PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of an acid dissociation constant

Reagents:
A solution of a weak monoprotic acid with a concentration of about 0.1 mol dm^{-3},
a solution of sodium hydroxide with a concentration of about 0.1 mol dm^{-3},
solutions of the indicators: methyl orange and phenolphthalein.

Equipment:
burette 25 cm^3,
calibrated pipette 20 cm^3,
two conical flasks 200 cm^3,
access to the *pH*-meter. An assistant will make one measurement only for each participant.

Questions:

1.1 Give the expression for the concentration dissociation constant of the acid HA.

1.2 Give your reasons for the choice of the indicator.

1.3 Give the results of titrations.

1.4 Write down your *pH* value (measured by assistant).

1.5 Show how you calculate the concentration pK_a value for the acid. Write down the value.

SOLUTION

1.1 $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (a)$$

1.2 Since the HA is a weak acid the colour transition of the indicator is expected in the basic region ($pH > 7$), and thus phenolphthalein is suitable.

1.3 and **1.4**

The results obtained by measuring volumes of the titrand and *pH* values were expected to be shown in the answer sheet.

1.5 The equation (a) can be transformed to equation (b) as follows:

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \qquad \text{(b)}$$

When $[A^-] = [HA]$, then $pH = pK_a$

Since the concentration of the sodium hydroxide solution is approximate only, it is not possible to calculate the exact concentration of the acid. Nevertheless, the combination of titration a measuring *pH* values gives the possibility to find the value of dissociation constant K_a.

PROBLEM 2 (Practical)

Determination of the formation (stability) constants of the complex ions $[Cu(NH_3)_4]^{2+}$ and $[Zn(NH_3)_4]^{2+}$

Equipment:

Two dry beakers with copper and zinc electrodes,
three bottles with aqueous solutions of $CuSO_4$, $ZnSO_4$ and NH_3, respectively,
one beaker with strips of filter paper for making a salt bridge,
one beaker with an aqueous solution of KNO_3,
three pipettes for delivering $CuSO_4$, $ZnSO_4$ and NH_3 solutions,
digital voltmeter for the EMF measurements,
red and blue leads (conductors) for connecting cell electrodes to the digital voltmeter,
rubber pipette filler,
appropriately marked glass stirring rods.

a) Procedure for setting up the Daniell cell:

1. Into the dry beakers containing Cu and Zn electrodes deliver 20 cm^3 of $CuSO_4$ and 20 cm^3 of $ZnSO_4$ using marked pipettes in order to get Cu/Cu^{2+} and Zn/Zn^{2+} half-cells.
2. Wet the filter paper strip with KNO_3 solution. The strip should only be moisten with the solution. Then place the strip ends into the $CuSO_4$ and $ZnSO_4$ solutions.
3. Connect the leads to the electrodes (red to Cu electrode and blue to Zn electrode).

a)

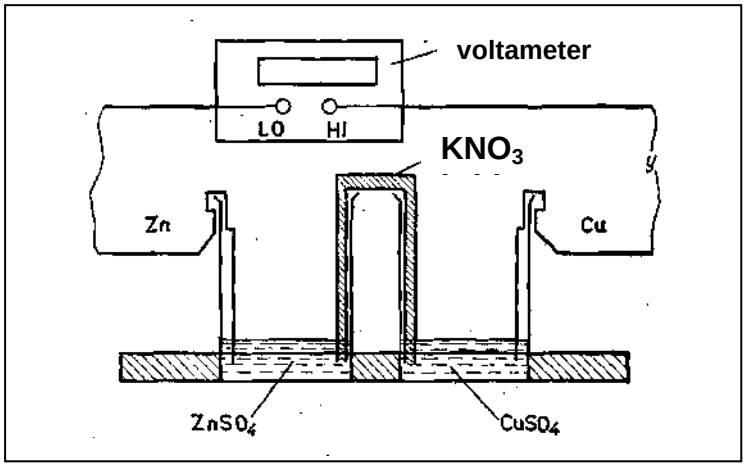


Fig. 1

b) Procedure for the EMF measurement of the Daniell cell (E_A):

Put the appropriately marked glass rods (red - Cu, blue - Zn) into the $CuSO_4$ and $ZnSO_4$ solutions. Having stirred the solutions gently with the rods, the rods should be left in the solutions throughout the course of the experiment. Start the EMF measurement of the cell by connecting the red lead to the voltmeter terminal (HI) and the blue one to the negative terminal (LO). If the EMF value changes by no more than 0.001 V, record the EMF (E_A).

c) Procedure for the EMF measurement of the cell (E_B) after the addition of the complexing agent (NH_3 solution) into the Cu/Cu^{2+} half-cell:

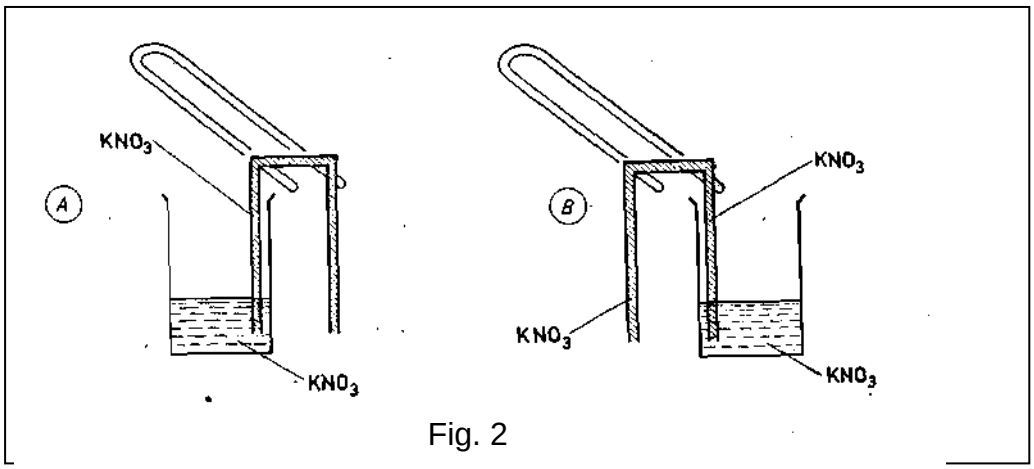


Fig. 2

Pipette 20 cm^3 of aqueous NH_3 solution into the $CuSO_4$ solution. Stir the solution with a glass rod gently until it becomes a clear dark blue. Leave the rod in the solution. Measure and record the new EMF (E_B), in the way described in part b).

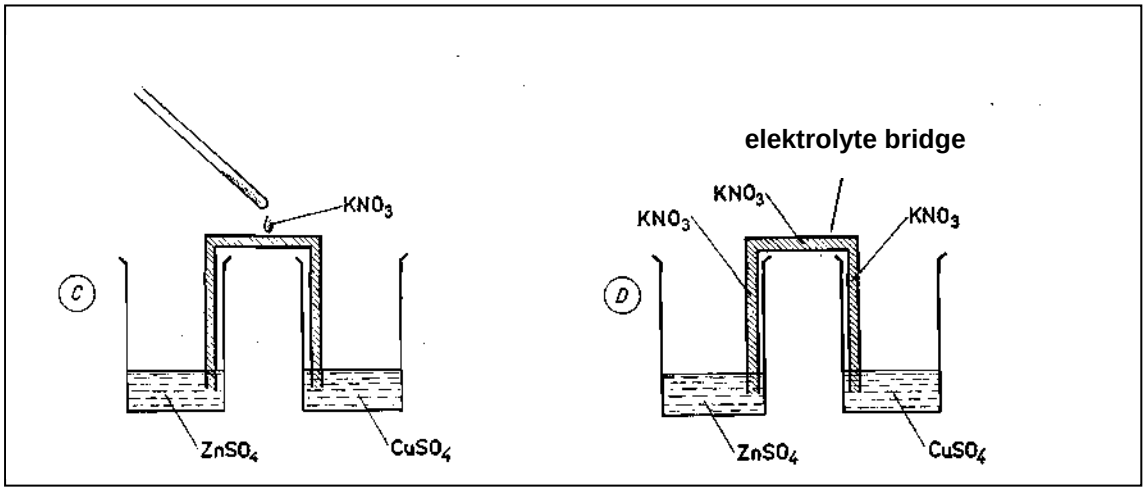


Fig. 3

d) Procedure for the EMF measurement of the cell (E_C) after the addition of the complexing agent (NH_3 solution) to the Zn/Zn^{2+} half-cell:

Leave the $Cu/[Cu(NH_3)_4]^{2+}$ half-cell unchanged. Add 20 cm^3 of NH_3 solution to the $ZnSO_4$ half-cell. Carry out the EMF measurement of the cell in the way described in part b). Write down the result (E_C).

Theoretical considerations:

Gas constant R = 8.314 J K^{-1} mol^{-1}

Faraday constant F = 96 487 C mol^{-1}

i) The concentrations of $CuSO_4$, $ZnSO_4$ and NH_3 aqueous solutions written on the bottles are expressed in mol kg^{-1}. Therefore they must be converted into appropriate concentrations expressed in mol dm^{-3}. The densities (d) of the solutions as functions of temperature are respectively:

$CuSO_4$: $d_1 = 1.0923$ (kg dm^{-3}) – 0.0002700 (kg $dm^{-3}K^{-1}$) T

$ZnSO_4$: $d_2 = 1.0993$ (kg dm^{-3}) – 0.0002900 (kg $dm^{-3}K^{-1}$) T

NH_3: $d_3 = 1.0740$ (kg dm^{-3}) – 0.0002800 (kg $dm^{-3}K^{-1}$) T

ii) In order to convert concentrations (c_i) into ionic activities (a_i), we need to calculate activities of the ions using the equation $a_i = f_i * c_i$. The activity coefficient values, f_i, of the ions involved are given in the answer sheet. The activity coefficient of ammonia should be assumed to be 1.

iii) To simplify the calculations it should be assumed that after the addition of the excess of complexing agent (NH_3) only Cu^{2+}_{aq}, Zn^{2+}_{aq}, $[Cu(NH_3)_4]^{2+}$, $[Zn(NH_3)_4]^{2+}$ ions exist in the respective solutions.

iv) Any diffusion potential occurring between both half-cells when the salt bridge is applied may be neglected in practice.

Questions:

2.1 Calculate the values of the concentrations of Cu^{2+} and Zn^{2+} ions in the Daniell cell before the introduction of the complexing agent (NH_3).

2.2 Calculate the standard EMF value E^o of your Daniell cell using the Nernst equation.

2.3 Calculate the concentrations of $[Cu(NH_3)_4]^{2+}$ and NH_3 in the B type cell, i.e. after the addition of NH_3 to the Cu/Cu^{2+} half-cell.

2.4 Determine the values of the thermodynamic formation (stability) constants K_B and ln K_B for the $[Cu(NH_3)_4]^{2+}$ ions.

2.5 Calculate the concentrations of $[Zn(NH_3)_4]^{2+}$ and NH_3 in the type C cell, i. e. after the addition of NH_3 to the Zn/Zn^{2+} half-cell.

2.6 Determine the values of the thermodynamic formation (stability) constant K_C and ln K_C for $[Zn(NH_3)_4]^{2+}$ ions.

SOLUTION

2.1 The mass of the solutions (kg) can be transformed to volumes of the solutions (dm^3) using the given densities. The concentrations are then given in units mol dm^{-3}.

2.2 $$E = \left(E^0(Cu^{2+}/Cu) + \frac{RT}{2F} \ln([Cu^{2+}] \times f_{Cu^{2+}}) \right) - \left(E^0(Zn^{2+}/Zn) + \frac{RT}{2F} \ln([Zn^{2+}] \times f_{Zn^{2+}}) \right) - E_{dif}$$

For $E_{dif} = 0$:

$$E_A = E^0(Cu^{2+}/Cu) - E^0(Zn^{2+}/Zn) + \frac{RT}{2F} \ln \frac{[Cu^{2+}] \times f_{Cu^{2+}}}{[Zn^{2+}] \times f_{Zn^{2+}}}$$

E_A can be measured. All other data required are given in the text of the problem or in the answer sheet.

2.3 Concentrations after the addition of NH_3:

$$[Cu(NH_3)_4^{2+}] = \frac{c(Cu^{2+}) \times V}{V + V_1}$$

$$[NH_3] = \frac{(c(NH_3) \times V_1) - (4\, c(Cu^{2+}) \times V)}{V + V_1}$$

2.4 After the addition of NH_3 the following complex equilibrium is established:

$$Cu^{2+} + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

$$\beta_4 = \frac{[Cu(NH_3)_4^{2+}] \times f_{Cu(NH_3)_4^{2+}}}{[Cu^{2+}] \times f_{Cu^{2+}} \times [NH_3]^4}$$

Then the Nernst equation has the form:

$$E_1^{'} = E^0(\mathrm{Cu^{2+}/Cu}) = \frac{RT}{2F} \ln \frac{[\mathrm{Cu(NH_3)_4^{2+}}] \times f_{\mathrm{Cu(NH_3)_4^{2+}}}}{\beta_4 \times [\mathrm{NH_3}]^4}$$

$$E_B = E'_1 - E_2 = E^0(\mathrm{Cu^{2+}/Cu}) - E^0(\mathrm{Zn^{2+}/Zn}) + \frac{RT}{2F} \ln \frac{[\mathrm{Cu(NH_3)_4^{2+}}] \times f_{\mathrm{Cu(NH_3)_4^{2+}}}}{[\mathrm{Zn^{2+}}] \times f_{Zn^{2+}} \times \beta_4 \times [\mathrm{NH_3}]^4}$$

From the above equation β_4 or $\ln\beta_4$ can be calculated since E_B can be measured, and all other data required are given in the text of the problem or in the answer sheet.

2.5 and **2.6**

The procedure in the calculation of β_4 or $\ln\beta_4$ for complex $\mathrm{Zn(NH_3)_4^{2+}}$ is analogical as that shown in parts (2.3) and (2.4) for complex $\mathrm{Cu(NH_3)_4^{2+}}$.