

### 1.a. Verification of Nernst's equation for $Ce^{+3}/Ce^{+4}$ redox system



**REDOX ELECTRODE.** The main part of the redox electrode is platinum platelet. The potential of electrode occurs if immersed in the solution with reduction oxidation system (for example mixture of  $Ce^{+3}$  and  $Ce^{+4}$  cations). The established redox potential is controlled by the Nernst's equation:

$$E_{Redox} = E_{Ce^{+3}/Ce^{+4}}^0 - \frac{RT}{nF} \ln \frac{a_{Ce^{+3}}}{a_{Ce^{+4}}} \cong E_{Ce^{+3}/Ce^{+4}}^0 - 0,059 \log \frac{[Ce^{+3}]}{[Ce^{+4}]} \quad (1.1.)$$

where  $E_{Ce^{+3}/Ce^{+4}}^0$  is standard redox potential of the  $Ce^{+3}/Ce^{+4}$  system,  $R$  is Gas constant,  $F$  is Faraday's constant,  $n$  is the number of transmitted electrons,  $a_{M^+}$  and  $[M^+]$  are activities and molarities of  $Ce^{+3}$  or  $Ce^{+4}$  cation respectively. The value 0.059 in equation (1.1) is the Nernst's electrode response in Volts at  $T = 298K$  (compare response for ISE).

The redox potential is measured by a combined redox electrode that contains the redox electrode and the reference electrode in one unit. The eqn  $E_{Redox} = EMV + E_{ref}$  is valid, where  $E_{ref}$  is constant potential of reference electrode and  $EMV$  is the electro motoric voltage (EMV) of the combined electrode.



**TASK:** Verify the Nernst's equation for the  $Ce^{+3}/Ce^{+4}$  system. Evaluate the experimental Nernst's response of the redox electrode and compare it with a theoretical value of 59 mV. Determine the  $[Ce^{+3}]/[Ce^{+4}]$  ratio in the unknown samples (e.g., in the Belousov-Zhabotinsky oscillating system).



**LABORATORY AIDS AND CHEMICALS:** combined Pt-redox electrode, potentiometer, electromagnetic stirrer, 2 beakers ( $100 \text{ cm}^3$ ), 3 scale glass pipettes ( $25$ ,  $10$  a  $5 \text{ cm}^3$ ), 10 volumetric flasks ( $50 \text{ cm}^3$ ), storage solution for redox electrode ( $5 \cdot 10^{-2} M$  KCl or saturated KCl). Stock solutions:  $0.006M$   $Ce(SO_4)_2$  in  $1.5 M$   $H_2SO_4$ ,  $0.006M$   $Ce_2(SO_4)_3$  in  $1.5 M$   $H_2SO_4$ .



**INSTRUCTIONS:** Get acquainted with the use of the potentiometer in mode mV reading.

**MEASUREMENT OF EMV FOR STANDARD SOLUTIONS.** Pipette the  $50ml$  of the  $0.006M$   $Ce^{3+}$  stock solution into beaker. Add the  $0.006M$   $Ce^{4+}$  stock solution in volume  $0.5 \text{ ml}$  and measure the electro motoric voltage (EMV) using combined redox electrode after stabilisation. Into the same solution, pipette gradually the  $0.006M$   $Ce^{4+}$  stock solution in volumes of 2.0, 2.5, 20 and 25 ml. Measure the EMV after each addition.

**MEASUREMENT OF UNKNOWN SOLUTION.** Measure the EMV of combined redox electrode of the system with unknown  $[Ce^{+3}]/[Ce^{+4}]$  ratio. Alternatively, record the EMV in the Belousov-Zhabotinsky oscillating system.



**REPORT: TABLE 1:** for  $0.006M$   $Ce^{3+}$  stock solution and all other prepared standard solutions: volume of  $0.006M$   $Ce^{4+}$ -addition, total volume, concentrations of  $Ce^{+3}$  and  $Ce^{+4}$ , value  $\log([Ce^{+3}]/[Ce^{+4}])$ , experimental EMV. **Graph 1:** Dependence of  $EMV = E_{Redox} - E_{ref}$  on value  $\log([Ce^{+3}]/[Ce^{+4}])$ . **NEXT:** experimental Nernst's response,  $[Ce^{+3}]/[Ce^{+4}]$  ratio of unknown sample. Alternatively, the  $[Ce^{+3}]/[Ce^{+4}]$  ratios at minimum and maximum of the EMV in the Belousov-Zhabotinsky oscillating system.