

Buffers for pH and Metal Ion Control

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convenient as pH standards, particularly as the solutions are rather insensitive to variations in concentration if the pH lies between about 3 and 11.

A much wider range of self buffers is encompassed when partially neutralized salts of substances with two or more pK_a values are involved. Phthalic acid is dibasic, with pK_a values at 25°C of 2.95 and 5.41; potassium hydrogen phthalate solutions have a pH roughly midway between these values (slightly lower because of ionic strength effects) and the buffer capacity is as expected for a solution 1.2 pH units removed from the pK_a . This is the basis of the use of 0.05M potassium hydrogen phthalate as the reference standard in pH measurement. Another example is potassium hydrogen tartrate (pK_a values of parent acid, 3.04 and 4.37) which has a better buffer capacity but is not very soluble. Sodium hydrogen malate (pK_a values of parent acid, 3.40 and 5.13) and potassium dihydrogen citrate (pK_a values of 3.13 and 4.76) could also be useful. The pH of a 0.05m KH_2 citrate solution is 3.68 at 25°C. A 0.2M solution of sodium hydrogen diglycollate (pK_a values 2.96 and 4.43) has a $pH = 3.40 \pm 0.02$ over the temperature range 10–35°C, has a slight $\Delta pH_{1/2}$ and has been proposed as a pH reference buffer (Keyworth and Hahn, 1958). On the other hand, the pK_a separations are too great for a salt such as potassium dihydrogen phosphate (pK_a values of phosphoric acid are 2.16, 7.21, 12.33) to be useful as a self buffer.

Mention has already been made of the self buffering by a salt of a weak acid and a weak base, such as ammonium acetate (pK_a values of 4.76 and 9.25). In this example the pH of a solution is near to 7 ($\approx \frac{1}{2}(pK_{HOAc} + pK_{NH_3})$), but the buffer capacity is small because the pH is more than 2 units away from either pK_a value. (In analytical chemistry this disadvantage is partially overcome by using high concentrations). Ammonium bicarbonate (pK_a values of 6.35, 9.25) or diammonium hydrogen phosphate (pK_a values 7.20, 9.25) giving pH values of approximately 7.4 and 8.0, respectively, for 0.05M solutions, have much better buffer capacities.

Piperazine phosphate monohydrate, $C_4H_{12}N_2HPO_4 \cdot H_2O$, is a very good self buffer (pK_a values of piperazine 5.333, 9.731; relevant pK_a value of phosphoric acid 7.198 at 25°C) and it has been proposed for use as a pH standard. Measured pH values for an 0.02m solution from 0 to 50°C are given in Table 2.5. For an 0.05m solution the pH values should be increased by 0.009.

Ampholytes (zwitterions) include an extensive range of substances that could be used as self buffers. Table 2.6 gives a list of isoionic ampholytes proposed for use as buffers in protein fractionation in a natural pH gradient (Svensson, 1962). Solutions of these substances in water have pH values close to the listed value of pI and when $pI - pK_1$ is less than 1.5 they can be considered to be self buffers.

2.9 Mixtures of buffers

The effective buffer range for a weak acid or base is approximately from $pH = pK_a + 1$ to $pH = pK_a - 1$. When two or more buffers are present, the effects are additive so that the buffering ability is spread over a wider pH range. Examples are McIlvaine's (1921) citric acid-phosphate mixtures for pH 2.6–8 (Table 10.45) and Smith and Smith's (1949) piperazine-glycylglycine mixtures for pH 4.4–10.8 (Table 10.46). The pK_a of ethanolamine (9.5) falls conveniently between two of the pK_a values of phosphoric acid (7.2, 12.3) so that ethanolamine-phosphate mixtures provide almost uniform buffer capacity between pH 6.7 and pH 12.8 (Thies and Kallinich, 1953).

If a buffer system has several successive pK_a values which differ by about 2 pH units, approximately linear buffer capacity results. This property has been exploited in 'universal' buffers having high buffer capacities over a wide pH range. Britton and Robinson (1931) used equimolar mixtures based on seven pK_a values of citric, phosphoric, boric and diethylbarbituric acids to cover the pH range 2.6–12, as listed in Tables 10.47 and 10.48. Coch Frugoni (1957) gave

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tables adapting these buffers to constant ionic strengths 0.005 and 0.02 by varying the amount of water added, and to $I = 0.1, 0.5$ and 1.0 by addition of sodium chloride.

2.10 Temperature dependence

The effect of temperature on the pH of a buffer solution depends on the temperature dependence of the activity coefficient terms and of the pK_a of the buffer species. The latter is usually much the more important. For systems of the type, B/BH^+ , the effect of temperature on the pK_a is given, to a first approximation, by

$$\frac{-d(pK_a)}{dT} = \frac{pK_a - 0.9}{T} \quad (2.22)$$

where T is in $^{\circ}K$ (Perrin, 1964). For dications, the equation is

$$\frac{-d(pK_a)}{dT} = \frac{pK_a}{T} \quad (2.23)$$

Around $25^{\circ}C$, for a base such as piperidine ($pK_a = 11.12$), the pK_a decreases by 0.034 units per degree. For carboxylic acids around ambient temperatures, on the other hand, changes in pK_a values are much smaller. The temperature coefficients for phenols are also smaller than for bases having comparable pK_a values.

2.11 Effect of pressure on buffers

High pressure increases the ionization of weak electrolytes, by enhancing the solvation of the ions, but the effect is not very great. At $25^{\circ}C$ and 3000 atmospheres, pK_a values are decreased as follows: formic acid, by 0.38 , acetic acid, by 0.50 , and propionic acid, by 0.55 (Hamann and Strauss, 1955). The logarithm of the basic dissociation constant of ammonia (into ammonium ion and hydroxyl ion) is increased by 1.14 for a pressure increase of 3000 atmospheres (Buchanan and Hamann, 1953) and by 2.72 for a pressure

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Table 10.13 *Formic acid, sodium formate buffer (0°C, 25°C)**

Contains x ml of M formic acid and y ml M NaOH, diluted to 100 ml

pH	I = 0.05			I = 0.1			I = 0.2		
	0°C x	25°C x	y	0°C x	25°C x	y	0°C x	25°C x	y
2.6	74.3	68.4	5.0	—	—	—	—	—	—
2.8	47.8	44.2	5.0	45.9†	84.4	10.0	—	—	—
3.0	31.7	29.4	5.0	61.3	56.6	10.0	—	—	—
3.2	21.7	20.3	5.0	42.2	39.3	10.0	41.6†	77.3	20.0
3.4	15.5	14.6	5.0	30.3	28.4	10.0	59.8	56.1	20.0
3.6	11.6	11.0	5.0	22.8	21.6	10.0	45.1	42.8	20.0
3.8	9.1	8.8	5.0	18.0	17.3	10.0	35.8	34.3	20.0
4.0	7.6	7.4	5.0	15.1	14.6	10.0	30.0	29.1	20.0
4.0	6.6	6.5	5.0	13.2	12.9	10.0	26.3	25.7	20.0
4.4	6.0	6.0	5.0	12.0	11.8	10.0	24.0	23.6	20.0
4.6	5.7	5.6	5.0	11.3	11.1	10.0	22.5	22.3	20.0
4.8	5.4	5.4	5.0	10.8	10.7	10.0	21.6	21.4	20.0

*Long (1961) †2M solution

Table 10.14 *Citric acid, sodium citrate buffer (23°C)**

Contains x ml 0.1M citric acid (21.01 g C₆H₈O₇·H₂O l⁻¹) and (50-x) ml 0.1M Na₃ citrate (29.41 g C₆H₅O₇Na₃·2H₂O l⁻¹), diluted to 100 ml

pH	x	pH	x
3.0	46.5	4.8	23.0
3.2	43.7	5.0	20.5
3.4	40.0	5.2	18.0
3.6	37.0	5.4	16.0
3.8	35.0	5.6	13.7
4.0	33.0	5.8	11.8
4.2	31.5	6.0	9.5
4.4	28.0	6.2	7.2
4.6	25.5		

*Gomori (1955)
For disodium hydrogen citrate, NaOH, HCl buffers covering the pH range 2.2–6.8, see Sørensen (1909, 1912)

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