

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY  
DEPARTMENT OF APPLIED CHEMISTRY  
SUPPLEMENTARY EXAMINATIONS – AUGUST 2014  
PHYSICAL CHEMISTRY II-SCH 2204 FOR SCH AND TTE  
TIME: (3) THREE HOURS

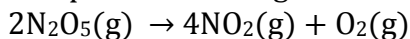
INSTRUCTIONS TO CANDIDATES

Answer ALL questions  
Answer each question on a FRESH page.

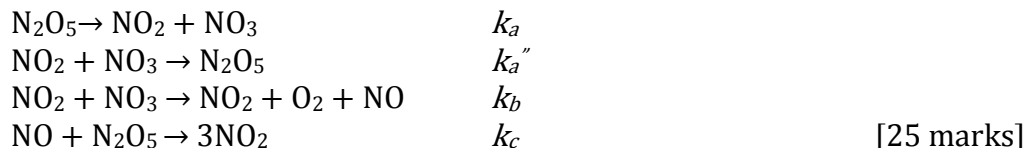
$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 0.08205 \text{ dm}^3 \text{ atm}^{-1} \text{ K}^{-1} \text{ mol}^{-1}.$$
$$F = eN_A = 96\,485 \text{ C mol}^{-1}$$

1.

$\text{N}_2\text{O}_5$  decomposes according to the following equation



Based on the following mechanism, and using the rate of formation of  $\text{NO}_2$ , devise the rate law for the decomposition process.



2.

a. A voltaic cell is set up at  $25^\circ\text{C}$  with the following half-cells:  $\text{Al}^{3+}$  (0.0010M)|Al and  $\text{Ni}^{2+}$  (0.50M)|Ni. Write an equation for the reaction that occurs when the cell generates an electric current, and determine the cell potential and calculate the equilibrium constant. [12 marks]

b. Silver bromide is a sparingly soluble salt. The salt dissolves to give the following equilibrium:  $\text{AgBr}_{(\text{s})} \rightleftharpoons \text{Ag}^+_{(\text{aq})} + \text{Br}^-_{(\text{aq})}$ . Form a cell that gives this net reaction and calculate its solubility product,  $K_{\text{sp}}$  and  $\Delta_{\text{R}}G^0$  at 298K. [13 marks]

3.

a. Compare and contrast *Chemisorption* and *Physisorption*. Discuss procedures that you need to carry out to distinguish chemisorption from Physisorption. [15 marks]

b. Discuss the assumptions of the Langmuir adsorption isotherm. [10 marks]

4.

Discuss what you understand by model fitting procedures and using examples explain their importance in chemical kinetics. [25 marks]

***END OF QUESTION PAPER!!!***

**ATTACHMENT: STANDARD REDUCTION POTENTIALS AT 25°C**

Half-reaction	E° (V)
$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\ell)$	+1.51
$\text{Au}^{3+} (\text{aq}) + 3\text{e}^- \rightarrow \text{Au} (\text{s})$	+1.50
$\text{ClO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 8\text{e}^- \rightarrow \text{Cl}^- (\text{aq}) + 4\text{H}_2\text{O} (\ell)$	+1.39
$\text{Cl}_2 (\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^- (\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-} (\text{aq}) + 14\text{H}^+ (\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} (\text{aq}) + 7\text{H}_2\text{O} (\ell)$	+1.33
$2\text{HNO}_3 (\text{aq}) + 4\text{H}^+ (\text{aq}) + 4\text{e}^- \rightarrow \text{N}_2\text{O} (\text{g}) + 3\text{H}_2\text{O} (\ell)$	+1.30
$\text{O}_2 (\text{g}) + 4\text{H}^+ (\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} (\ell)$	+1.23
$\text{MnO}_2 (\text{s}) + 4\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 2\text{H}_2\text{O} (\ell)$	+1.22
$\text{Br}_2 (\text{aq}) + 2\text{e}^- \rightarrow 2\text{Br}^- (\text{aq})$	+1.07
$\text{Hg}_2^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Hg} (\ell)$	+0.85
$\text{ClO}^- (\text{aq}) + \text{H}_2\text{O} (\ell) + 2\text{e}^- \rightarrow \text{Cl}^- (\text{aq}) + 2\text{OH}^- (\text{aq})$	+0.84
$\text{Ag}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Ag} (\text{s})$	+0.80
$\text{NO}_3^- (\text{aq}) + 2\text{H}^+ (\text{aq}) + \text{e}^- \rightarrow \text{NO}_2 (\text{g}) + \text{H}_2\text{O} (\ell)$	+0.80
$\text{Fe}^{3+} (\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+} (\text{aq})$	+0.77
$\text{O}_2 (\text{g}) + 2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 (\ell)$	+0.70
$\text{I}_2 (\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^- (\text{aq})$	+0.54
$\text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\ell) + 4\text{e}^- \rightarrow 4\text{OH}^- (\text{aq})$	+0.40
$\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu} (\text{s})$	+0.34
$\text{SO}_4^{2-} (\text{aq}) + 4\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 (\text{aq}) + \text{H}_2\text{O} (\ell)$	+0.17
$\text{Sn}^{4+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+} (\text{aq})$	+0.15
$\text{S} (\text{s}) + 2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{S} (\text{aq})$	+0.14
$\text{AgBr} (\text{s}) + \text{e}^- \rightarrow \text{Ag} (\text{s}) + \text{Br}^- (\text{aq})$	+0.07
$2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2 (\text{g})$	0.00
$\text{Pb}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Pb} (\text{s})$	-0.13
$\text{Sn}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Sn} (\text{s})$	-0.14
$\text{AgI} (\text{s}) + \text{e}^- \rightarrow \text{Ag} (\text{s}) + \text{I}^- (\text{aq})$	-0.15
$\text{Ni}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Ni} (\text{s})$	-0.26
$\text{Co}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Co} (\text{s})$	-0.28
$\text{PbSO}_4 (\text{s}) + 2\text{e}^- \rightarrow \text{Pb} (\text{s}) + \text{SO}_4^{2-} (\text{aq})$	-0.36
$\text{Se} (\text{s}) + 2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{Se} (\text{aq})$	-0.40
$\text{Cd}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cd} (\text{s})$	-0.40
$\text{Cr}^{3+} (\text{aq}) + \text{e}^- \rightarrow \text{Cr}^{2+} (\text{aq})$	-0.41
$\text{Fe}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Fe} (\text{s})$	-0.45
$\text{NO}_2^- (\text{aq}) + \text{H}_2\text{O} (\ell) + \text{e}^- \rightarrow \text{NO} (\text{g}) + 2\text{OH}^- (\text{aq})$	-0.46
$\text{Ag}_2\text{S} (\text{s}) + 2\text{e}^- \rightarrow 2\text{Ag} (\text{s}) + \text{S}^{2-} (\text{aq})$	-0.69
$\text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Zn} (\text{s})$	-0.76
$2\text{H}_2\text{O} (\ell) + 2\text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq})$	-0.83
$\text{Cr}^{3+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cr} (\text{s})$	-0.91
$\text{Se} (\text{s}) + 2\text{e}^- \rightarrow \text{Se}^{2-} (\text{aq})$	-0.92
$\text{SO}_4^{2-} (\text{aq}) + \text{H}_2\text{O} (\ell) + 2\text{e}^- \rightarrow \text{SO}_3^{2-} (\text{aq}) + 2\text{OH}^- (\text{aq})$	-0.93
$\text{Al}^{3+} (\text{aq}) + 3\text{e}^- \rightarrow \text{Al} (\text{s})$	-1.66
$\text{Mg}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Mg} (\text{s})$	-2.37
$\text{AgCl} (\text{s}) + \text{e}^- \rightarrow \text{Ag} (\text{s}) + \text{Cl}^- (\text{aq})$	+0.22