

UNIVERSITY OF TORONTO
FACULTY OF APPLIED SCIENCE AND ENGINEERING
Final Examination April 16, 2001

EDC230S ENVIRONMENTAL CHEMISTRY
Examiner : G.J. Evans

Closed Book Exam (2.5 hours)

Only non-programmable calculators are allowed

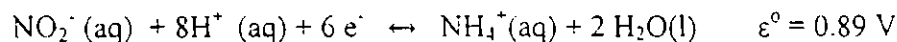
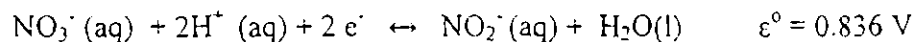
ANSWER ALL FIVE (5) QUESTIONS (two Pages + equation sheet)

CONSTANTS $R = 0.08206 \text{ L-atm/K-mol} = 8.314 \text{ J/mol-K}$

(10%) 1) Define the following terms: i) bio-magnification, ii) excess free energy, iii) $\text{PM}_{2.5}$, iv) COD, v) variable charge.

(25%) 2) Nitrogen is usually present in water in forms ranging from NH_4^+ to NO_3^- depending on the redox potential of the system.

Based on the reactions



- Calculate the pE at which the concentration of $\text{NO}_3^- (\text{aq})$ is 100 times that of $\text{NO}_2^- (\text{aq})$ for water with a pH of 6.
- Calculate the pE at which $\text{NO}_3^- (\text{aq})$ and $\text{NH}_4^+ (\text{aq})$ have equal concentrations in water with a pH of 8.
- Calculate the concentration of $\text{NH}_4^+ (\text{aq})$ in water with a pH of 4 and pE = 0, in equilibrium with air.

(25%) 3) Consider the following set of reactions occurring in the troposphere:

- | | |
|--|---|
| 1) $\text{NO}_2 \rightarrow \text{NO} + \text{O}$ | |
| 2) $\text{O} + \text{M} + \text{O}_2 \rightarrow \text{O}_3$ | $k = 6 \times 10^{-34} \text{ cm}^3/\text{molec-s}$ |
| 3) $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}^\bullet$ | |
| 4) $\text{O}^\bullet + \text{M} \rightarrow \text{O}$ | $k = 2.9 \times 10^{-11} \text{ cm}^3/\text{molec-s}$ |
| 5) $\text{O}^\bullet + \text{H}_2\text{O} \rightarrow 2 \text{OH}$ | $k = 2.2 \times 10^{-10} \text{ cm}^3/\text{molec-s}$ |
| 6) $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ | $k = 2.7 \times 10^{-13} \text{ cm}^3/\text{molec-s}$ |
| 7) $\text{OH} + \text{TCE} \rightarrow \text{products}$ | $k = ???$ |
| 8) $\text{OH} + \text{CH}_4 \rightarrow \text{products}$ | $k = 8.4 \times 10^{-15} \text{ cm}^3/\text{molec-s}$ |

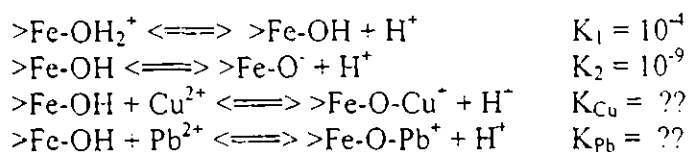
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- a) On a summer morning with $T = 25^{\circ}\text{C}$ and $P = 1 \text{ atm}$, some trichloroethylene (TCE) is released to the atmosphere and found to have a mean lifetime of 6 hours. In contrast the mean lifetime of CO is 51.1 hours. Assuming that both TCE and CO are only eliminated through reaction with OH, calculate the rate constant for the reaction of OH and TCE (reaction 7).
- b) By the middle of the afternoon, the rate of O^{\bullet} production through reaction 3 has tripled as compared to that in the morning and the partial pressure of water has increased from 1.5 kPa to 3.0 kPa (although the total pressure is still 101 kPa). Calculate the mean lifetime of TCE under these afternoon conditions. Assume that the release rates of TCE, CH_4 and CO increase in the afternoon such that their concentrations remain same as in morning.

(20%) 4) 1g of Mg^{2+} saturated clay is mixed with 100 ml of a solution that initially contains $2 \times 10^{-2} \text{ M}$ of Cd^{2+} .

- a) At equilibrium, 40% of the Cd^{2+} is adsorbed by the surface. Given that at the pH of the solution used the CEC of this clay is 2 meq/g, calculate the selectivity coefficient for this physical adsorption of Cd^{2+} .
- b) The pH of the clay/solution mixture from part "a" is increased such that the CEC increases to 3 meq/g. Calculate the concentration of Cd^{2+} in solution once the system has equilibrated.

(20%) 5) A Graduate student is investigating the chemisorption of Cu^{2+} and Pb^{2+} by an iron oxide based soil with 10^{-3} moles/g of surface sites. One gram of this soil is suspended in 1L of a pH = 6 solution that initially contains $5.25 \times 10^{-4} \text{ M}$ of Cu^{2+} and the same concentration of Pb^{2+} . The following reactions then occur:



- a) At equilibrium, Pb^{2+} occupies 45% of the surface sites while 15% are occupied by Cu^{2+} . Calculate the values of K_{Cu} and K_{Pb} , the equilibrium constants for the chemisorption of Cu^{2+} and Pb^{2+} by $>\text{Fe}-\text{OH}$.
- b) The pH of the solution is increased from 6 to 7 and, once the system has again equilibrated, the concentration of $\text{Pb}^{2+}(\text{aq})$ is found to be $2 \times 10^{-5} \text{ M}$. What is the concentration of $\text{Cu}^{2+}(\text{aq})$? Assume that the change in pH does not affect the total number of sites on the surface.
- c) The pH of the solution is increased again, this time from 7 to 8. Estimate the concentration of $\text{Cu}^{2+}(\text{aq})$ once the system has equilibrated.

EQUATIONS AID SHEET

$$\Delta G = \Delta H - T\Delta S$$

$$q = \frac{q_m C}{(a + C)}$$

$$\varepsilon = \varepsilon^\circ - \frac{RT}{nF} \ln Q$$

$$\varepsilon^\circ = \frac{RT}{nF} \ln K = \frac{0.0591}{n} \log K (at 298 K)$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta E = h\nu \quad \nu = \frac{c}{\lambda}$$

$$\Delta G_w = RT \ln x_w^{sat} \gamma_w \quad C_w^{sat} = \frac{l}{V_{H_2O} \gamma_w}$$

$$\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = 2kt \quad t_{\frac{1}{2}} = \frac{1}{2k[A]_0}$$

$$[A] = [A]_0 \exp(-kt) \quad t_{\frac{1}{2}} = \ln \frac{2}{k}$$