

OBAFEMI AWOLowo UNIVERSITY, ILE-IFE  
B.Sc. (Chemistry) Degree Examination

Part II  
Harmattan Semester Examination

CHM 203 – BASIC PHYSICAL CHEMISTRY

Answer ALL questions and answer each section on separate booklet

July, 2011

Time Allowed: 2½ hrs

SECTION A

- State the important postulates of kinetic theory of gases.
  - A quantity of dry air at 27°C is compressed slowly to one-third of its original volume. What is the percentage change in pressure?
  - At what temperature, pressure remaining constant will the root-mean-square velocity becomes double its value at  $T_1 = 273$  K. Let  $C_1$  and  $C_2$  be the velocities corresponding to  $T_1$  and  $T_2$ .
  - The volume of an ideal gas goes through a temperature change from 20°C to 60°C. Obtain the relation between the average molecular energy at 20°C ( $E_1$ ) to that at 60°C ( $E_2$ )
- In the presence of a metallic catalyst, nitrogen and hydrogen react to form ammonia in a process called the Haber process. The Haber reaction is:  
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H^\circ = -92.22 \text{ kJ at } 298.15 \text{ K}$$
  - Compute  $K_p$  for the reaction at 298.15 K
  - Compute the equilibrium constant at 500 K. (You may assume that  $\Delta H^\circ$  is a constant equal to its value at 298.15 K)
  - At what temperature would the equilibrium constant  $K_p = 1$ . Use the same assumption as (b) above
  - Explain how change in pressure will affect the production of ammonia. (Given  $\mu^\circ = 0.00, 0.00$  and  $-16.46 \text{ kJ mol}^{-1}$  for  $\text{N}_2(\text{g}), \text{H}_2(\text{g})$  and  $\text{NH}_3(\text{g})$  respectively.)
- State Kohlrausch's law and give its application(s) [Not more than 5 lines]
  - The molar conductivities at infinite dilution (at 25°C) of  $\text{NaI}, \text{NaCH}_3\text{CO}_2$  and  $\text{Mg}(\text{CH}_3\text{CO}_2)_2$  are  $12.69 \text{ mS m}^2 \text{ mol}^{-1}, 9.10 \text{ mS m}^2 \text{ mol}^{-1}$ , and  $18.78 \text{ mS m}^2 \text{ mol}^{-1}$ , respectively. What is the limiting molar conductivity of  $\text{MgI}_2$  at this temperature?
  - The standard potentials at 25 °C are:  
$$\text{Pd}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pd}(\text{s}) \quad \epsilon^\circ = 0.83 \text{ V}$$
$$\text{PdCl}_4^{2-}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pd}(\text{s}) + 4\text{Cl}^-(\text{aq}) \quad \epsilon^\circ = 0.64 \text{ V}$$
Calculate the equilibrium constant for the reaction  
$$\text{Pd}^{2+}(\text{aq}) + 4\text{Cl}^- \rightleftharpoons \text{PdCl}_4^{2-}(\text{aq})$$
Calculate the  $\Delta G^\circ$  for this reaction

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### SECTION B

- 4a. Define "heat of combustion of hydrocarbons"
- b. The bacterium *Acetobacter suboxyans* obtains energy for growth by oxidizing ethanol in two stages as follows:
- i.  $C_2H_5OH(l) + \frac{1}{2}O_2(g) \rightarrow CH_3CHO(l) + H_2O(l)$
  - ii.  $CH_3CHO(l) + \frac{1}{2}O_2(g) \rightarrow CH_3COOH(l)$

The enthalpy change in the complete combustion { to  $CO_2(g)$  and  $H_2O(l)$  } of the three compounds are:

Compound	$\Delta H_c^\circ (kJ\ mol^{-1})$
Ethanol (l)	-1171.6
Acetaldehyde (i)	-1168.1
Acetic acid (l)	-876.7

Calculate  $\Delta H^\circ$  values for reactions (i) and (ii)

- 5a. > \* If the decomposition reaction,  $2N_2O_5 \rightarrow 4NO_2 + O_2$  has the general rate law:

$$\text{Rate} = m \frac{d[N_2O_5]}{dt} = p \frac{d[NO_2]}{dt} = -q \frac{d[O_2]}{dt}$$

- i. Write down the values of m, p and q.
  - ii. If oxygen gas is produced at the average rate of  $9.1 \times 10^{-4} \text{ mol} \cdot \text{litre}^{-1} \cdot \text{s}^{-1}$ . Over the same period, what are the average rates of the production of nitrogen dioxide and the loss of nitrogen pentoxide?
- b. At  $27^\circ C$ , a certain reaction is 50% complete in 20.0 minutes. At  $57^\circ C$ , the same reaction is 50% complete in 5.0 minutes. Calculate the activation energy for the reaction (Given:  $R = 1.987 \text{ cal/K/mole}$ ).
- c. For the reaction  $2HI \rightarrow H_2 + I_2$  at 700K, The collision frequency obtained is  $10^{34} \text{ m}^{-2} \text{ s}^{-1}$  by collision theory. However the experimental value is  $10^{20} \text{ m}^{-2} \text{ s}^{-1}$ . Explain this observation in just one sentence and give 2 reasons for the observed difference. (Give two reasons why most molecular collisions do not lead to a reaction).

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