·457	4·407
			$K_2 \times 10^6$	15·0	21·0	25·3	29·3	34·9	39·2
			$k_2 \times 10^6$	5·9	6·9	7·3	7·6	7·7	7·8
N-KCl	1·5	0·845	*E.M.F.*	0·5417	0·5389	0·5365	0·5340	0·5315	0·5294
			p_H	4·957	4·910	4·871	4·828	4·787	4·752
			$K_2 \times 10^6$	11·0	12·3	13·5	14·9	16·3	17·7
			$k_2 \times 10^6$	5·2	4·6	4·6	4·7	4·6	4·7
M/4-$MgSO_4$	1·5	0·466	*E.M.F.*	0·5373	0·5326	0·5290	0·5263	0·5225	0·5199
			p_H	4·884	4·806	4·745	4·700	4·637	4·594
			$K_2 \times 10^6$	13·1	15·6	18·0	20·0	23·1	25·5
			$k_2 \times 10^6$	5·2	5·2	5·3	5·3	5·2	5·2

Salt.	A.	B.	C.c. added	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·3601	0·4000	0·4352	0·4667	0·4948	0·5200
N-NaCl	1·5	0·759	*E.M.F.*	0·5266	0·5256	0·5246	0·5232	0·5227	0·5220
			p_H	4·706	4·689	4·673	4·649	4·640	4·629
			$K_2 \times 10^6$	19·7	20·5	21·2	22·4	22·9	23·5
			$k_2 \times 10^6$	4·6	4·6	4·6	4·8	4·8	4·8
M/3-K_2SO_4	1·5	0·961	*E.M.F.*	0·5320	0·5310	0·5306	0·5300	0·5292	0·5290
			p_H	4·796	4·779	4·773	4·762	4·749	4·745
			$K_2 \times 10^6$	16·0	16·6	16·9	17·3	17·8	18·0
			$k_2 \times 10^6$	4·5	4·5	4·5	4·6	4·7	4·7
M/3-$BaCl_2$	1·5	0·435	*E.M.F.*	0·5064	0·5049	0·5033	0·5020	0·5012	0·5010
			p_H	4·367	4·344	4·318	4·296	4·284	4·280
			$K_2 \times 10^6$	42·8	45·3	48·1	50·6	52·0	52·5
			$k_2 \times 10^6$	7·8	7·6	7·6	7·6	7·5	7·3
N-KCl	1·5	0·845	*E.M.F.*	0·5280	0·5277	0·5270	0·5264	0·5259	0·5251
			p_H	4·730	4·724	4·713	4·702	4·693	4·680
			$K_2 \times 10^6$	18·6	18·9	19·4	19·9	20·3	20·9
			$k_2 \times 10^6$	4·7	4·6	4·6	4·6	4·7	4·8
M/4-$MgSO_4$	1·5	0·466	*E.M.F.*	0·5180	0·5164	0·5150	0·5139	0·5130	0·5121
			p_H	4·563	4·536	4·513	4·494	4·480	4·465
			$K_2 \times 10^6$	27·4	29·1	30·7	32·1	33·1	34·3
			$k_2 \times 10^6$	5·1	5·0	5·0	5·0	4·9	5·0

Mean value of $k_2 = 4·65 \times 10^{-6}$.

potassium sulphate, *M*/3-barium chloride, or *M*/4-magnesium sulphate were added, and the *E.M.F.* at each stage was determined. The salts were Kahlbaum's "for analysis, with certificate of guarantee."

The values of k given in Tables II—IX were computed by means of the expression $p_k = p_H + A\sqrt{\mu} - B\mu$. In general, k is constant within the limits of experimental error, *i.e.*, throughout the range of salt concentrations studied (0·0—0·5*N*), the activation effect is in accordance with the Debye–Hückel theory. Apparent deviations are met with (*a*) in strongly acid mixtures in the presence of potassium and magnesium sulphates, (*b*) in slightly alkaline mixtures on the addition of magnesium sulphate and barium chloride. It is probable that in these cases we are dealing, not with a simple

TABLE VII.

Glycerylphosphoric acid mixture.

[HA′] = [A″] = 0·01.

Salt.	*A.*	*B.*	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·040	0·0680	0·0857	0·1273	0·1652	0·200	0·2616
N-KCl	1·5	0·837	*E.M.F.*	0·6296	0·6258	0·6240	0·6206	0·6185	0·6170	0·6139
			p_H	6·452	6·389	6·359	6·304	6·268	6·244	6·192
			$K \times 10^7$	3·5	4·1	4·4	5·0	5·4	5·7	6·4
			$k \times 10^7$	1·8	1·9	1·9	1·9	1·8	1·8	1·8
N-NaCl	1·5	0·629	*E.M.F.*	0·6296	0·6254	0·6238	0·6204	0·6174	0·6149	0·6117
			p_H	6·452	6·383	6·357	6·300	6·250	6·209	6·155
			$K \times 10^7$	3·5	4·1	4·4	5·0	5·6	6·2	7·0
			$k \times 10^7$	1·8	1·8	1·8	1·8	1·8	1·8	1·7
M/3-K_2SO_4	1·5	0·965	*E.M.F.*	0·6296	0·6260	0·6250	0·6225	0·6204	0·6194	0·6170
			p_H	6·452	6·392	6·375	6·334	6·299	6·282	6·241
			$K \times 10^7$	3·5	4·1	4·2	4·6	5·0	5·2	5·7
			$k \times 10^7$	1·8	1·9	1·8	1·8	1·8	1·7	1·8
M/3-$BaCl_2$	1·5	0·256	*E.M.F.*	0·6296	0·6190	0·6149	0·6095	0·6044	0·6008	0·5962
			p_H	6·452	6·275	6·207	6·119	6·033	5·973	5·896
			$K \times 10^7$	3·5	5·3	6·2	7·6	9·3	10·6	12·7
			$k \times 10^7$	1·8	2·2	2·4	2·4	2·5	2·6	2·5
M/4-$MgSO_4$	1·5	0·288	*E.M.F.*	0·6296	0·6180	0·6144	0·6062	0·6010	0·5985	0·5935
			p_H	6·452	6·260	6·200	6·064	5·977	5·936	5·852
			$K \times 10^7$	3·5	5·5	6·3	8·6	10·5	11·6	14·1
			$k \times 10^7$	1·8	2·3	2·4	2·7	2·9	2·8	2·8
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·3143	0·3601	0·4000	0·4352	0·4667	0·4948	0·5200
N-KCl	1·5	0·837	*E.M.F.*	0·6120	0·6109	0·6099	0·6090	0·6083	0·6078	0·6072
			p_H	6·159	6·142	6·126	6·110	6·099	6·091	6·081
			$K \times 10^7$	6·9	7·2	7·5	7·8	8·0	8·1	8·3
			$k \times 10^7$	1·8	1·8	1·8	1·8	1·8	1·8	1·9
N-NaCl	1·5	0·629	*E.M.F.*	0·6089	0·6072	0·6056	0·6043	0·6032	0·6028	0·6020
			p_H	6·108	6·080	6·053	6·032	6·013	6·006	5·994
			$K \times 10^7$	7·8	8·3	8·9	9·3	9·7	9·9	10·1
			$k \times 10^7$	1·8	1·8	1·8	1·8	1·8	1·8	1·8
M/3-K_2SO_4	1·5	0·965	*E.M.F.*	0·6154	0·6142	0·6136	0·6129	0·6128	0·6122	0·6115
			p_H	6·216	6·195	6·186	6·175	6·173	6·163	6·152
			$K \times 10^7$	6·1	6·4	6·5	6·7	6·7	6·9	7·0
			$k \times 10^7$	1·8	1·8	1·8	1·8	1·8	1·8	1·8
M/3-$BaCl_2$	1·5	0·256	*E.M.F.*	0·5921	0·5903	0·5881	0·5855	0·5850	0·5840	0·5829
			p_H	5·829	5·799	5·762	5·719	5·711	5·694	5·676
			$K \times 10^7$	14·8	15·9	17·3	19·1	19·5	20·2	21·1
			$k \times 10^7$	2·6	2·5	2·5	2·5	2·4	2·4	2·4
M/4-$MgSO_4$	1·5	0·288	*E.M.F.*	0·5902	0·5880	0·5862	0·5845	0·5834	0·5825	0·5815
			p_H	5·798	5·761	5·731	5·703	5·684	5·669	5·653
			$K \times 10^7$	15·9	17·3	18·6	19·8	20·7	21·5	22·3
			$k \times 10^7$	2·8	2·8	2·7	2·7	2·7	2·6	2·6

Mean value of $k_2 = 1·80 \times 10^{-7}$.

activation effect, but with a displacement of the acid–base equilibria. Ionic reactions, such as (*a*) $SO_4'' + H^{\cdot} \rightleftharpoons HSO_4'$, (*b*) $Ba^{\cdot\cdot} + OH' \rightleftharpoons Ba(OH)^{\cdot}$, which tend to diminish the hydrogen- (or hydroxyl-) ion concentration, lead to an alteration of the ratio [acid]/[salt]. In such circumstances it is no longer correct to assume, as is done in computing both K and k, that this ratio is independent of salt concentration.

Conclusions.

(1) The buffer unit of Van Slyke, *viz.*, $\beta = dB/dp_H$, is not in itself a true criterion of buffer efficiency. It is suggested that this value should be supplemented by the unit $\pi = dp_H/d\sqrt{\mu}$ expressing the dilution and neutral-salt errors.

TABLE VIII.

Pyrophosphoric acid mixture (i).

$[H_2A''] = [HA'''] = 0{\cdot}02.$

Salt.	*A.*	*B.*	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·2400	0·2625	0·2762	0·3093	0·3392	0·3665	0·4156
N-KCl	2·5	1·29	*E.M.F.*	0·5922	0·5886	0·5876	0·5859	0·5845	0·5832	0·5813
			p_H	5·797	5·737	5·720	5·693	5·669	5·646	5·615
			$K_3 \times 10^7$	16·0	18·3	19·1	20·3	21·4	22·6	24·3
			$k_3 \times 10^7$	1·9	2·1	2·1	2·1	2·1	2·1	2·0
N-NaCl	2·5	0·983	*E.M.F.*	0·5922	0·5838	0·5872	0·5846	0·5826	0·5806	0·5776
			p_H	5·797	5·657	5·714	5·670	5·637	5·664	5·554
			$K_3 \times 10^7$	16·0	22·0	19·3	21·4	23·1	24·9	27·9
			$k_3 \times 10^7$	1·6	2·1	1·8	1·8	1·7	1·7	1·7
M/3-K_2SO_4	2·5	1·48	*E.M.F.*	0·5922	0·5911	0·5901	0·5888	0·5878	0·5868	0·5853
			p_H	5·797	5·779	5·762	5·740	5·724	5·707	5·683
			$K_3 \times 10^7$	16·0	16·6	17·3	18·2	18·9	19·6	20·8
			$k_3 \times 10^7$	2·2	2·1	2·2	2·1	2·1	2·1	2·1
M/4-$MgSO_4$			*E.M.F.*	0·5922	0·5755	0·5644	0·5398	0·5250	0·5159	0·5062
			p_H	5·797	5·518	5·333	4·925	4·679	4·528	4·366
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·9
			μ	0·4573	0·4936	0·5250	0·5527	0·5777	0·6003	0·6200
N-KCl	2·5	1·29	*E.M.F.*	0·5798	0·5788	0·5777	0·5769	0·5763	0·5758	0·5753
			p_H	5·590	5·573	5·555	5·543	5·530	5·524	5·516
			$K_3 \times 10^7$	25·7	26·7	27·9	28·6	29·5	29·9	30·5
			$k_3 \times 10^7$	2·0	2·0	2·0	2·0	2·1	2·1	2·1
N-NaCl	2·5	0·983	*E.M.F.*	0·5755	0·5737	0·5718	0·5703	0·5693	0·5683	0·5676
			p_H	5·518	5·489	5·458	5·433	5·417	5·399	5·388
			$K_3 \times 10^7$	30·3	32·4	34·8	36·9	38·3	39·9	40·9
			$k_3 \times 10^7$	1·7	1·7	1·8	1·8	1·8	1·8	1·8
M/3-K_2SO_4	2·5	1·48	*E.M.F.*	0·5843	0·5838	0·5830	0·5825	0·5818	0·5816	0·5807
			p_H	5·666	5·657	5·644	5·635	5·623	5·620	5·606
			$K_3 \times 10^7$	21·6	22·0	22·7	23·2	23·8	24·0	24·8
			$k_3 \times 10^7$	2·1	2·1	2·1	2·1	2·1	2·1	2·2
M/4-$MgSO_4$			*E.M.F.*	0·5004	0·4968	0·4941	0·4921	0·4903	0·4888	0·4878
			p_H	4·270	4·210	4·165	4·132	4·102	4·078	4·061

Mean value of $k_3 = 1{\cdot}98 \times 10^{-7}$.

TABLE IX.

Pyrophosphoric acid mixture (ii).

$[HA'''] = [A''''] = 0{\cdot}02.$

Salt.	*A.*	*B.*	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·3400	0·3598	0·3715	0·4003	0·4262	0·4498	0·4926
N-KCl	3·497	1·33	*E.M.F.*	0·7410	0·7380	0·7369	0·7335	0·7318	0·7292	0·7260
			p_H	8·307	8·256	8·237	8·181	8·153	8·108	8·056
			$K_4 \times 10^{10}$	49·3	55·5	57·9	65·9	70·3	78·0	87·9
			$k_4 \times 10^{10}$	1·3	1·3	1·3	1·4	1·3	1·4	1·4
N-NaCl	3·22	0·687	*E.M.F.*	0·7410	0·7376	0·7358	0·7303	0·7265	0·7237	0·7190
			p_H	8·307	8·249	8·219	8·127	8·063	8·017	7·939
			$K_4 \times 10^{10}$	49·3	56·4	60·4	74·6	86·5	96·2	115·1
			$k_4 \times 10^{10}$	1·1	1·2	1·2	1·3	1·3	1·4	1·4
M/3-K_2SO_4	3·69	1·74	*E.M.F.*	0·7410	0·7392	0·7384	0·7365	0·7349	0·7337	0·7320
			p_H	8·307	8·275	8·262	8·230	8·204	8·185	8·156
			$K_4 \times 10^{10}$	49·3	53·1	54·7	58·9	62·5	65·3	69·8
			$k_4 \times 10^{10}$	1·4	1·4	1·4	1·3	1·3	1·3	1·3
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·5288	0·5604	0·5875	0·6115	0·6332	0·6531	0·6700
N-KCl	3·497	1·33	*E.M.F.*	0·7239	0·7222	0·7207	0·7195	0·7185	0·7178	0·7170
			p_H	8·021	7·991	7·968	7·947	7·930	7·920	7·907
			$K_4 \times 10^{10}$	95·3	102	108	113	118	120	124
			$k_4 \times 10^{10}$	1·4	1·4	1·3	1·3	1·3	1·3	1·3
N-NaCl	3·22	0·687	*E.M.F.*	0·7152	0·7125	0·7102	0·7084	0·7067	0·7052	0·7041
			p_H	7·877	7·830	7·793	7·764	7·736	7·711	7·691
			$K_4 \times 10^{10}$	133	148	161	172	184	195	204
			$k_4 \times 10^{10}$	1·4	1·4	1·4	1·4	1·4	1·4	1·3
M/3 K_2SO_4	3·69	1·74	*E.M.F.*	0·7308	0·7289	0·7282	0·7273	0·7268	0·7263	0·7257
			p_H	8·136	8·104	8·091	8·076	8·069	8·060	8·050
			$K_4 \times 10^{10}$	73·1	78·7	81·1	84·0	85·3	87·1	89·1
			$k_4 \times 10^{10}$	1·3	1·3	1·3	1·3	1·2	1·2	1·2

Mean value of $k_4 = 1{\cdot}32 \times 10^{-10}$.

(2) The limiting dilution error is independent of the strength and specific nature of the buffer electrolyte, depending only on the valency type.

(3) The limiting dilution error of a monobasic buffer mixture is $\pi = -0{\cdot}5$; that of an n-valent mixture is approximately $(2n - 1)$ times as great.

(4) The neutral-salt error is described by the Debye–Hückel equation in the form $p_k = p_K + A\sqrt{\mu} - B\mu$. The value of A for an n-valent buffer mixture is approximately $(n - 0{\cdot}5)$. The value of B depends on the specific nature of the salt, and on the strength and valency of the buffer electrolyte.

(5) The "thermodynamic dissociation constants" of aspartic (k_{A_1}), acetic, cacodylic, o-phthalic (k_2), α-glycerylphosphoric (k_2), and pyrophosphoric (k_3, k_4) acids, and of arginine (k_{B_1}) have been determined.

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