

**Autoevaluation TEST N°2 (Topics 3-5)**

Family name and name \_\_\_\_\_

**Important:** Write your name before beginning the test. No additional material will be provided. Books, class notes are not allowed. Calculators are allowed. Use margins for drafts or calculus. **Mark with a cross the correct answer in the box at your left when you are completely sure. No crossings out and no additional comments are allowed. Correct answers mark as +1. Errors mark -0.1. Blanks mark as 0. The final score can not be less than 0.** There is only one correct answer in each question.

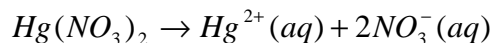
- A) When 3.24 g of  $\text{Hg}(\text{NO}_3)_2$  are dissolved in 1000 g of water the freezing point of the solution is -0.0558 °C. When 10,84 g of  $\text{HgCl}_2$  are dissolved in 1000 g water, the freezing point of the solution is -0.0744 °C.  $K_c$  for water is 1.86. Are ionized any of these salts in water?  $M(\text{Hg})=200.6$ ;  $M(\text{N})=14$ ;  $M(\text{Cl})=35.5$ ;  $M(\text{O})=16$

**Solution**

Freezing point depression of electrolyte solutions is calculated from the equation  $\Delta T = i \cdot K_c \cdot m$ , where  $m$  is the molality and  $i$ , the Van't Hof coefficient. Molality (moles of solute per kg solvent) of the solution is  $m = 3.24 / (2 \cdot 14 + 6 \cdot 16 + 200.6) = 0.00998$  mol/kg. Molality of the  $\text{HgCl}_2$  solution is  $m = 10.84 / (2 \cdot 35.5 + 200.6) = 0.0399$  mol/kg.

Assuming no ionization for both salts,  $i = 1$ .  $\Delta T(\text{the})$  for  $\text{Hg}(\text{NO}_3)_2$  would be  $\Delta T(\text{the}) = 1.86 \cdot 0.00998 = 0.0186$  °C. And for  $\text{HgCl}_2$   $\Delta T(\text{the}) = 1.86 \cdot 0.0399 = 0.0742$  °C. We notice that freezing point depression for the later coincides with the experimental data so the non ionization hypothesis is correct for this salt. This means that this salt dissolves forming ionic pairs  $\text{HgCl}_2(\text{aq})$  and not hydrated isolated ions

On the other hand, the Van't Hof coefficient for the nitrate solution can be calculated as  $\Delta T(\text{exp}) / \Delta T(\text{the}) = 3$ , which corresponds with the stoichiometry of the salt



- B) Consider the Daniell galvanic cell  $\text{Zn} | \text{Zn}^{2+}(\text{ac})(1\text{M}) || \text{Cu}^{2+}(\text{ac})(1\text{M}) | \text{Cu}$ . A solution of sodium sulfide ( $\text{Na}_2\text{S}$ ) was added to the Zn electrode to precipitate the Zn(II) cations in the form of ZnS. The final concentration of sulfide anions was 1 M and the cell potential was +1.78V.
- The flow of electrons goes from Zn electrode to Cu electrode or the other way round?
  - Calculate the solubility constant for ZnS.

Data:  $E^\circ_{(\text{Cu}(\text{II})/\text{Cu})} = 0,34$  V,  $E^\circ_{(\text{Zn}(\text{II})/\text{Zn})} = -0,76$  V

**Solution**

According to the notation for galvanic cells, anode is written at the left and anode at the right. Zn electrode is the anode, where oxidation takes place  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ . Cathode is the Cu electrode, where reduction takes place  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ . The standard potential of this cell is therefore  $E^\circ = 0.34 - (-0.76) = 1.10$  V. Electrons are produced in the anode and consumed in the cathode so flow of electrons goes from the anode to the cathode.

When ZnS is added, ZnS precipitates decreasing the  $\text{Zn}^{2+}$  concentration. We don't know this concentration but we know that the cell potential is 1.78 V. Therefore, from the Nernst equation we can calculate it. The overall reaction is  $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$ , so Nernst equation will be  $E = E^\circ - (0.059/n) \log([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$ ; since there are 2 exchanged electrons in the process and

$[Cu^{2+}]=1M$ , we reach to  $\log[Zn^{2+}]=2 \cdot (E^\circ - E)/0.059 = -23.05$ ;  $[Zn^{2+}] = 8.895 \cdot 10^{-24}$ . This is the concentration of Zn cations in equilibrium with solid ZnS. The solubility equilibrium is

$ZnS \leftrightarrow Zn^{2+} + S^{2-}$ . The solubility product is  $K_s = [Zn^{2+}] \cdot [S^{2-}]$ . Since  $[S^{2-}] = 1 M$  and  $[Zn^{2+}] = 8.895 \cdot 10^{-24}$ ,  $K_s = 8.895 \cdot 10^{-24}$ .

**C) Hydrazine is a base ( $K_b = 3 \cdot 10^{-6}$ ) that dissociates in aqueous solution as  $NH_2-NH_2 + H_2O \leftrightarrow NH_2-NH_3^+ + OH^-$ . 1 mL of a 0.02 M NaOH solution was added to 200 mL of 0.1 M hydrazine. Calculate the pH of the solution.**

**Solution**



Initial concentration:  $(0.2L \cdot 0.1 M) / 0.201$  0  $(0.001L \cdot 0.02M) / 0.201$

Equilibrium conc.:  $9.95 \cdot 10^{-2} - x$  x  $9.95 \cdot 10^{-5} + x$

$$K_b = \frac{[Hz^+][OH^-]}{[Hz]} = \frac{(9.95 \cdot 10^{-5} + x) \cdot x}{9.95 \cdot 10^{-2} - x} \approx \frac{(9.95 \cdot 10^{-5} + x) \cdot x}{9.95 \cdot 10^{-2}} = 3 \cdot 10^{-6}$$

$x = 4.989 \cdot 10^{-4}$ ;  $[OH^-] = 4.989 \cdot 10^{-4} + 9.95 \cdot 10^{-5} = 5.984 \cdot 10^{-4} M$ ; pOH = 3.22; pH = 10.78

**D)  $\Delta G_f^\circ$  for the following reaction  $S (s) + 3/2 O_2 (g) \leftrightarrow SO_3 (g)$  is  $\Delta G_f^\circ = -370.7 \text{ kJ} \cdot \text{mol}^{-1}$  at 298 K. Calculate  $K_p$  at 298K,  $K_c$  at 1000 K. How shifts equilibrium if T is decreased at constant pressure?**

**Solution**

$K_p$  and  $\Delta G_f^\circ$  are related through  $\Delta G_f^\circ = -RT \ln K_p$ ;  $K_p(298) = \exp(370.7 \cdot 10^3 / 8.314 \cdot 298) = 9.55 \cdot 10^{64}$ .  $K_p$  and  $K_c$  are related through  $K_p = K_c(RT)^{-\Delta n}$ ;  $K_c = 9.55 \cdot 10^{64} \cdot (8.314 \cdot 298)^{1/2} = 4.74 \cdot 10^{66}$ . If other values for the R constant are used, the numerical values of both  $K_p$  and  $K_c$  would change accordingly.

To calculate  $K_c$  at 1000 K, we need the reaction enthalpy value. Since it is not given in the wording, we can make a rough approximation.  $\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$ . Usually, entropy change in reactions between gases is relatively low so we can assume

$$\ln K_p = -\frac{\Delta \tilde{G}^0}{RT} = -\frac{\Delta \tilde{H}^0}{RT} + \frac{\Delta \tilde{S}^0}{RT} \approx -\frac{\Delta \tilde{H}^0}{RT}$$

$$\ln \frac{K_p(T_1)}{K_p(T_2)} = -\frac{\Delta \tilde{G}^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Therefore

$$\ln \frac{K_p(1000)}{K_p(298)} = \ln \frac{K_p(1000)}{9.55 \cdot 10^{64}} = -\frac{370.7 \cdot 10^3}{8.314} \left( \frac{1}{298} - \frac{1}{1000} \right)$$

and  $K_p(1000) = 2.31 \cdot 10^{19}$ .  $K_c = 2.31 \cdot 10^{19} \cdot (8.314 \cdot 1000)^{1/2} = 2.1 \cdot 10^{21}$ .