Measurement of electric potential of silver electrodes

Rui Li

Qiushi science class (chemistry)
Chu Kochen Honor College

Electric potential of several types of silver electrodes is measured using potentiometer, and the density as well as temperature is investigated.

Keywords: electric potential, potentiometer

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I. INTRODUCTION

Electrode potential is derived from the thermodynamics' second law that for an arbitrary process occurred in a system, the maximum non-volume work is given by

$$W_{\text{non-}pV} \leq -\Delta G, \tag{1}$$

and for a process involving electron transfer, electric work dominates the non-volume work. Faraday pointed out its linearity towards the amount of electrons transferred, as is natural in electric circuits,

$$W_{\text{non-}pV,\max} = -\Delta G = nFE \tag{2}$$

where n is the total amounts of electrons transferred, F the Faraday constant representing electric charges of 1 mol electrons, and E represents the electric potential in the circuit provided by the reaction. Thus it is evident that Any reaction that involves electron transfer and a decrease in Gibbs free energy can be applied as an electric power source.

Nernst equation is deduced in the system of chemical equilibrium, from the equation of which was deduced in the former report,

$$\Delta G_m = \Delta G^{\ominus} + RT \ln Q = \Delta G_m^{\ominus} + RT \ln \frac{\alpha_{\text{product}}^{c_i}}{\prod \alpha_{\text{reactant}}^{c_j}} \tag{3}$$

and when decomposing it into half-electrode reactions for oxidants and redox, combining it with the Faraday equation, it is deduced that

$$E_{\text{red}} = E_{\text{red}}^{\ominus} - \frac{RT}{zF} \ln Q' = E_{\text{red}}^{\ominus} - \frac{RT}{zF} \ln \frac{\alpha_{\text{red}}}{\alpha_{\text{Ox}}} \tag{4}$$

where α represents the fugacity of the matter in the solution, and z the amount of electrons per mole of reaction that transferred. The same can be deduced for the redox reaction.

TABLE I. The potential of the cells of different electrodes measured at 25 °Cusing potassium nitrate as the salt bridge

Group	c/M				
A	0.1116	0.0832	0.06929	0.06041	0.05454
B	0.4373	0.4627	0.4722	0.4833	0.4917
C	0.2086	0.3835	0.4080	0.4288	0.4339
D	0.05658	0.03192	0.01917	0.01133	0.005567

A:Hg|Hg$_2$Cl$_2$,KCl(Sat.)||KCl(c),AgCl|Ag
B:Hg|Hg$_2$Cl$_2$,KCl(Sat.)||AgNO$_3$(c)|Ag
C:Ag|AgCl,KCl(c)||AgNO$_3$(c)|Ag
D:Ag|AgNO$_3$(c)||AgNO$_3$(0.100 M)|Ag

According to Kirchhoff's circuit laws, the current will cause an decrease in the measurement of the potential of a battery using simple electric circuits due to inevitable resistance for the battery. Thus an apparatus that can measure a potential with no current through the battery needs to be adopted, linear sweep vltammetry as one of the examples. The apparatus in this experiment is much simpler, involving several variable resistances with battery that provides a standard electric potential, which can help deduce the electric potential of the target battery according to the Kirchhoff's circuit laws.

II. METHODS AND PROCEDURES

A series of standard solution of KCl and standard solution of AgNO$_3$ in different concentrations was prepared respectively. Each battery consists of a pair from four electrodes - saturated calomel electrode in saturated KCl solution, silver chloride electrode in different concentration of KCl solution, silver electrode in different concetration of AgNO$_3$ solution - is measured using Model UJ-25 high voltage DC potentiometer. The electrric potential of battery that consists of saturated calomel electrode in saturated KCl solution and silver chloride electrode in 0.0900 M of KCl solution is measured at different temperatures.

III. RESULT AND ANALYSIS

The data is shown in Table.I,II, with figures shown in Fig.1,2. Relatively nice linearity is obtained in Fig.1,

TABLE II. The potential of $Hg|Hg_2Cl_2,KCl(Sat.)||KCl(0.09$ M),AgCl|Ag measured at different temperatures using potassium nitrate as the salt bridge

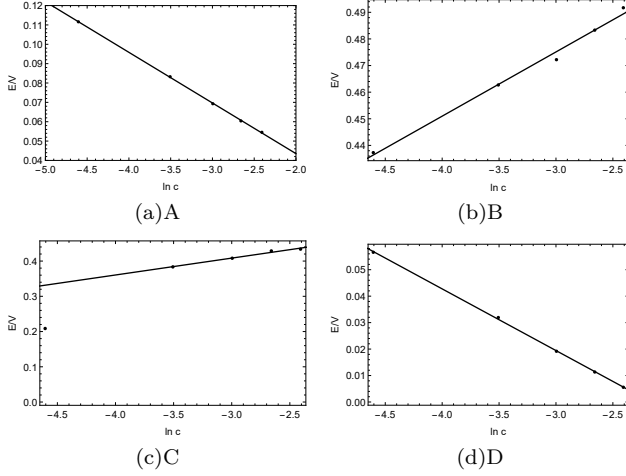| T/K	298.15	303.15	308.15	313.15	318.15
E/V	0.054537	0.055457	0.055823	0.055947	0.056093

(a)A　　　　　　　　(b)B

(c)C　　　　　　　　(d)D

FIG. 1. The E-$\ln c$ curve of the cells of different electrodes measured at 25 °C using potassium nitrate as the salt bridge

where the lines are interpreted as

$$\begin{cases} E_A = -0.00880485 - 0.0261599 \ln c \\ E_B = 0.547491 + 0.024127 \ln c \\ E_C = 0.552076 + 0.0478942 \ln c \\ E_D = -0.0504885 - 0.0233089 \ln c \end{cases} \quad (5)$$

with

$$\begin{cases} R_A^2 = 0.999794 \\ R_B^2 = 0.991412 \\ R_C^2 = 0.984017 \\ R_D^2 = 0.999645 \end{cases} \quad (6)$$
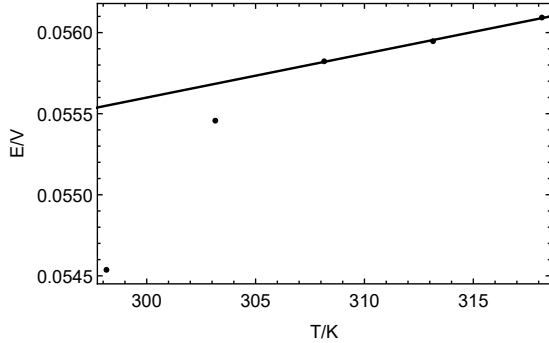

FIG. 2. The E-T plot of the potential of saturated calomel electrode combined with silver chloride electrode in 0.09 M KCl measured at different temperatures using potassium nitrate as the salt bridge

if excluding the error point in the C group. Substituting c with 1, it is easily obtained that

$$\begin{cases} E_{AgCl/Ag}^{\ominus} = -0.008805\,\text{V} \\ E_{Ag^+/Ag}^{\ominus} = 0.5475\,\text{V} \end{cases} \quad (7)$$

in the reference to saturated calomel electrode. Subtracting them gives 0.5563 V, which is identical to the result from the C group (0.5521 V). The slopes deviate slightly from RT/nF, namely 0.02569, which might be attributed to limited conductance of the ions in the solution that influences the measurement, and inevitable consumation of the reactant during the measurement. It also gives

$$K^{\ominus}(\text{AgCl}) = \exp\frac{-nFE}{RT} = 2.535 \times 10^{-9} \quad (8)$$

which also differs from the standard data(1.8×10^{-10}), which owes itself to the non-one fugacity coefficient of the ions in the solution.

It fails to give linearity in Fig.2, which might be due to non-zero gradient of temperature over the system, especially in the salt bridge, which is outside the thermostat. It affects the fugacity of the ions as well as producing flows of the solution, which is certain to cause unpredictable errors. Picking the last three data points to fit a straight line returns

$$E = 0.0474993 + 0.000027T \quad (9)$$

which is of low confidence. Considering that

$$\Delta_r G_m = \Delta_r H_m - T\Delta_r S_m, \quad (10)$$

it can be interpreted that for the cell $Hg|Hg_2Cl_2,KCl(Sat.)||KCl(0.09$ M),AgCl|Ag there is

$$\begin{cases} \Delta_r G_m = 5360\,\text{J/mol} \\ \Delta_r S_m = 2.605\,\text{J/(K·mol)} \\ \Delta_r H_m = 4583\,\text{J/mol} \end{cases} \quad (11)$$

However, the line is too far from the data point of 25 °C, indicating the indifference of calculating $\Delta_r G_m, \Delta_r S_m, \Delta_r H_m$ as well as correcting the density of Cl^-.