THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Assignment I (Test) — 2013/2014

CMU 2220/CME 4220 — Concepts in Chemistry

1 hour

25th February 2014 (Tuesday) 2.45 p.m. — 3.45 p.m.

- Answer all 25 questions (25 x 4 = 100 marks)
- Choose the most correct answer to each of the questions and mark this answer with an "X" on the answer script in the appropriate box.
- Use a **PEN** (not a PENCIL) in answering.
- Any answer with more than **one** "X" marked will be considered as an *incorrect* answer.
- Marks will be deducted for incorrect answers (0.6 per incorrect answer).
- The use of a non-programmable electronic calculator is permitted.
- Mobile phones are **not** allowed.

Gas constant (R)	=	$8.314 \ \mathrm{JK^{-1}mol^{-1}}$
Avogadro constant (N_A)	=	$6.023 \times 10^{23} \ \mathrm{mol^{-1}}$
Faraday constant (F)	=	$96{,}500 \ \mathrm{C\,mol^{-1}}$
Planck constant (h)	=	$6.63 \times 10^{-34} \ \mathrm{J\,s}$
Velocity of light (c)	=	$3.0 \times 10^{8} \ \mathrm{m\,s^{-1}}$
Protonic charge (e)	=	1.602177×10^{-19} C
Standard atmospheric pressure	=	$10^5 \ \mathrm{Pa}\left(\mathrm{N\,m^{-2}}\right)$
$\mathrm{Log}_e(X)$	=	$2.303 \ \mathrm{Log}_{10}(X)$

1. A student kept a red coloured solid object X in sunlight for a period of time, t. The student observed an increase in the temperature of this object during this time period. Consider the following statements about the observations of the student.

   (i) One can definitely say that some of the photons coming from sun got absorbed by X.

   (ii) The gaps between some energy levels of some molecules in X are equal to the energy of some photons in sunlight.

   (iii) One can definitely say that there are **no** transitions among energy levels of molecules in X which are allowed by selection rules in absorption spectroscopy.

   The correct statements out of (i), (ii) and (iii) above are
   (a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
   (d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

2. A student was asked to determine the number of photons crossing a cross section of a parallel beam of monochromatic radiation of wavelength 20 nm provided to him. He measured the cross sectional are of the beam to be $2.0 \ \mathrm{cm^2}$. His measurement of the rate of flow of energy of the beam gave a value of $0.035 \ \mathrm{W\,m^{-2}}$. What is the rate of flow of photons through a cross section of the beam?
   (a) $5.0 \times 10^{11} \ \mathrm{s^{-1}}$ (b) $6.0 \times 10^{11} \ \mathrm{s^{-1}}$ (c) $7.0 \times 10^{11} \ \mathrm{s^{-1}}$
   (d) $8.0 \times 10^{11} \ \mathrm{s^{-1}}$ (e) $9.0 \times 10^{11} \ \mathrm{s^{-1}}$

3. What is the number density of photons in the beam described in question 2 above.

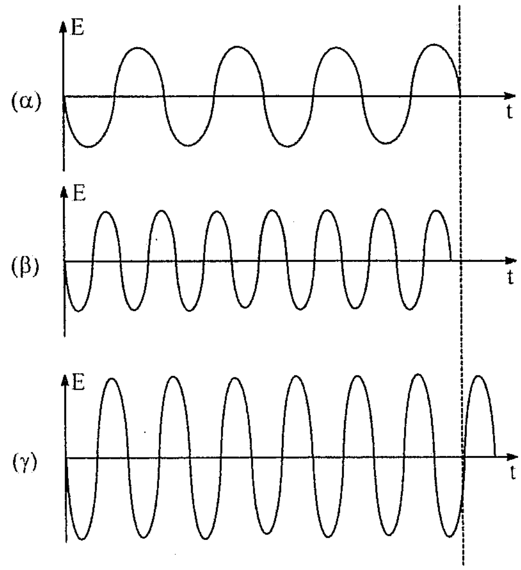
(a) $1.5 \times 10^5\ m^{-3}$ (b) $6.7 \times 10^4\ m^{-3}$ (c) $2.3 \times 10^7\ m^{-3}$
(d) $5.3 \times 10^6\ m^{-3}$ (e) $1.2 \times 10^7\ m^{-3}$

4. The electric field strength, E, versus time, t, drawn on the same scales, of three different monochromatic parallel beams of radiation, (α), (β) and (γ) are shown in the figure. Consider the following statements about these three beams.

(i) Photons in beam (γ) has the highest energy.

(ii) Radiation in beam (β) has the highest frequency.

(iii) Highest rate of flow of energy is in beam (γ).



The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

Use the following data in answering questions 5, 6 and 7.

A student was given a solution, A, of a pure compound X in water. He dissolved a small quantity of a pure compound Y in A to obtain a solution B. There was no change in the volume of solution in this process so that the concentration of X is the same in both solutions. The concentrations of X and Y in B were equal to $0.3\ mol\ dm^{-3}$ and $0.5\ mol\ dm^{-3}$, respectively. He filled a sample cell of path length 1 cm with solution B and placed in a sample chamber of a double beam spectrometer. Then he filled an identical sample cell with water used in preparing A and placed it in the reference chamber of the same double beam spectrometer. The absorbance reading was 2.6. He then replaced the water in the reference cell with solution A and placed it in the reference chamber and observed the absorbance reading to be 1.4. Both absorbance readings were taken with radiation of wavelength 20 nm. [Assume that X and Y do not interact with each other and the student has made no error in this experiment.]

5. Consider the following statements.

(i) One can definitely say that X absorbs radiation at wavelength of 20 nm.

(ii) One can definitely say that water absorbs radiation at wavelength of 20 nm.

(iii) The absorbance due to X and Y in the sample cell is 2.6.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

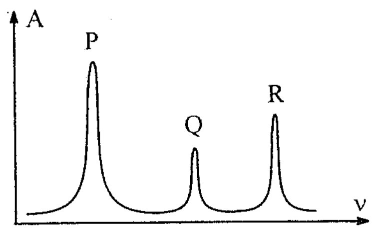
6. What is the molar extinction coefficient of Y?

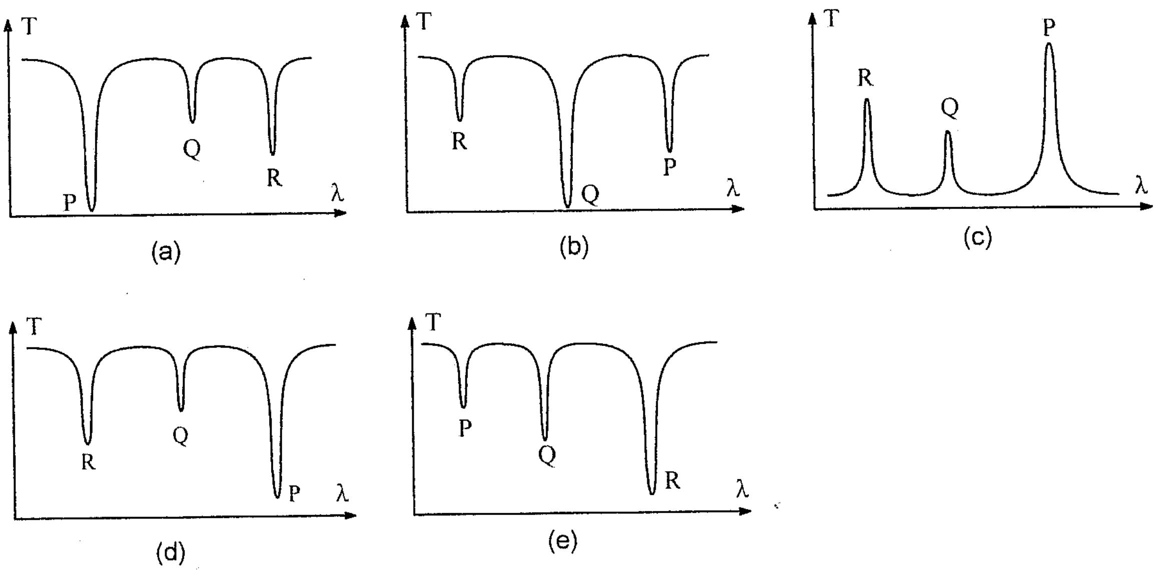
(a) 5.2 $dm^3\ mol^{-1}\ cm^{-1}$ (b) 1.3 $dm^3\ mol^{-1}\ cm^{-1}$ (c) 0.7 $dm^3\ mol^{-1}\ cm^{-1}$
(d) 2.8 $dm^3\ mol^{-1}\ cm^{-1}$ (e) 2.4 $dm^3\ mol^{-1}\ cm^{-1}$

7. What is the molar extinction coefficient of X?

(a) 5.2 $dm^3\ mol^{-1}\ cm^{-1}$ (b) 2.0 $dm^3\ mol^{-1}\ cm^{-1}$ (c) 0.7 $dm^3\ mol^{-1}\ cm^{-1}$
(d) 2.4 $dm^3\ mol^{-1}\ cm^{-1}$ (e) 4.0 $dm^3\ mol^{-1}\ cm^{-1}$

8. The spectrum of a compound X on an absorbance, A, versus frequency, ν, plot is shown in the figure to the right. It has three peaks, P, Q and R. Which of the following figures best represents the same spectrum (three peaks) on a transmittance, T, versus wavelength, λ, plot?





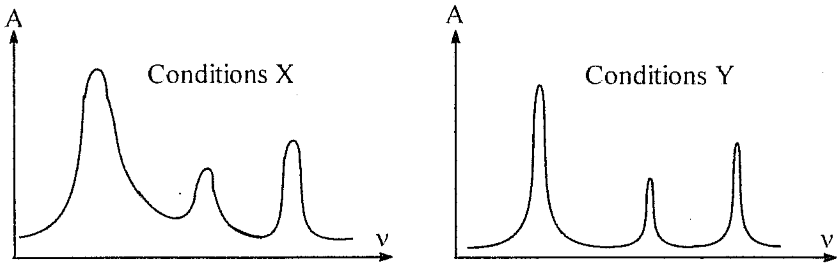
9. The ionic character of the HBr is 17% whose bond length is 0.127 nm. What is the dipole moment of the molecule?

(a) 3.46×10^{-25} C m (b) 3.46×10^{-22} C m (c) 3.46×10^{-25} C m
(d) 3.46×10^{-27} C m (e) 3.46×10^{-30} C m

10. Consider a (hypothetical) gaseous molecule which has only five energy levels. It is known that the populations of the three upper most levels are zero at $30^{\circ}C$. What is the maximum number of peaks that may be observed in the absorption spectrum of this molecule at $30^{\circ}C$?

(a) 10 (b) 9 (c) 8 (d) 7 (e) 6

11. The spectra of two gaseous samples of Br_2 obtained by a student under two different sets of physical conditions using the same spectrometer are shown below.



Consider the following statements about the conditions X and Y.

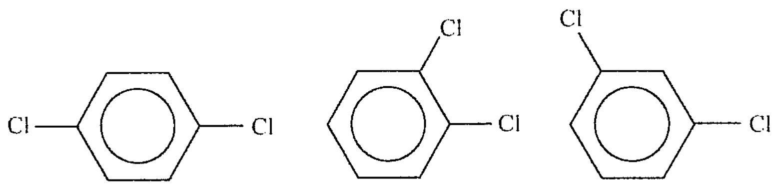
(i) X may have had a higher pressure than Y and the same temperature.

(ii) Y may have had a lower temperature than X and the same pressure.

(iii) X may have had a lower pressure and a lower temperature than Y.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

12. What is the decreasing order (largest first and smallest last) of dipole moment in dichlorobenzene molecules shown in the following figure?



(i) (ii) (iii)

(a) (i), (ii), (iii) (b) (ii), (iii), (i) (c) (iii), (ii), (i)
(d) (ii), (i), (iii) (e) (i), (iii), (ii)

13. Consider the following statements about the Bohr condition in spectroscopy.

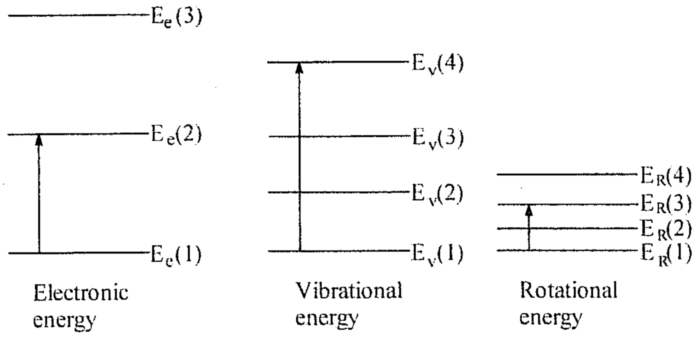
(i) Bohr condition is a relationship between the difference in energy of two levels of a molecule involved in a transition in absorption spectroscopy and the energy of the absorbed photon.

(ii) Bohr condition has to be satisfied for an incoming photon, for it to get absorbed by a molecule.

(iii) Some times, even when the Bohr condition is satisfied, a transition between some energy levels may not take place with the absorption of an incoming photon.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

14. Often you assume that the rotational, vibrational and electronic energy levels of a molecule are separately quantised. First few levels in each of these energies of a molecule and a particular mixed transition is schematically represented in the diagram to the right in standard notation. $E_\alpha(\beta)$ indicates the energy of the β^{th} level in electronic, vibrational and rotational energy depending on $\alpha = e$, v or R respectively.



Consider the following statements about the transitions.

(i) The spectral line corresponding to the mixed transition represented in the diagram most probably appears in the UV-Visible region of the electromagnetic spectrum.

(ii) Most probably frequency, ν', given by $\nu' = (E_v(3) - E_v(2))/h$ will be in the microwave region of the electromagnetic spectrum.

(iii) The frequency, ν, of the photon absorbed in the mixed transition represented in the diagram is given by $\nu = (E_e(2) + E_v(4) + E_R(3) - E_e(1) - E_v(1) - E_R(1))/h$ where h is the Plank constant.

The correct statements out of (i), (ii) and (iii) above are

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

15. An excited quantum state of a molecule cannot have an infinite life time. Always it has a finite lifetime. Which processes, out of the three processes indicated below, are responsible for a finite life time of a molecule?

(i) Stimulated emission.

(ii) Spontaneous emission.

(iii) Collisional deactivation.

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

16. What is meant by the natural width of a peak in a spectrum?

(a) The peak width due to Doppler broadening which arises due to spontaneous emission.

(b) The peak width due to lifetime broadening which arises due to stimulated emission.

(c) The peak width due to lifetime broadening which arises due to spontaneous emission.

(d) The peak width due to Doppler broadening which arises due to stimulated emission.

(e) None of the answers (a), (b), (c) or (d) above is correct.

17. Three microscopic processes, $(\alpha), (\beta)$ and (γ), that occur in a sample of molecules, M, placed in an absorption spectrometer are shown below in standard notation.

(α) $M^* \rightarrow M + h\nu$

(β) $M + h\nu \rightarrow M^*$

(γ) $M^* + h\nu_1 \rightarrow M + h\nu_1 + h\nu_2$

Where (γ) represents the stimulated emission process.

Consider the following statements about these processes.

(i) Process (α) is called spontaneous emission.

(ii) In stimulated emission, the frequency of the <u>incoming</u> photon must satisfy the Bohr condition, $\nu_1 = (E_i - E_f)/h$, where E_i and E_f are the initial and final energy levels of the molecule involved in the <u>stimulated emission process</u> and h is the Plank constant.

(iii) If the sample absorbs radiation at a particular frequency then the rate of (α) has to be smaller than that of (β) at that frequency (within the sample).

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the <u>answers</u> (a), (b), (c) or (d) is correct.

18. Consider the following reaction scheme

$RCHO \xrightarrow{k_1} R + CHO$

$RCHO + R \xrightarrow{k_2} RH + RCO$

$RCO \xrightarrow{k_3} R + CO$

$2\,RCO \xrightarrow{k_4} RCOCOR$

Based on the principle of the steady state assumption for the radical R, the concentration of R is best represented by

(a) $[R] = \dfrac{k_3[RCO] - k_1[RCHO]}{k_2[RCHO]}$

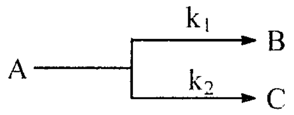
(b) $[R] = \dfrac{k_3[RCO] + k_1[RCHO]}{k_2[RCHO]}$

(c) $[R] = \dfrac{k_3[RCHO] + k_1[RCO]}{k_2[RCHO]}$

(d) $[R] = \dfrac{k_3[RCO] + k_4[RCO]^2}{k_2[RCHO]}$

(e) $[R] = k_3[RCO] + k_1[RCHO] - k_2[RCHO]$

19. Consider the reaction shown below.



The rate equation for the above reaction is of the form $\frac{d[x]}{dt} = (k_1 + k_2)[a - x]$ (the symbols used have the usual meanings). Consider the following statements.

(i) The above reaction is an example of a consecutive reaction.

(ii) The integrated form of the rate equation is $\ln\left[\frac{a}{a-x}\right] = (k_1 + k_2)t$.

(iii) The above reaction is a first order reaction.

The correct statements out of (i), (ii) and (iii) above are

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) Only (ii). (e) Only (iii).

20. Consider he following four statements which refer to a reaction of the form $2A + B + C \rightarrow P + Q$. Its rate equation was experimentally determined to be $-\frac{d[A]}{dt} = k[A][B][C]^2$.

(i) The rate of the reaction is proportional to $[A]^2[B][C]$.

(ii) The rate of the reaction is proportional to $[A][B][C]^2$.

(iii) The overall order of the reaction is 4.

(iv) If the concentration of A and B are in excess relative to C, then it can be considered as a pseudo first order reaction.

The correct statements out of (i), (ii), (iii) and (iv) above are

(a) Only (i), (ii) and (iii). (b) Only (ii), (iii) and (iv). (c) Only (iii), (iv) and (i).
(d) Only (i) and (iii) (e) Only (ii) and (iii).

Use the information given below in answering questions 21 and 22.

A kinetic experiment involving the hydrolysis reaction between methyl acetate and sodium hydroxide was carried out. You have been asked to mix $10.00\ cm^3$ of methyl acetate with distilled water and 2.0 M NaOH such that the total volume is $250.00\ cm^3$ and the concentration of NaOH equals that of methyl acetate.

[Assume density of methyl acetate = $740.0\ kg\,m^{-3}$.
Relative atomic masses: H= 1.0; C = 12.0; O = 16.0]

21. The initial concentration of the ester $(\mathbf{in\ mol\,dm^{-3}})$ in the reaction mixture is

(a) 1.00 (b) 0.40 (c) 0.25 (d) 0.20 (e) 0.10

22. The volume of 2.0 M NaOH $(\mathbf{in\ cm^3})$ used in preparing the above solution is

(a) 200 (b) 100 (c) 50 (d) 40 (e) 25

Use the information given below in answering questions 23 and 24.

Consider a <u>second order</u> reaction of the form $A \rightarrow$ Products carried out at $27^{\circ}C$.

Rate constant for the above reaction, $\mathbf{k} = 2.0\times10^{-5}\ mol^{-1}\ m^{3}\ min^{-1}$

The initial concentration of A, $\mathbf{a} = 5.0\times10^{-2}\ mol\,dm^{-3}$.

23. The integrated form of the rate equation for this reaction is (where **x** is the concentration of A reacted after time, **t**)

(a) $\ln\left[\frac{a}{a-x}\right] = kt$ (b) $\frac{1}{a} - \frac{1}{a-x} = kt$ (c) $\left[\frac{x}{a(a-x)}\right] = kt$

(d) $\left[\frac{a}{x(a-x)}\right] = kt$ (e) $x = kt$

24. The half – life of the above reaction (**in minutes**) is about

(a) 35 (b) 70 (c) 35×10^{3} (d) 10^{3} (e) 10^{6}

25. Consider the following statements.

(i) The over-all order of a reaction may be equal to the sum of the stoichiometric coefficients of the balanced equation of the reaction.

(ii) According to Arhennius equation, rate constant is proportional to temperature.

(iii) According to Arhennius equation, a plot of $\ln(k)$ versus T is a straight line.

The correct statements out of (i), (ii) and (iii) above are

(a) Only (i). (b) Only (ii). (c) Only (iii).

(d) Only (i) and (iii). (e) Only (ii) and (iii).