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Uva Wellassa University, Sri Lanka

BTech. Degree Program 2006/07

End Semester Examination - Semester 1

January 2008

CHE 281-2 Physical Chemistry

Answer for **three (03)** questions **only. All questions carry equal marks**
Total number of questions: Five (05)

Time: Two hours

Universal gas law constant, R = 8.314 $JK^{-1}mol^{-1}$
Faraday constant, F: 1F = 96500 $Cmol^{-1}$
At T = 298 K

(a). RT = 2.4790 $kJ.mol^{-1}$
(b). RT/F = 29.693 mV
(c). 2.303RT/F = 59 mV

At very small x, exp(x) ~1+x

ln(x)=2.303log(x)

Question 1[100 marks]:

(a). Determine the solubility product of calcite at 25 ^{0}C? The following data are given **[25 marks]:**

Species	ΔG^0 *kJ.mol^{-1}*
Ca^{2+}	-553.6
CO_3^{2-}	-527.0
$CaCO_3$	-1128.0

(b). A natural well water sample contains Ca^{2+} of $10^{-3.05}$ and CO_3^{2-} of $10^{-3.56}$ $mol.L^{-1}$. Calculate the ion activity product (IAP) **[25 marks]?**

(c). Calculate saturation index (SI) of calcite **[25 marks]?**

(d). What does the saturation index indicate about the state of saturation with respect to calcite **[25 marks]?**

Question 2 [100 marks]:

A lanthanum fluoride (LaF_3) solid-state electrode can be used to follow the progress of a potentiometric titration of fluoride ion (F^-) with a standard solution of lanthanum (La^{3+}) and can be used for the direct measurement of the fluoride ion concentration (activity) in a solution.

Exactly 100.0 mL of a 0.03095 M F^- solution was titrated with 0.03318 M La^{3+} solution, the titration reaction being

$$La^{3+} + 3F^- \rightleftharpoons LaF_3(s)$$

A solid-state LaF_3 membrane indicator electrode and a saturated calomel reference electrode (SCE) were employed, and the following data were obtained:

Volume of La^{3+}, mL	*E_{cell}, volts*
0	–0.1046
50.00	+0.1118

(a). If the response of the LaF_3 electrode is given by the relation $E_{cell} = K - 0.0592 \log [F^-]$ calculate K using the initial F^- concentration **[20 marks].**

(b). Using the result from part (a), calculate $[F^-]$ after the addition of 50.00 mL of the La^{3+} solution **[30 marks].**

(c). Using the result from part (b), calculate the concentration of free (unprecipitated) La^{3+} remaining after the addition of 50.00 mL of the La^{3+} solution **[25 marks].**

(d). Using the results from parts (b) and (c), calculate the solubility product (K_{sp}) for $LaF_3(s)$ **[25 marks].**

Question 3 [100 marks]:

(a). Given following half-cells

$Cu^{2+}|Cu$ $E^0 = 0.34$ V

$Zn^{2+}|Zn$ $E^0 = -0.76$ V

$Fe^{3+}, Fe^{2+}|Pt$ $E^0 = 0.77$ V

Write the reaction potential of cells that have following properties: (i). a cell which copper dissolves; (ii). The cell with the largest E^0 **[20 marks]**

(b). The potential of a hydrogen electrode (p_{H2} = 1 atm, T 298 K) measured against a saturated calomel electrode (E_{SCE}^0 = 0.282 V) is -0.151 V. Using Nernst equation calculate solution pH **[30 marks]**?

(c). Much of the life goes on because of the ability of biological systems to concert sugars into useable energy. Write the half reaction for the combustion of glucose and hence the overall reaction **[25 marks]**.

(d). Write the cell reaction and the electrode half-reactions and the standard emf of the following cell:

$$Pt|Fe^{3+}_{aq}, Fe^{2+}_{aq} \| Sn^{4+}_{aq}, Sn^{2+}_{aq}|Pt$$

(Given: $Fe^{3+}_{aq}, Fe^{2+}_{aq} | Pt$, $E^0 = 0.771$ V and $Sn^{4+}_{aq}, Sn^{2+}_{aq}|Pt$ $E^0 = 0.150$V) **[25 marks]**

Question 4 [100 marks]:

The Butler-Volmer (BV) equation is

$$i = i_0\left(exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) - exp\left(\frac{-\alpha\, nF\eta}{RT}\right)\right)$$

(a). State all terms stated in the equation. State the conditions under which the BV equation holds **[20 marks].**

(b). Define i_0 **[20 marks].**

(c). Derive limiting forms of the BV equation when (i). η is small and (ii). η is large **[30 marks].**

(d). The exchange current density for the evolution of the hydrogen at platinum is 8 Am^{-2}. What is the current density at 298 K for an η of 2mV? (hint: use the simplication (i) made under section (c)) **[30 marks].**

Question 5 [100 marks]:

(a). What are the units of the rate coefficients of first second-, and third order reactions if the concentrations are expressed in (mol L^{-1}) and the time is given in seconds **[20 marks]**?

(b). The gas phase reaction $2NO + O_2 \rightarrow 2NO_2$ is observed to be third order. There are several mechanisms that could lead to this observed reaction order. One possible mechanism is

(1) $NO + O_2 \rightleftharpoons NO_3$

(2) $NO_3 + NO \rightarrow^{"} 2NO_2$

Assuming that reaction (1) is very fast in both directions compared to reaction (2), derive a rate expression for the overall reaction in terms of the concentrations of NO and O_2 **[30 marks]**.

(b) A second possible mechanism is

(1) $NO + NO \rightleftharpoons N_2O_2$

(2) $N_2O_2 + O_2 \rightarrow^{"} 2NO_2$

Assuming that N_2O_2 is present in concentrations much smaller than the other species, derive a rate expression for the overall reaction in terms of the concentrations of NO and O_2 **[30 marks].**

(d) In which mechanism pseudo steady state approximation was assumed **[20 marks]?**