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by D H Everett FRS, *University of Bristol*

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pH AND ITS MEASUREMENT

Arthur Covington

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pH AND ITS MEASUREMENT

Arthur K Covington

Arthur K Covington received the degrees of BSc, PhD and DSc from the University of Reading where he worked with the late Professors J E Prue and E A Guggenheim. After a period in industry he went, in 1958, to Kings College in the University of Durham, which later became the University of Newcastle-upon-Tyne, to join the electrochemistry group of the late Professor Lord Wynne-Jones. He became Senior Lecturer in 1969, Reader in Physical Chemistry in 1971, and was awarded a personal Chair in Electro-analytical Chemistry in 1985.

Professor Covington's research interests include pH measurements and standardisation, pH titrimetry and complex ion-formation constant determinations, ion-selective electrodes and ChemFETs and particularly their application to clinical chemistry. He was 1983-84 R A Robinson Medallist and Lecturer, and in 1986 recipient of the Award and Medal for electroanalytical chemistry, of the Royal Society of Chemistry.

As Chairman of British Standards Institution Technical Committee LBC/16 since 1973 he has been responsible for the preparation of British Standards on pH measurement, pH meters, glass and reference electrodes, and ion-selective electrodes. He is UK National Representative on the International Union of Pure and Applied Chemistry Commission (V5) on Electroanalytical Chemistry and on the Electrochemistry Commission (I3). He has also been concerned with standardisation work with various other international bodies, and currently the International Federation of Clinical Chemistry Blood Gases and Electrolytes Subcommittee.

He is author of another Chemistry Cassette in this series on *Ion-Selective Electrodes*.

CHEMISTRY CASSETTES

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ACKNOWLEDGEMENTS

Thanks are due to CIBA CORNING DIAGNOSTICS, KENT INDUSTRIAL MEASUREMENTS and RUSSELL pH for providing illustrative material for frames 4, 10, 11, 12, 15, 16 and 17, and especially to DR ISABEL FERRA for reading the text and checking the exercises.

1

$$\text{pH} = -\lg c_{\text{H}^+}$$

or

$$\text{pH} = -\lg c_{\text{H}^+}/c^\circ$$

where $c^\circ = 1 \text{ mol dm}^{-3}$

NB. pH does not have units.

Notional definition: $\text{pH} = -\lg a_{\text{H}^+} = -\lg c_{\text{H}^+} \gamma_{\text{H}^+} / c^\circ$ (1)

where γ_{H^+} is the single ion activity coefficient of the hydrogen ion on the molarity scale.

Usual range of pH for aqueous solutions is determined by the ionic product, or autoprotolysis constant, of water:

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} (\text{mol dm}^{-3})^2 \text{ at } 298 \text{ K}$$

where [] indicates, for the moment, substance concentrations,

$$\text{so } [\text{H}^+] = [\text{OH}^-] = K_w^{0.5} = 10^{-7} \text{ mol dm}^{-3}$$

and for solutions no more concentrated than 1 mol dm^{-3} , the range of pH is 0 (acid) to 14 (alkaline) with neutrality at $\text{pH} = 7$. This is only true at 298 K; neutrality is 6.5 at 358K and 7.5 at 273K because K_w is strongly temperature dependent.

2**Operational cell scheme:**

$\text{Hg} \mid \text{Hg}_2\text{Cl}_2 \mid \text{KCl} (< 3.5 \text{ mol dm}^{-3}) \parallel \text{X} \mid \text{H}_2 \mid \text{Pt}$ (I)
 where X is the solution whose pH it is required to measure.

Applying the Nernst equation to the spontaneous cell reaction:

$E = E^\circ + k \lg a_{\text{H}^+} a_{\text{Cl}^-} + E_J$,
 where $k = (RT/F) \ln 10 = 59.16 \text{ mV}$ at 298 K (often called the 'slope factor')
 and E_J is the liquid junction potential between X and KCl.

Substituting the notional definition for pH from FRAME 1,

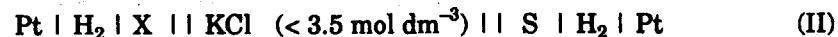
$E = E^\circ - k \text{pH} + E_J + k \lg a_{\text{Cl}^-} = (E^\circ + E_J) - k \text{pH}$
 where the constant chloride ion activity term has been combined with E° as E° .

Rearranging

$$\text{pH} = [(E^\circ + E_J) - E] / k \quad (2)$$

The term in () is often referred to as 'the standard potential'.

Using pH standard solutions, the operational cell is used to compare standard S with sample X, so the cell is effectively



and the reference electrode serves only to assist in making the measurement, particularly when a glass electrode replaces the hydrogen gas electrode.

Now

$$\text{pH(X)} = \text{pH(S)} - \{E(\text{X}) - E(\text{S})\} / k + \{E_J(\text{X}) - E_J(\text{S})\} / k \quad (3)$$

where $\{E(\text{X}) - E(\text{S})\}$ is the potential difference of the above cell, or alternatively $E(\text{X})$ and $E(\text{S})$ are the potential differences of the operational cell containing X or S, and the last term is called the 'residual liquid junction potential'. It is the change in liquid junction potential against KCl when X is replaced by S in the operational cell. This term is assumed to be zero in order to calculate pH(X) . Any error in making this assumption is subsumed into pH(X) .

3**pH Glass Electrode****Pioneers in its Development:**

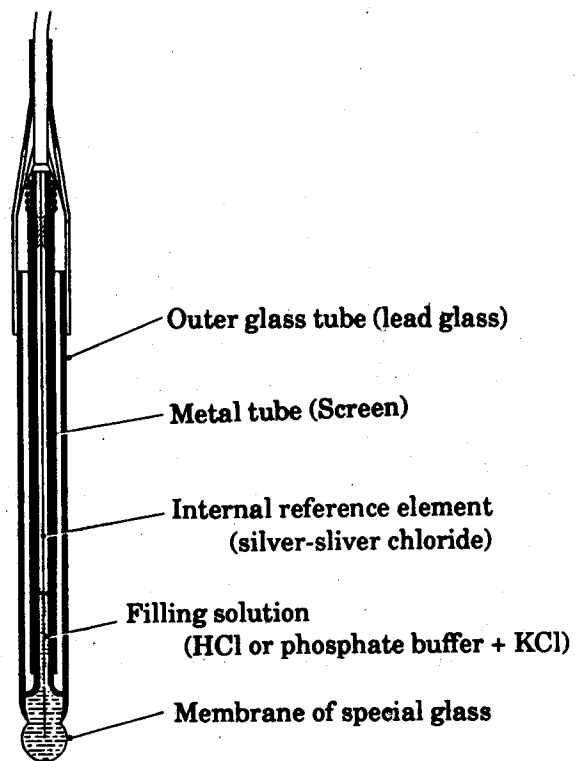
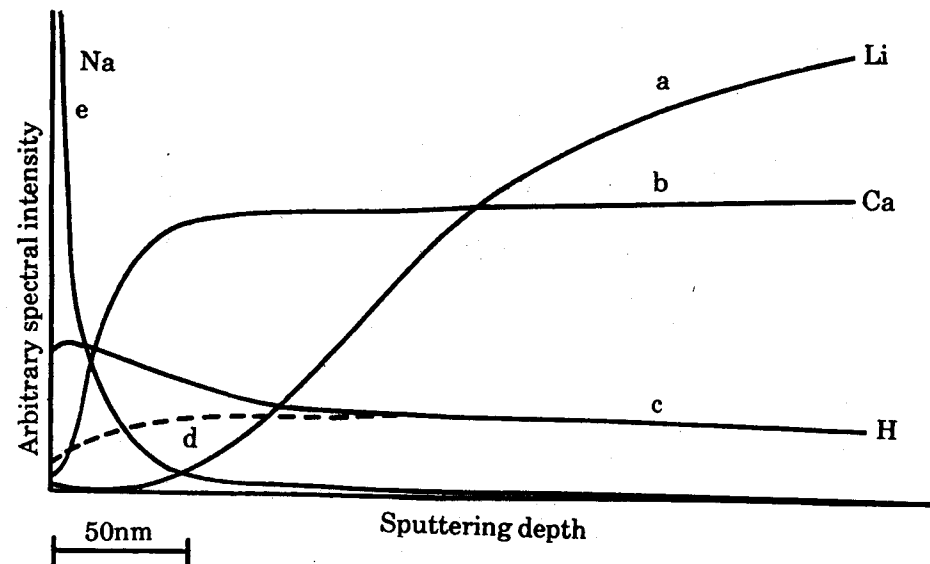
- 1906: Cremer, a biologist, discovered the effect
- 1909: Haber and Klemensiewicz did the first systematic study
- 1930: MacInnes and Dole did a systematic study to find the optimum sodium calcium silicate glass composition
- 1949: Perley reported on the optimising of commercial glass compositions using lithium glasses

Asymmetry Potential:

- i) caused by differences between inside and outside surfaces.
- ii) varies with time, hence recalibration necessary.

Conditioning before use:Necessary to develop by ion-exchange a 'gel' layer of silanol ($\equiv \text{SiOH}$) groups on the surface; water swollen, alkali metal-free.**Errors (extent depends on glass composition):**

- i) Acid errors - entry of anions into gel layer.
- ii) Alkaline errors entry of Na^+ , Li^+ into gel layer.

4**Conventional screened glass electrode.****5**

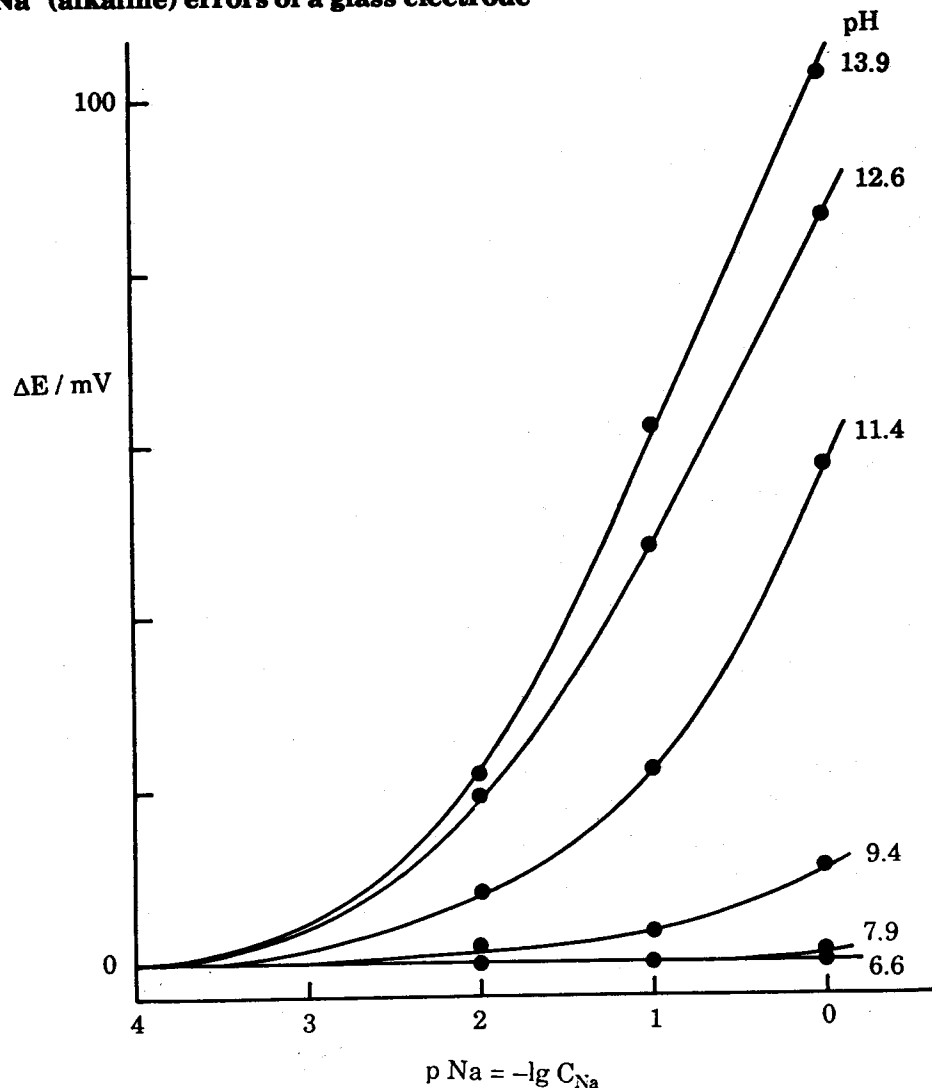
Concentration profiles in a lithia lime silica glass (20-5-75 mol%) after soaking in 0.1 mol/l H_2SO_4 for three days.

(a) Li; (b) Ca; (c) H immediately after exposure to low pressure; (d) as (c) but after exposure to low pressure for one hour; (e) penetration of Na after soaking repolished specimen in 0.1 mol/l NaOH for 24 hrs.

Source: JCS Chem. Comm. 1972, 792

6

Na⁺ (alkaline) errors of a glass electrode



7

Reference Electrodes.

Values of E_0' / mV^* for some common sat. KCl reference electrodes

Hg	Hg ₂ Cl ₂	KCl	Calomel	-241.3
Ag	AgCl	KCl	Silver-silver chloride	-195.4
Tl(Hg)	TlCl	KCl	'Thalimid'	+575.0
Pt I ₂	KI ₃	KCl	Ross	-822.0

Problems with Reference Electrodes

Design of liquid junction $\rightarrow E_J$ variation

Contamination of sample $\rightarrow E$ changes

Ingress of sample $\rightarrow E_0'$ changes

Ingress of water $\rightarrow E_J, E_0'$ changes

* Eqn. 2 of FRAME 2: see Appendix 8 for a note on sign conventions.

8

Requirements for Stable Liquid Junctions

1) Gravitational Stability.

The less dense solution should be on top

2) Fixed and Constant Geometry

A clearly defined and constant transition layer between the two solutions formed by free diffusion, constrained in ceramic or polymer, or by flow.

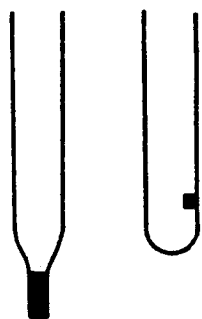
3) Cylindrical Symmetry

Lines of electric force should be in the same direction as the density gradient.

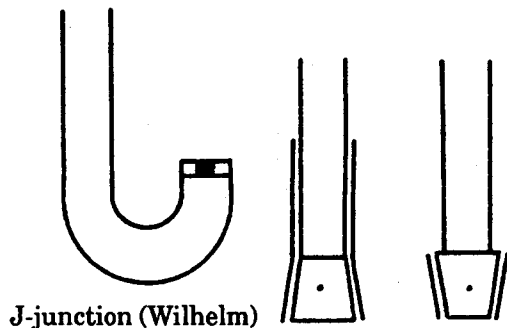
These requirements are not met by any commercial design of junction and certainly not by ceramic plug or ground glass sleeve junctions (see FRAME 9).

9

Methods of forming liquid junctions.

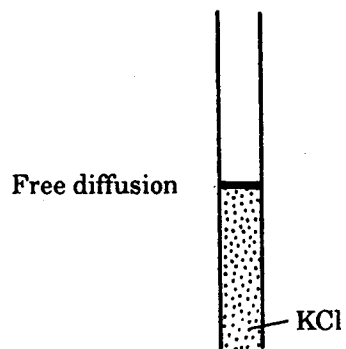


Porous ceramic



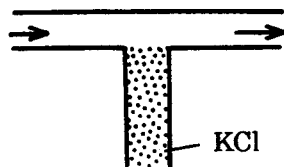
J-junction (Wilhelm)

Ground glass 'sleeve' type
(may be cleaned and renewed)



Free diffusion

KCl

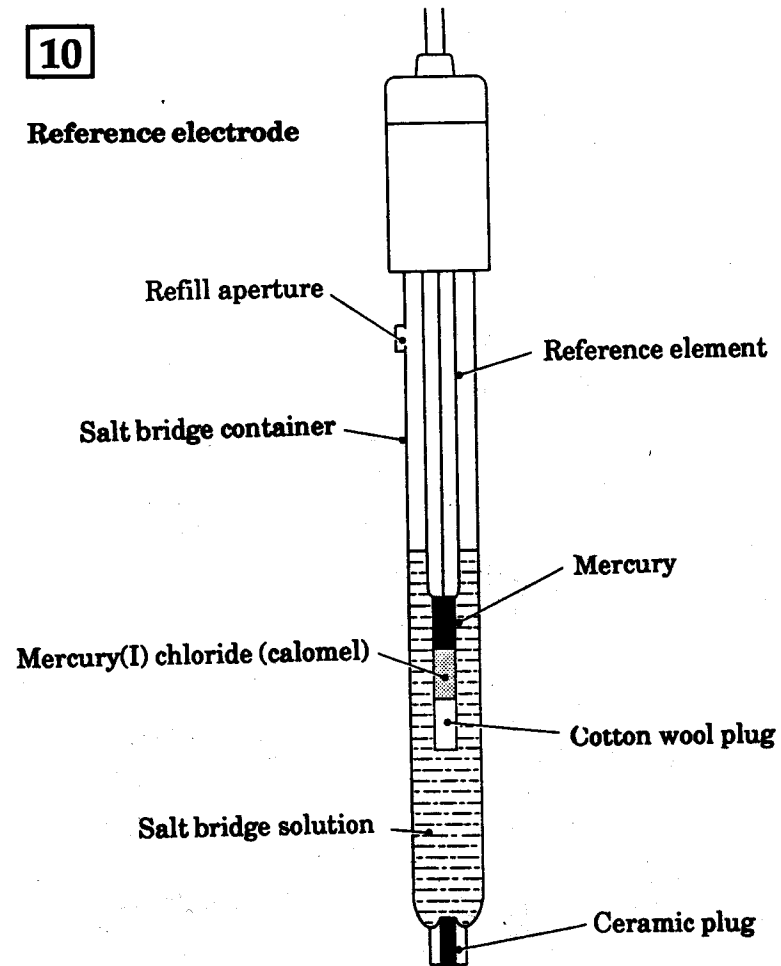


Flowing junctions

KCl

10

Reference electrode



Refill aperture

Reference element

Salt bridge container

Mercury

Mercury(I) chloride (calomel)

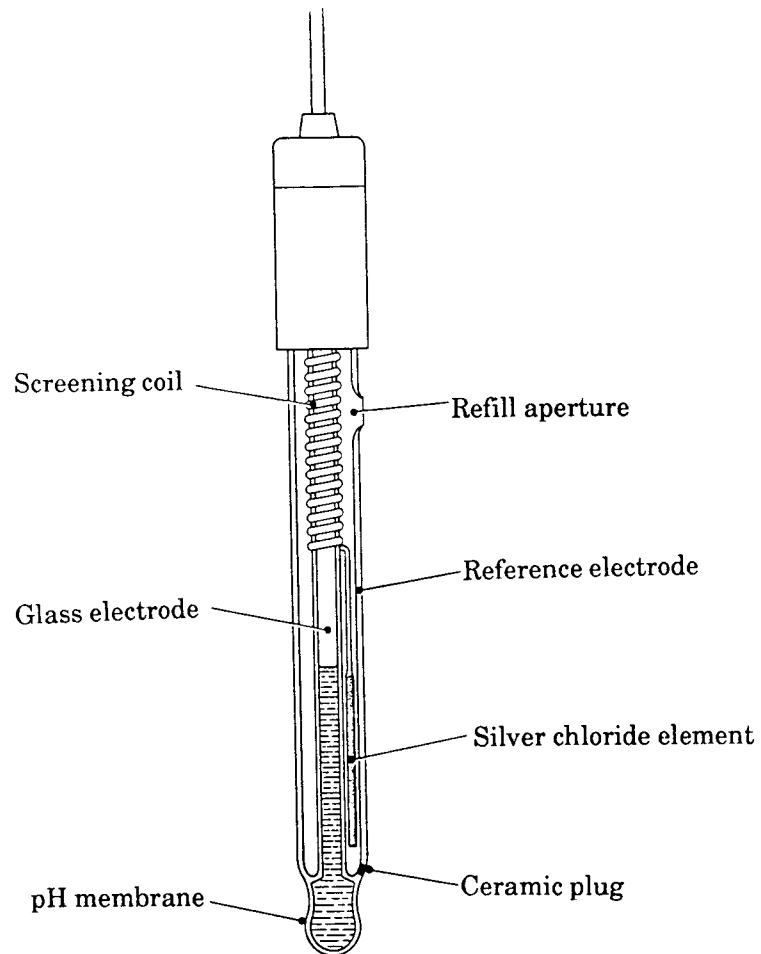
Cotton wool plug

Salt bridge solution

Ceramic plug

11

Combination (dual) electrode



12

Glass electrode production/testing facility



13**Requirements of pH meters**

A pH meter is a high impedance millivoltmeter with a facility for converting mV to pH.

Input ± 900 mv with source resistance 5×10^9 ohm at 273 K.

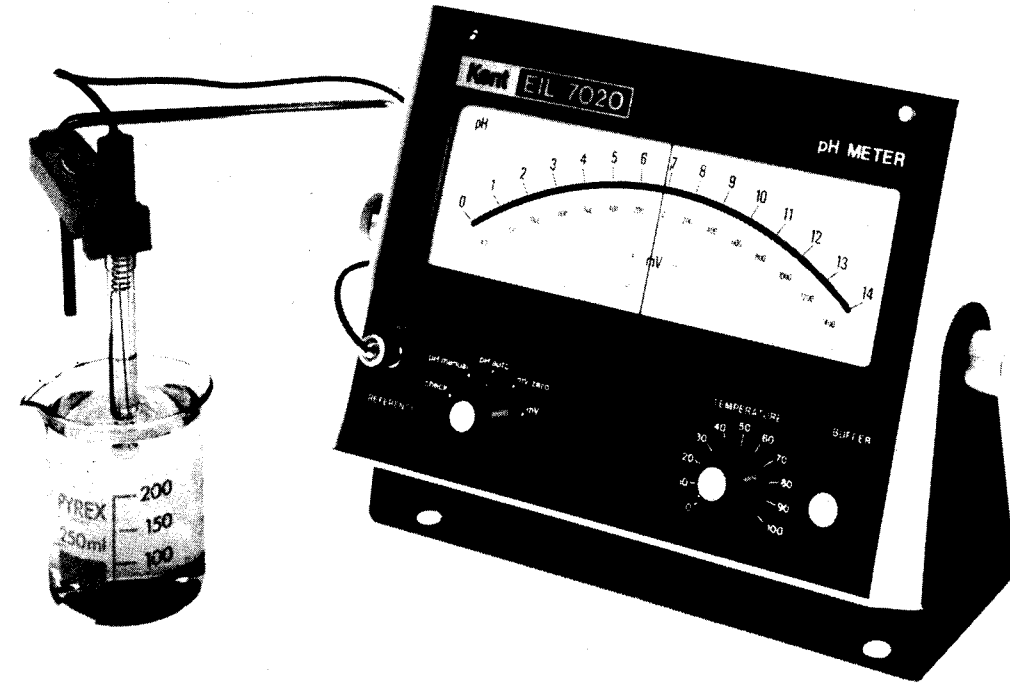
Output: mV/pH with provision for driving display

Display: Linear (mV/pH) or logarithmic (concentration).

Form of Display: Moving index, digital (LED, LCD), recording (strip chart, print out, RS232).

14**Controls on pH Meters**

Name	Function
Set Buffer Adjustment (buffer, set zero, intercept, asymmetry, standardise, calibrate)	Input signal offset
Slope Temperature Factor Adjustment (slope factor, temperature)	Divide signal by k (amplifier gain)
Slope Factor Adjustment (sensitivity, span, scale length)	%k (amplifier fine gain)
Isopotential (set iso, zero control, set standard point)	Output Offset (pH where temperature control is ineffective)

15**Analogue display pH meter.**

16

Research analogue pH meter showing controls.



17

Digital pH meter.



Temperature Compensation

1) Manual

0.01 pH error results from 1°C error in setting control when $\Delta\text{pH} = \text{pH}(\text{S}) - \text{pH}(\text{X}) = 3$ but resistor linearity is not usually better than 1%.

2) Automatic

Nickel or platinum resistance thermometer which replaces part or all of the amplifier feedback resistor. (It is impossible to find material with exactly the right non-linearity of temperature coefficient. Each device has to be matched to an individual pH meter).

3) Isopotential Correction

There are two separate cases (both of which should be avoided if at all possible), each requiring separate and different corrections:

- When sample and standard differ in temperature
- When reference electrode is remote and at a different temperature from the sample and standard reference buffer.

If $E(\text{X}) = a + bT + k'T \text{pH}(\text{X})$, where $k' = k/T$, then E is not a function of temperature when $-bT = k'T \text{pH}(\text{X})$ or the isopotential pH_i , $\text{pH}_i = -b/k' = -(1/k') dE^0/dT$. This pH_i value relates to a particular type of glass-reference electrode pair.

pH Values of Some Standard Buffers (see Appendices 2 & 3 for more values and details)

	pH (298 K)
Potassium hydrogen phthalate (0.05 mol kg ⁻¹) (KHP _h - H ⁺ , HPh ⁻ , Ph ²⁻)	4.01
Potassium dihydrogen phosphate (0.025 mol kg ⁻¹) + disodium hydrogen phosphate (0.025 mol kg ⁻¹) (→ H ⁺ , HPO ₄ ²⁻ , H ₂ PO ₄ ⁻)	6.86
Disodium tetraborate (0.01 mol kg ⁻¹) (B ₄ O ₇ ²⁻ + 7H ₂ O → 2B(OH) ₄ ⁻ + 2B(OH) ₃)	9.18

20a

For phosphoric acid, H_3A , there are three pKs

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]}$$

$$K_2 = \frac{[\text{H}^+][\text{HA}^{2-}]}{[\text{H}_2\text{A}^-]}$$

$$K_3 = \frac{[\text{H}^+][\text{A}^{3-}]}{[\text{HA}^{2-}]}$$

The total concentration is

$$c = [\text{H}_3\text{A}] + [\text{H}_2\text{A}^-] + [\text{HA}^{2-}] + [\text{A}^{3-}]$$

and the fraction with zero hydrogen ions

$$\alpha_0 = \frac{[\text{A}^{3-}]}{c}$$

$$= \left[\frac{[\text{H}_3\text{A}]}{[\text{A}^{3-}]} + \frac{[\text{H}_2\text{A}^-]}{[\text{A}^{3-}]} + \frac{[\text{HA}^{2-}]}{[\text{A}^{3-}]} + 1 \right]^{-1}$$

$$= \left[\frac{[\text{H}^+]}{K_1 K_2 K_3} + \frac{[\text{H}^+]}{K_2 K_3} + \frac{[\text{H}^+]}{K_3} + 1 \right]^{-1}$$

and hence $\alpha_1 = \frac{\alpha_0 [\text{H}^+]}{K_3}$

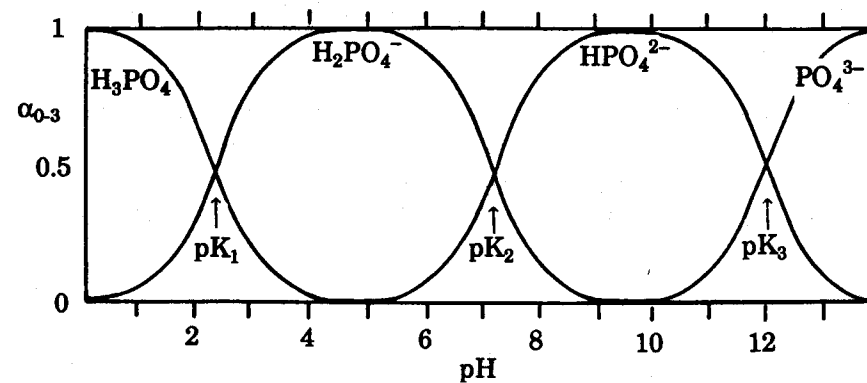
$$\alpha_2 = \frac{\alpha_0 [\text{H}^+]^2}{K_2 K_3}$$

$$\alpha_3 = \frac{\alpha_0 [\text{H}^+]^3}{K_1 K_2 K_3}$$

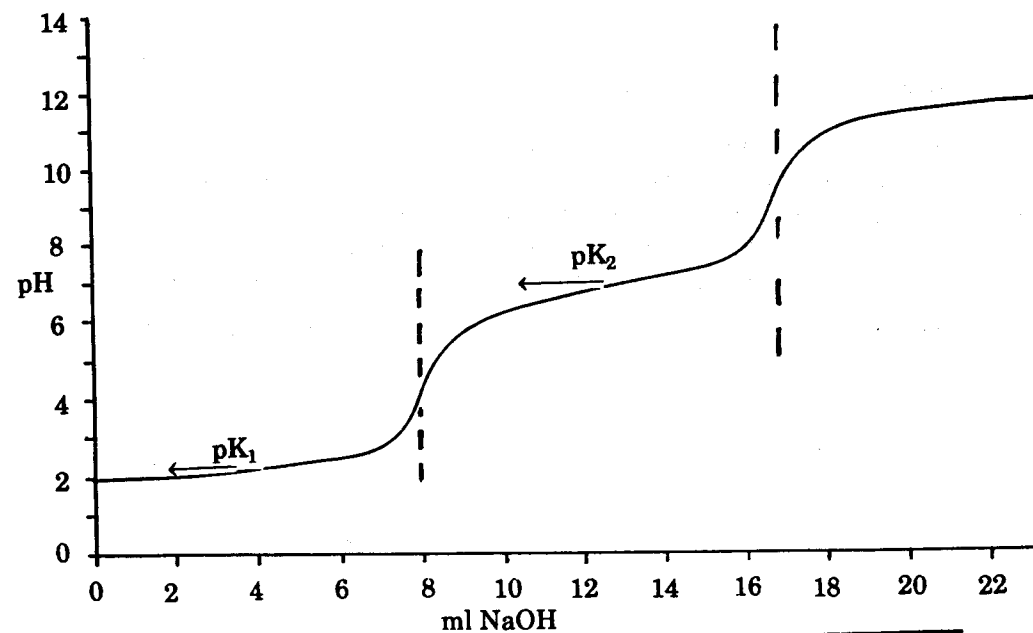
so the species concentration diagram (frame 20b) can be constructed from knowledge of the pKs.

20b

Species concentration diagram for phosphoric acid

**20c**

Titration curve for phosphoric acid



Measurement of pH**Choice of Standard Reference Solution**

1a) If pH is not required to better than ± 0.05 any standard reference solution may be selected.

1b) If pH is required to ± 0.002 and interpretation in terms of hydrogen ion concentration or activity is desired, choose a standard reference solution to match X as closely as possible in terms of pH, composition and ionic strength. Even so, the uncertainty in hydrogen ion concentration will be given by

$$\text{pH} = -\lg(c_{\text{HY}^{\pm}} / c^{\circ}) \pm 0.02$$

where y_{\pm} is the mean ionic activity coefficient of a typical 1:1 electrolyte. The uncertainty of 0.02 corresponds to an uncertainty of $\pm 3.9\%$ in concentration.

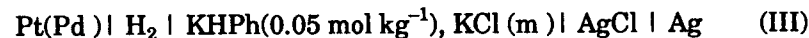
2) Alternatively, a bracketing procedure may be adopted whereby two standard reference solutions are chosen whose pH values, pH(S1), pH(S2) are on either side of pH(X). Then if the corresponding potential difference measurements are E(S1), E(S2), E(X), then pH(X) is obtained from

$$\text{pH}(X) = \text{pH}(S1) + [E(X) - E(S1)] / \%k$$

where $\%k = 100[E(S2) - E(S1)] / [\text{pH}(S2) - \text{pH}(S1)]$ is the apparent percentage slope. This procedure is very easily done on some pH meters simply by adjusting downwards the slope factor control with the electrodes in S2. The purpose of the bracketing procedure is to compensate for deficiencies in the electrodes and measuring system.

Determination of pH standard values for potassium hydrogen phthalate pH(RVS)

The cell without liquid junction, called the Harned cell, is



where, in this example, KHPH = potassium hydrogen phthalate, and Pt(Pd) is a palladised platinum electrode in which the lower catalytic activity of palladium compared with platinum is used to reduce the possibility of chemical reduction of the benzene ring in the phthalate.

Using again the operator $p = -\lg$, we define

$$p(a_{\text{H}} \gamma_{\text{Cl}}) = -\lg(m_{\text{H}} \gamma_{\text{H}} \gamma_{\text{Cl}}) = (E - E^{\circ}) / k + \lg m \quad (4)$$

and the molality scale (mol kg^{-1}) is preferred as it is temperature independent and γ refers to single ion activity coefficients on this scale.

E° refers to the standard potential of the Ag | AgCl electrode, whose value is known, or can be redetermined with a known concentration of HCl in the Harned cell. First, a small extrapolation is done to remove the effect of KCl(m), added so that we can use the Ag | AgCl electrode directly in the solution. Now the assigned value of pH, pH(RVS), can be obtained if we adopt a convention for γ_{Cl} .

That chosen is called the Bates-Guggenheim convention. It is intended for solutions of ionic strength* $I \leq 0.1 \text{ mol/l}$. It is based on the Debye-Hückel theory for the activity coefficient with an assumed ion-size parameter of close to 5 Ångströms.

$$\lg \gamma_{\text{Cl}} = -A\sqrt{I} / [1 + 1.5\sqrt{I}] \quad (\text{Bates-Guggenheim Convention}) \quad (5)$$

which can be substituted into $\text{pH(RVS)} = (p a_{\text{H}} \gamma_{\text{Cl}})^{\circ} + \lg \gamma_{\text{Cl}}$,

where $^{\circ}$ signifies extrapolation to zero KCl added, to obtain pH(RVS)

The measurements are then repeated at 5° intervals and the results expressed by smoothing equations such as

$$\text{pH(RVS)}_{\text{T}} = A/T + B + CT + DT^2$$

The same procedure is applied to primary standard solutions to obtain pH(PS) values.

* ionic strength $I = \frac{1}{2} \sum_i z_i^2 m_i$

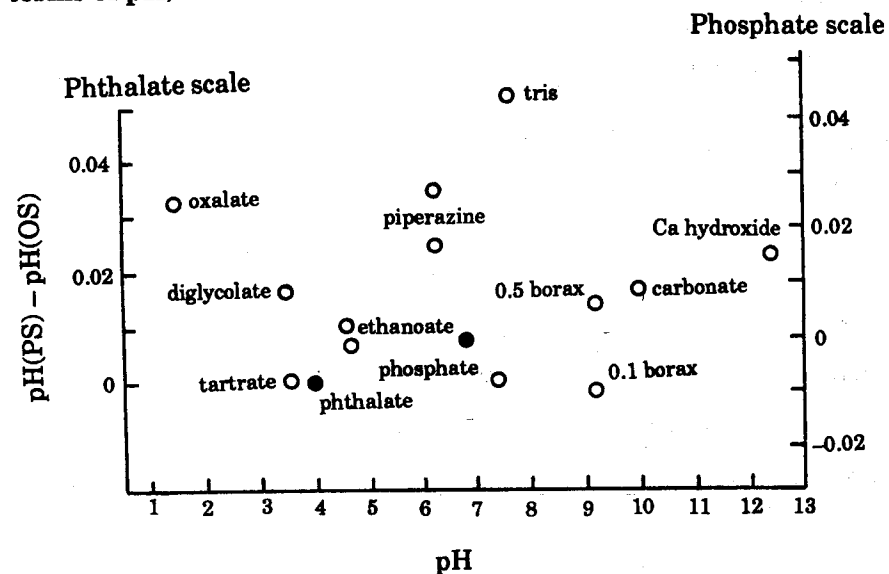
($I = m$ for 1:1 electrolytes, e.g NaCl; $I = 3m$ for 1:2 electrolytes, etc.)

Choice of standard reference materials for primary pH buffers

The ideal properties of pH standard reference substances are:

1. Good buffer capacity.
2. Good crystallization conditions, i.e. on crystallization from aqueous solution which contains an excess of acid or alkaline components, crystals of the proper composition must be formed.
3. Moderate solubility at room temperature so that easy purification of the salt can be obtained by recrystallization.
4. pH in solution should show only slight dependence on concentration.
5. pH in the solution should show only slight dependence on temperature.
6. The requirement of low residual liquid junction potential.
7. A single component buffer (e.g. potassium hydrogen phthalate) is simpler to prepare than a two component one.

Conventional residual liquid junction potentials (expressed in terms of pH)



Source: Anal. Chim. Acta 1987, 200, 245

Tests of the Nernstian response of some electrodes

EMF of cells:

(I) SCE(Y) | X | H₂ | Pt; with Y = cylindrical liquid junction (clj); ceramic plug (cp); asbestos fibre (af); glass sleeve junction (gs) and (II) SCE(clj) | X | GE at 25°C.

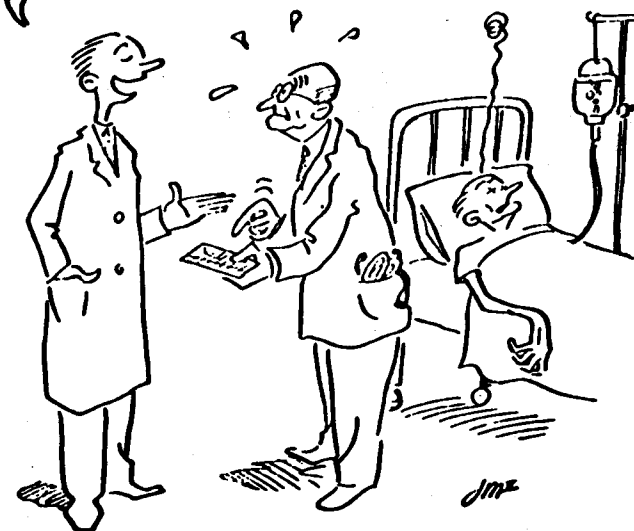
X	-E _i /mV					-ΔE _i /mV				error of GE/mV
	clj	cp	af	gs	GE	E _{clj} -E _{cp}	E _{clj} -E _{af}	E _{clj} -E _{gs}	E _{clj} -E _i (clj)	
0.05m tetroxalate	343.29	344.82	342.56	341.69	529.63	-1.54	0.73	1.6	186.34	0.36
0.05m NaHdiglycollate	452.21	450.47	447.91	451.20	638.56	1.71	4.3	1.01	186.35	0.37
0.05m KHphthalate	482.66	481.61	479.16	481.79	668.64	1.03	3.5	0.87	185.98	★0.00
0.1 mol/l ethanoic acid + 0.1 mol/l sodium ethanoate	520.57	519.18	517.77	519.58	706.55	1.36	2.8	0.99	185.98	0.00
0.025m phosphate	650.64	648.76	647.94	649.68	836.46	1.87	2.7	0.96	185.82	+0.16
0.008695m KH ₂ PO ₄ + 0.003043m Na ₂ HPO ₄	683.85	681.77	681.05	682.84	869.85	2.08	2.8	1.00	186.0	-0.02
0.05 mol/l borax	789.00	787.02	786.30	788.02	974.39	2.00	2.7	0.98	185.39	+0.59
Slope E vs. pH(PS)	59.23	58.78	59.04	59.28	59.12					
S.D.	±0.10	±0.07	±0.05	±0.13	±0.09					
Slope E vs. pH(OS)	59.15	58.75	59.04	59.20	59.04					
S.D.	±0.02	±0.16	±0.20	±0.03	±0.02					

★ Assumed to be zero

Source: A K Covington, *Anal. Chim. Acta* 1981, 127, 1.

M J F Rebelo, *PhD Thesis*, University of Newcastle upon Tyne, 1983.

RESIDUAL LIQUID-JUNCTION POTENTIALS, BUFFER ACCURACY, ELECTRODE & BUFFER TEMPERATURE COEFFICIENTS, ELECTRODE IMPEDANCES ARE ALL AMONG THE FACTORS THAT CAN PRODUCE UNDETECTED ERRORS IN MEASUREMENTS WHOSE MAGNITUDE.....



Recommended Reading

R.G. Bates, *Determination of pH. Theory and Practice. Second Edition.* Wiley, New York 1973.

[This is the definitive text, alas now out of print]

A.K. Covington, R.G. Bates and R.A. Durst, *Pure and Applied Chemistry* 1985, 57, 531-542.

[contains the compromise IUPAC recommendations]

A.K. Covington, *Anal Chim. Acta* 1981, 127, 1.

R.G. Bates, *Crit. Rev. Anal. Chem.* 1981, 10, 247.

[present the two sides of the controversy]

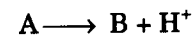
EXERCISES

- 1 For the 1 : 3.5 physiological or 'blood' phosphate buffer at 25°C, the potential differences of the Harned cell were 803.20, 785.09 and 774.36 mV for additions of potassium chloride so that the chloride concentrations in the buffer were 0.005, 0.010 and 0.015 mol/kg respectively. Take $E^\circ = 222.34$ mV and calculate $p_{\text{aH}^+/\text{Cl}^-}$ for each chloride concentration. Extrapolate the data to zero chloride concentration. Calculate the single ion activity coefficient of the chloride ion at the ionic strength of the buffer using the Bates-Guggenheim Convention ($A = 0.5108 \sqrt{\text{kg mol}^{-1}}$). Hence calculate pH(PS) of the 'blood' buffer solution.
- 2 In 1 : 1 phosphate, phthalate and carbonate buffers, a glass-reference electrode pair gave potential difference readings of -3, 161, and -178 mV respectively at 25°C. Calculate, using values from Appendix 4, (i) the percentage variation from the theoretical, Nernstian slope; (ii) the pH value for the phosphate buffer by the bracketing procedure taking the other two as standard buffers; (iii) the pH value for the phosphate buffer taking the phthalate as the standard buffer and the Nernst slope. Calculate the pH(X) of an unknown X, which gave a potential difference reading of -260 mV, on the basis of phthalate as the standard buffer with (a) the Nernst slope and (b) the practical slope calculated in (i). Which would be nearer correct?
- 3 The same glass electrode-reference electrode pair gave the following readings in the three buffers of Exercise 2: -2, 155 and -174 mV at 5°C and -5, 170 and -186 mV at 60°C. Calculate the value of the isopotential, pH_i .
- 4 Which shows the smaller sodium error, the glass electrode used for the results of FRAME 6 or FRAME 25?
- 5 Using the glass electrode data of FRAME 25, evaluate the standard potential, E° , and the zero point (pH when $E = 0$).

Appendix 1

Brönsted Definitions of acids and bases. Dissociation constants.

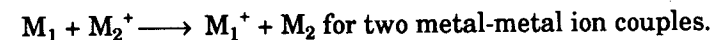
Brönsted definition: An acid (A) is a substance that dissociates to yield a base (B) and a bare proton (H⁺); likewise a base accepts a proton to yield an acid. A and B are called conjugate acid-base pairs.



Since the bare proton does not exist in aqueous solutions all acid-base reactions are coupled



which is a proton exchange reaction between two conjugate acid-base pairs. This may be compared with electron exchange reaction e.g.



We can write an equilibrium constant K for the pairs A₁-B₁, A₂-B₂:

$$K = [B_1][A_2] / [B_2][A_1]$$

It is usual in water to take the conjugate pair H₃O⁺ - H₂O as a reference pair, therefore we can define the acid dissociation constant

$$K_a = K[H_2O] = [B][H_3O^+] / [A]$$

where [] indicate activities. Likewise for the ionic product or autoprotolysis constant

$$K_w = K[H_2O] = [H_3O^+][OH^-]$$

Note: In the Frames, [H⁺] has been used as shorthand for [H₃O⁺].

Rewriting the equation for K_a as

$$[H^+] = K_a[A] / [B], \text{ then } [A] / [B] \text{ is called the buffer ratio.}$$

Taking logarithms, then

$$pH = -\lg [H^+] = pK_a - \lg [A] / [B]$$

which is called the Henderson-Hasselbalch equation.

When [A] / [B] = 1, then pH = pK_a and this is one method of determining K_a and it is also the condition for a solution to have maximum buffering capacity (least variation of pH when increments of a strong acid or base are added).

- 6 Dr. P. H. Noggins was suspicious about the calomel reference electrode that he was using for a series of pH measurements. He quickly substituted for it another reference electrode, which he found lying around in his laboratory without looking at it too closely or recalibrating. He was amazed to find that the pH(X) of his unknown was now about 13 instead of 3 as he had expected. Assuming that his calomel electrode was in fact all right, what type of reference electrode had he picked up?
- 7 In what ways do ethanoic acid/ethanoate buffers fail to satisfy the criteria of FRAME 23 for choice as primary standard buffers.

Appendix 2

Values of pH(RVS) for the reference value standard of 0.05 mol kg⁻¹ potassium hydrogen phthalate at various temperatures.

t/°C	pH(RVS)	t/°C	pH(RVS)	t/°C	pH(RVS)
0	4.000	35	4.018	65	4.097
5	3.998	37	4.022	70	4.116
10	3.997	40	4.027	75	4.137
15	3.998	45	4.038	80	4.159
20	4.001	50	4.050	85	4.183
25	4.005	55	4.064	90	4.21
30	4.011	60	4.080	95	4.24

Source: *Pure & App. Chem.* 1985, 57, 531-542

Appendix 3

Values of pH(PS) for Primary Standard Reference Solutions

Primary Reference Standard	0	5	10	15	20	25	30	35
Saturated potassium hydrogen tartrate (at 25°C)						3.557	3.552	3.549
0.1 mol/kg potassium dihydrogen citrate	3.863	3.840	3.820	3.802	3.788	3.776	3.766	3.759
0.025 mol/kg disodium hydrogen phosphate + 0.025 mol/kg potassium dihydrogen phosphate	6.984	6.951	6.923	6.900	6.881	6.865	6.853	6.844
0.03043 mol/kg disodium hydrogen phosphate + 0.008695 mol/kg potassium dihydrogen phosphate	7.534	7.500	7.472	7.448	7.429	7.413	7.400	7.389
0.01 mol/kg disodium tetraborate	9.464	9.395	9.332	9.276	9.225	9.180	9.139	9.102
0.025 mol/kg sodium hydrogen carbonate + 0.025 mol/kg sodium carbonate	10.317	10.245	10.179	10.118	10.062	10.012	9.966	9.926

Note: Based on an uncertainty of ± 0.2 mV in determined ($E - E^\circ$), the uncertainty is ± 0.003 in pH in the range 0 - 50°C

Source: *Pure & App. Chem.* 1985, 57, 531-542

t/°C							
37	40	50	60	70	80	90	95
3.548	3.547	3.549	3.560	3.580	3.610	3.650	3.674
3.756	3.754	3.749					
6.841	6.838	6.833	6.836	6.845	6.859	6.876	6.886
7.386	7.380	7.367					
9.088	9.068	9.011	8.962	8.921	8.884	8.850	8.833
9.910	9.889	9.828					

Appendix 4

pH (OS) values for operational Reference Solutions.

Operational Standard Reference Solution	t/°C	0	5	10	15	20	25
0.1 mol/kg potassium tetroxalate ^a						1.475	1.479
0.05 mol/kg potassium tetroxalate ^a				1.638	1.642	1.644	1.646
0.05 mol/kg sodium hydrogen diglycolate ^b			3.466	3.470	3.476	3.484	3.492
Saturated (at 25°C) potassium hydrogen tartrate							3.556
0.05 mol/kg potassium hydrogen phthalate (RVS)		4.000	3.998	3.997	3.998	4.000	4.005
0.1 mol/dm ³ ethanoic acid + 0.1 mol/dm ³ sodium ethanoate		4.664	4.657	4.652	4.647	4.645	4.644
0.01 mol ethanoic acid + 0.1 mol sodium ethanoate		4.729	4.722	4.717	4.714	4.712	4.713
0.02 mol/kg piperazine phosphate ^c			6.477	6.419	6.364	6.310	6.259
0.025 disodium hydrogen phosphate + 0.025 mol/kg potassium dihydrogen phosphate		6.961	6.935	6.912	6.891	6.873	6.857
0.03043 mol/kg disodium hydrogen phosphate + 0.008695 mol/kg potassium disodium phosphate		7.506	7.482	7.460	7.441	7.423	7.406
0.04 mol/kg disodium hydrogen phosphate + 0.01 mol/kg potassium disodium phosphate			7.512	7.488	7.466	7.445	7.428
0.05 mol/kg tris hydrochloride + 0.01667 mol/kg tris ^d		8.399	8.238	8.083	7.933	7.788	7.648
0.05 mol/kg disodium tetraborate (Na ₂ B ₄ O ₇)		9.475	9.409	9.347	9.288	9.233	9.182
0.01 mol/kg disodium tetraborate (Na ₂ B ₄ O ₇)		9.451	9.388	9.329	9.275	9.225	9.179
0.025 mol/kg sodium hydrogen carbonate + 0.025 mol/kg sodium carbonate		10.273	10.212	10.154	10.098	10.045	9.995
Saturated (at 20°C) calcium hydroxide		13.360	13.159	12.965	12.780	12.602	12.431

Note: Uncertainty is ±0.003 in pH between 0 and 60°C rising to ±0.01 above 70°C.

^a potassium trihydrogen dioxalate (KH₃C₄O₆) ^b sodium hydrogen 2,2' oxydiethanoate

^c C₄H₁₀N₂H₃PO₄ ^d 2-amino-2-(hydroxymethyl)-1,3 propanediol or tris(hydroxymethyl)aminomethane

	30	37	40	50	60	70	80	90	95
	1.483	1.490	1.493	1.503	1.513	1.52	1.53	1.53	1.53
	1.648	1.649	1.650	1.653	1.660	1.671	1.689	1.72	1.73
	3.502	3.519	3.527	3.558	3.595				
	3.549	3.544	3.542	3.544	3.553	3.570	3.596	3.627	3.649
	4.011	4.022	4.027	4.050	4.080	4.115	4.159	4.21	4.24
	4.643	4.647	4.650	4.663	4.684	4.713	4.75	4.80	4.83
	4.715	4.722	4.726	4.743	4.768	4.800	4.839	4.88	4.91
	6.209	6.143	6.116	6.030	5.952				
	6.843	6.828	6.823	6.814	6.817	6.830	6.85	6.90	6.92
	7.390	7.369							
	7.414	7.404							
	7.513	7.332	7.257	7.018	6.794				
	9.134	9.074	9.051	8.983	8.932	8.898	8.88	8.84	8.89
	9.138	9.086	9.066	9.009	8.965	8.932	8.91	8.90	8.89
	9.948	9.889	9.866	9.800	9.753	9.728	9.725	9.75	9.77
	12.267	12.049	11.959	11.678	11.423	11.192	10.984	10.80	10.71

Source: *Pure & App. Chem.* 1985, 57, 531-542

Appendix 5

Useful data on some standard buffer solutions.

	Molecular formula	Molality mol/kg	Relative molar mass	Density at 20°C ^o g/cm ³	Molarity at 20°C mol/l	Mass of 1 l at 20°C g	Mass tolerance for 0.001 pH [*] g	Mass tolerance as a percentage
potassium tetraoxalate	KH ₃ C ₄ O ₈ ·2H ₂ O	0.1	254.1913	1.0091	0.09875	25.1017	0.07	0.27
potassium tetraoxalate	KH ₃ C ₄ O ₈ ·2H ₂ O	0.05	254.1913	1.0038	0.04965	12.6202	0.034	0.26
disodium hydrogen orthophosphate	Na ₂ HPO ₄ anhyd.	0.025	141.9588	1.0038	0.02492	3.5379	0.02	0.56
potassium dihydrogen orthophosphate	KH ₂ PO ₄ anhyd.	0.025	136.0852			3.3912	0.02	0.58
disodium tetraborate	Na ₂ B ₄ O ₇ ·10H ₂ O	0.05	381.367	1.0075	0.04985	19.0117	0.9	4.73
disodium tetraborate	Na ₂ B ₄ O ₇ ·10H ₂ O	0.01	381.367	1.0001	0.009981	3.8064	0.19	0.49
sodium carbonate	Na ₂ CO ₃	0.025	105.9887	1.0021	0.02494	2.6428	0.017	0.064
sodium hydrogen carbonate	NaHCO ₃	0.025	84.0069			2.0947	0.013	0.62

* Calculated from known dilution value of solution.

Appendix 6

Henderson equation for the liquid junction potential of a continuous mixture junction

Consider a junction between two solutions

I | II

where solutions I and II contain only singly charged ions which mix linearly in accordance with the equation

$$c_i = xc_i^{II} + (1-x)c_i^I$$

$$= x(c_i^{II} - c_i^I) + c_i^I$$

where x is a mixing parameter.

The transport number is defined by

$$t_i = U_i c_i / \sum U_i c_i$$

where U_i = mobility of ion (its velocity under unit potential gradient).

$$\text{So } t_i = U_i c_i / [(1-x)\sum c_i^I U_i + x\sum c_i^{II} U_i]$$

By considering the differences between successive layers across the junction differing infinitesimally in concentration it can be shown that:

$$-E_J = \frac{RT}{F} \int_{II}^I \sum t_i d \ln c_i$$

$$= \frac{RT}{F} \int_{II}^I \frac{\sum U_i (c_i^{II} - c_i^I) dx}{[c_i^I U_i + x \sum (c_i^{II} - c_i^I) U_i]}$$

since $d \ln c_i = dc_i / c_i$ and $dc_i = (c_i^{II} - c_i^I) dx$ (but the solutions have been treated as ideal i.e. activity coefficients $y_i = 1$).

If mobilities of ions are constant across boundary, this integral is a standard one of the form

$$\int_0^1 \frac{dx}{a + bx} = \frac{1}{b} \ln(1 + b/a)$$

So,

$$-E_J = \frac{RT}{F} \frac{\sum U_i (c_i^{II} - c_i^I)}{\sum U_i (c_i^{II} - c_i^I)} \ln \frac{\sum c_i^{II} U_i}{\sum c_i^I U_i}$$

But $U_i = \lambda_i / F$ where F is the Faraday constant.

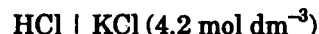
$$-E_J = \frac{RT}{F} \frac{(\lambda_+ c_+ - \lambda_- c_-)^I - (\lambda_+ c_+ - \lambda_- c_-)^{II}}{(\lambda_+ c_+ + \lambda_- c_-)^I - (\lambda_+ c_+ + \lambda_- c_-)^{II}} \ln \frac{(\lambda_+ c_+)^{II} + (\lambda_- c_-)^{II}}{(\lambda_+ c_+)^I + (\lambda_- c_-)^I}$$

Henderson Equation.

Appendix 7

Reduction of Liquid Junction Potentials

Consider a very simple junction

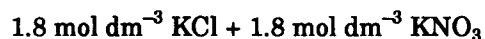
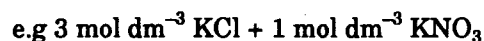


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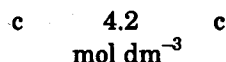
From the Henderson equation

$$-E_D = RT \cdot 4.2 (\lambda_K - \lambda_{Cl}) - c(\lambda_H - \lambda_{Cl}) \ln 4.2 (\lambda_K + \lambda_{Cl}) \\ F \cdot 4.2 (\lambda_K + \lambda_{Cl}) - c(\lambda_H + \lambda_{Cl}) \quad c (\lambda_H + \lambda_{Cl})$$

If $c \ll 4.2$, and if $\lambda_K = \lambda_{Cl}$, then the pre-log term is zero. This is the basis for the use of a high concentration of 'equitransferent' salt as the bridge solution. Other equitransferent high concentration bridge solutions have been suggested



For the double junction $\text{HCl} \mid \text{KCl} \mid \text{NaCl}$



Then for the *residual* liquid junction potential

$$-\Delta E_J = \frac{RT}{F} \left[\frac{4.2 (\lambda_K - \lambda_{Cl}) - c(\lambda_H - \lambda_{Cl}) \ln \frac{4.2 \Lambda_{KCl}}{c \Lambda_{HCl}}}{4.2 \Lambda_{KCl} - c \Lambda_{HCl}} - \frac{4.2 (\lambda_K - \lambda_{Cl}) - c(\lambda_{Na} - \lambda_{Cl}) \ln \frac{4.2 \Lambda_{KCl}}{c \Lambda_{NaCl}}}{4.2 \Lambda_{KCl} - c \Lambda_{NaCl}} \right]$$

If $c \ll 4.2$, then

$$-\Delta E_J = \frac{RT}{F} \cdot \frac{1}{4.2 \Lambda_{KCl}} \left[c(\lambda_{Na} - \lambda_{Cl}) \ln \frac{4.2 \Lambda_{KCl}}{c \Lambda_{NaCl}} - c(\lambda_H - \lambda_{Cl}) \ln \frac{4.2 \Lambda_{KCl}}{c \Lambda_{HCl}} \right. \\ \left. + 4.2 (\lambda_K - \lambda_{Cl}) \ln \Lambda_{NaCl} / \Lambda_{HCl} \right]$$

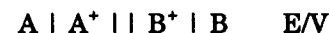
Therefore ΔE_J depends principally on the mobilities in the dilute solutions,

Appendix 8

A note on sign conventions for electrochemical cells.

The sign convention for electrochemical cells is the Stockholm Convention agreed at a meeting of the International Union of Pure and Applied Chemistry in Stockholm in 1953. This agreement ended a confusion where different sign conventions were used in Europe and in USA.

For the electrochemical cell written as



the potential difference is assigned on the basis of the convention that the polarity of the electrode on the right hand side is positive. If on measurement of the cell voltage, the polarity of this electrode is found to be negative, then E has negative values.

The single standard electrode potentials to be reported are *reduction potentials* when the electrode is combined with the standard hydrogen gas electrode. So in the above example if $A \mid A^+$ were the standard hydrogen electrode and its polarity in the cell was negative, then E would be positive and that would be the magnitude and sign of the single electrode potential of $B^+ \mid B$.

However, in 1977 the IUPAC meeting in Warsaw agreed that a reference electrode in a cell with liquid junction (such as used for ion-selective electrode or pH measurements), should always be written on the left hand side of the cell scheme irrespective of the cell polarity. The cell polarity always changes during pH measurements anyway, as usually at pH = 7, E = 0 (the zero point). This 1977 convention has been used in FRAME 2 for the operational cell. In practice, the polarity of the hydrogen electrode is negative, and the operational cell I of FRAME 2 has negative values of E increasing negative as the pH increases. With a zero point 7 glass electrode, the values of E are positive in acid solution going negative in alkaline solution. The reason for the 1977 convention was to bring the accepted practice for pH glass electrode measurements in to line with that for cation responsive ion-selective electrode measurements. There is an inconsistency, however, in that the values for E° , defined in equation 2 of FRAME 2 for cell I, which are listed for

some saturated potassium chloride reference electrodes in FRAME 7, are opposite in sign to E° values found in a tables of (Stockholm Convention) Electrode Potentials. This does not cause confusion, normally, in practical glass electrode pH measurements unless one attempts to make calculations similar to that of EXERCISE 6.

ANSWERS TO EXERCISES

- 1 $p_{\text{H}}\gamma_{\text{Cl}}$ values are 7.5183, 7.5131, 7.5078 leading to an intercept of 7.5235.
 $I = 0.1 \text{ mol/kg}$. $\lg \gamma_{\text{Cl}} = -0.10956$. $\text{pH(PS)} = 7.414$
Source: *J. Res. NBS* 1961, **65A**, 267-270.
- 2 (i) Practical slope 56.74 mV. Percentage $k = 95.9$.
(ii) 6.91 (iii) 6.78.
(a) 11.12 (b) 11.42.
The answer from (b).
- 3 pH_i is the isopotential pH, the pH where E is independent of temperature. It is therefore given by the intersection of the three lines for the three temperatures. Solving the two simultaneous linear equations for the 5° and 60° data gives $\text{pH}_i = 6.1$. In Germany, this intersection is called 'the isothermal crossing point', which is a much better name for it than isopotential even if it is longer. (It is one word in German: *isothermenschnittpunkt*).
- 4 That of FRAME 25.
- 5 $E^\circ = -432 \text{ mV}$; zero point $\text{pH} = -7.31$. It was, in fact, a Schott glass electrode with Thallamid internal reference in $0.1 \text{ mol/dm}^{-3} \text{ HCl}$ solution. Normally the inner and outer reference electrodes are the same so there is no large offset. A symmetrical cell has some advantages in terms of smaller temperature coefficient of E .
- 6 See Frame 7; Ross. Whenever you change reference electrode you should recalibrate because there can be small differences of $\pm 10 \text{ mV}$ between different samples of the same type.
- 7 2,3 and 6.