8. SIMULTANEOUS EQUILIBRIA IN SOLUTIONS OF ELECTROLYTES

Dissociation constant of a base (in earlier tables) is the equilibrium constant K_B of the reaction

$$B + H_2O = BH^+ + OH^-$$

Dissociation constant of an acid conjugate of this base is equilibrium constant K_{BH^+} of the reaction

$$BH^+ = B + H^+$$

Both constants are related by an equation (K_w is ionic product of water)

$$K_B \cdot K_{BH^+} = K_w$$

Dissociation and acidity constants of some weak bases at 25 °C
(standard state c^{st} = 1 mol dm^{-3})

Base B		K_B	Conjugate acid BH^+	K_{BH^+}
piperidine	$C_5H_{10}NH$	$1.34 \cdot 10^{-3}$	$C_5H_{10}NH_2^+$	$7.52 \cdot 10^{-12}$
methylamine	CH_3NH_2	$4.58 \cdot 10^{-4}$	$CH_3NH_3^+$	$2.2 \cdot 10^{-11}$
ethylamine	$C_2H_5NH_2$	$4.58 \cdot 10^{-4}$	$C_2H_5NH_3^+$	$2.2 \cdot 10^{-11}$
propylamine	$C_3H_7NH_2$	$4.0 \cdot 10^{-4}$	$C_3H_7NH_3^+$	$2.5 \cdot 10^{-11}$
ammonia	NH_3	$1.80 \cdot 10^{-5}$	NH_4^+	$5.6 \cdot 10^{-10}$
pyridine	C_6H_5NH	$1.71 \cdot 10^{-9}$	$C_6H_5NH_2^+$	$5.9 \cdot 10^{-6}$
aniline	$C_6H_5NH_2$	$4.0\ \ 10^{-10}$	$C_6H_5NH_3^+$	$2.5 \cdot 10^{-5}$
diphenylamine	$(C_6H_5)_2NH$	$6.90 \cdot 10^{-14}$	$(C_6H_5)_2NH_2^+$	0.146

Problem 8-01 pH – Strong bases

Calculate pH of aqueous solution of NaOH prepared at 17 °C

(a) by dilution of 1 cm^3 of NaOH solution with concentration of $1 \cdot 10^{-4}$ mol dm^{-3} to volume 10 dm^3

(b) by dilution of 1 cm^3 of NaOH solution with concentration of 0.1 mol dm^{-3} to volume 10 dm^3.

Is it possible to neglect the protolysis of water? Ionic product of water at the temperature of 17 °C is $5.83 \cdot 10^{-15}$ (standard state: infinite dilution, c^{st} = 1 mol dm^{-3}). Activity coefficients can be taken as equal to one.

[(a) pH = 7.146; (b) pH = 9.234;
Protolysis can be neglected in case (b): (a) pH = 6.234; (b) pH = 9.234]

Problem 8-02 Solution of weak acid – dissociation constant

pH of aqueous solution of weak acid HA, prepared at 18 °C in concentration $2.5 \cdot 10^{-5}$ mol dm^{-3}, was determined to be 6.8. Calculate the value of the dissociation constant for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3} (assume that all activity coefficients are equal to one). Ionic product of water K_w at these conditions has the value of $5.826 \cdot 10^{-15}$.

[$K_{HA} = 7.755 \cdot 10^{-10}$]

Problem 8-03 Solution of weak acid – concentration from pH

The dissociation constant of acrylic acid for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3}, has the value of $5.5 \cdot 10^{-5}$. Assuming that all activity coefficients are equal to one and that you can neglect the water protolysis, calculate what amount of acrylic acid (in grams) you must dissolve in 100 cm^3 of water at 20 °C to obtain a solution with pH = 4.2. Ionic product of water K_w at these conditions has the value of $6.8 \cdot 10^{-15}$.

[$m_0 = 9.763 \cdot 10^{-4}$ g]

Problem 8-04 Solution of two weak acids – dissociation constant

pH of the solution containing 0.001 mol dm^{-3} of acetic acid (HA) together with other monobasic acid (HB) in concentration 0.001 mol dm^{-3} was determined to be 3.78. The dissociation constant of the acetic acid (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}) is $K_{HA} = 1.75 \cdot 10^{-5}$. Find the value of the dissociation constant of acid HB. Ionic product of water K_w at these conditions has the value of $1.008 \cdot 10^{-14}$. Assume that all activity coefficients are equal to one

[$K_{HB} = 1.26 \cdot 10^{-5}$]

Problem 8-05 Solution of weak base – pH

What is pH value of the ammonia solution with concentration of 0.002 mol dm^{-3} at the temperature of 20 °C. The value of acidity constant of ion NH_4^+ is $5.56 \cdot 10^{-10}$ and the ionic product of water is $K_w = 6.8 \cdot 10^{-15}$ (both for standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). You can assume that the amount of hydrogen ions formed by water autoprotolysis is negligible small and all activity coefficients are equal to one.

[pH = 10.345]

Problem 8-06 Solution of weak base – acidity and dissociation constants

The measurement of pH of methylamine solution of the concentration 0.002 mol dm^{-3} at the temperature of 30.1 °C yielded the value pH = 10.87. Calculate the acidity constant of $CH_3NH_3^+$ and the dissociation constant of methylamine (both for standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). Ionic product of water at 30.1 °C is $K_w = 1.484 \cdot 10^{-14}$ and all the activity coefficients can be taken as equal to one.

[$K_{BH+} = 1.104 \cdot 10^{-11}$, $K_{dis} = 1.344 \cdot 10^{-3}$]

Problem 8-07 Solution of the salt of the weak base and weak acid

Aqueous solution of the salt of weak acid (AH) and weak base (BOH) at the temperature of 25 °C and concentration of 0.0025 mol dm^{-3} has pH = 9.65. Calculate the dissociation constant of the weak acid in question, if you know that the dissociation constant conjugated to the weak base BOH has the value of $K_{B+} = 1.32 \cdot 10^{-9}$ (all for standard state of infinite dilution, c^{st} = 1 mol dm^{-3}, and unit activity coefficients).

[$K_{dis\,(HA)} = 3.26 \cdot 10^{-11}$]

Problem 8-08 Charge numbers

What ratio of concentrations $c(CH_3NH_2) : c(CH_3NH_3^+)$ will be found, if you add a small amount of methylamine to the buffer solution with pH = 10? Acidity constant of methylammonia is $pK_a(CH_3NH_3^+) = 10.64$ (standard state: infinite dilution, c^{st} = 1 mol dm^{-3})

[$c(CH_3NH_2) : c(CH_3NH_3^+) = 0.229$; pH < p$K$, the share of protonated form is greater]

Problem 8-09 Charge numbers

Find the equilibrium concentration ratio $c(CO_2) : c(HCO_3^-) : c(CO_3^{2-})$ in blood (pH = 7.4)? The acidity constants are: $pK_a(CO_2) = 6.37$ (including H_2CO_3), $pK_a(HCO_3^-) = 10.25$.

[$c(CO_2) : c(HCO_3^-) : c(CO_3^{2-}) = 0.0933 : 1 : 0.00141$]

Problem 8-10 Balance of simultaneous equilibria in electrolyte solutions

0.2 mol of salmiac (NH_4Cl) together with 0.001 mol of ammonia (NH_3) were dissolved in 2 dm^3 of water.

(a) Write the equations which would permit to calculate pH. Don't solve.

(b) Calculate pH of the solution assuming that the water protolysis can be neglected. Acidity constant of NH_3 has the value of $5.6 \cdot 10^{-10}$ (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}).

[(a) $K_1 = \dfrac{(c_{A0} + x) \cdot (x + y)}{(c_{S0} - x)}$, $K_2 = y \cdot (x + y)$; (b) pH = 6.951]

Problem 8-11 Balance of simultaneous equilibria in electrolyte solutions

What is pH of the solution containing in 2 dm^3 0.01 mol HCl and 0.04 mol NH_4Cl at the temperature of 25 °C? Acidity constant of NH_3 has the value of $K_a = 5.6 \cdot 10^{-10}$, ionic product of water $K_w = 1.008 \cdot 10^{-14}$. [pH = 2 (the solution is not a buffer)]

Problem 8-12 Balance of simultaneous equilibria in electrolyte solutions

2 dm^3 of aqueous solution contain 0.2 mol of HCl and 0.4 mol of NH_4Cl. What is pH of this solution at the temperature of 25 °C? Acidity constant of NH_3 has the value of $K_a = 5.6 \cdot 10^{-10}$, ionic product of water $K_w = 1.008 \cdot 10^{-14}$. [pH = 8.949]

Problem 8-13 Buffers

0.096 mol of sodium acetate was dissolved in v 800 cm^3 of acetic acid solution of concentration 0.1 mol dm^{-3}.

(a) What is pH of this buffer solution?

(b) What change in pH will cause an addition of 2 cm^3 HCl solution of concentration 4 mol dm^{-3} (neglect the mixing change in volume)?

(c) What change in pH will occur if you dissolve 8 mmol of NaOH in this buffer solution?

[(a) pH = 4.838 ; (b) ΔpH = 0.078 ; (c) ΔpH = –0.046]

Problem 8-14 Buffers

Buffer consisting of 0.2 mol dm^{-3} of acetic acid and 0.2 mol dm^{-3} of sodium acetate has pH = 4.75. What change will cause the addition of 0.05 mol dm^{-3} KOH solution?

[$pH_1 = pK_{HAc} = 4.75$, $pH_2 = 4.97$]

Problem 8-15 Buffers

System dihydrogen phosphate ($H_2PO_4^-$)/hydrogen phosphate (HPO_4^{2-}) represents a classical buffer significantly involved in keeping the intracellular value of pH. For the equilibrium constant of the reaction

$$H_2PO_4^- = HPO_4^{2-} + H^+$$

applies pK = 7.2 (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). pH inside the cell is 7.4 and the total concentration of phosphate 0.02 mol dm^{-3}. What are the concentrations of single components of this buffer? Instead of the activities you can use the relative concentrations.

[[HPO_4^{2-}] = 7.737 mmol dm^{-3} ; [$H_2PO_4^-$] = 12.263 mmol dm^{-3}]

Problem 8-16 Ampholytes – Amino acids

What is the share of single ionic forms in the alanine solution of the concentration 0.02 mol dm^{-3} at pH = 5.2 and temperature 25 °C. The dissociation constants have the following values (standard state of infinite dilution, c^{st} = 1 mol dm^{-3})

$$pK_1(\text{–COOH}) = 2.34 \quad , \quad pK_2(\text{–}NH_3^+) = 9.69$$

[0.0032 % Ala^- ; 0.138 % Ala^+ ; 99.859 % Ala^0]

Problem 8-17 Ampholytes – Amino acids

At what pH will the 0.03 molar solution of methionine contain 1.2 mol. % of Met^+ form and 0.008 mol. % of Met^- form? The dissociation constants of methionine (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}) at 25 °C have the following values:

$$pK_1(\text{–COOH}) = 2.28 \quad , \quad pK_2(\text{–}NH_3^+) = 9.21$$

What pH value corresponds to the isoelectric point of methionine?

[pH = 4.66 ; pI = 5.745]