6X 358

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

AUTUMN EXAMINATIONS 2002

THIRD YEAR CHEMISTRY

Physical Chemistry (CH 313)

All questions carry equal marks.

Answer *four* (4) questions.

Professor K Waugh
Professor R N Butler
Professor B Ó Cochláin
Dr J M Simmie
Dr W M Carroll

Time allowed : ***Two*** hours

Gas Constant, $R = 8.314\ J\ K^{-1}\ mol^{-1}$	Avogadro constant, $N_A = 6.022 \times 10^{23}\ mol^{-1}$
Planck's constant, $h = 6.626 \times 10^{-34}\ J\ s$	Velocity of light, $c = 2.998 \times 10^{8}\ m\ s^{-1}$
Electronic mass, $m_e = 9.109 \times 10^{-31}\ kg$	Boltzmann constant, $k = 1.381 \times 10^{-23}\ J\ K^{-1}$
Electronic charge, $e = 1.602 \times 10^{-19}\ C$	Bohr magneton, $\mu_B = 9.274 \times 10^{-24}\ J\ T^{-1}$
Faraday constant, $F = 96485\ C\ mol^{-1}$	Atmosphere $= 101325\ N\ m^{-2}$

1. The vapour pressure of water is 23.76 mm Hg at 25 °C; derive an expression for the variation of the vapour pressure of water with temperature in the range 25 to 100 °C (the normal boiling point).
Use your equation to obtain the boiling point of water under a pressure of 485 mm Hg and ΔS_{vap} (the entropy of evaporation at the normal boiling point).

[25 marks]

---

2. **Answer <u>EITHER</u> (a) <u>OR</u> (b).**

(a) The standard enthalpy of decomposition of $CaCl_2 \cdot NH_3(s)$ into $CaCl_2(s)$ and $NH_3(g)$ is nearly constant between 350 and 470 K. ΔG° in the same temperature range follows the relationship

$$\Delta G^\circ / \text{kJ mol}^{-1} = 78 + 0.161T .$$

Calculate the standard enthalpy of decomposition and the equilibrium pressure of ammonia in the presence of $CaCl_2 \cdot NH_3(s)$ at 400 K.

[25 marks]

(b) Answer any <u>three</u> of the following:

(i) Derive the Gibbs-Helmholtz equation

[9 marks]

(ii) Show that for an ideal binary solution, a consideration of freezing point depression is equivalent to a consideration of the variation of solubility as a function of temperature.

[8 marks]

(iii) It has been claimed that Le Chatelier's Principle is not original, but was 'copied' from the van't Hoff equation $\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H}{RT^2}$.

Show that this could be so.

[8 marks]

(iv) Show how the Second Law of thermodynamics (a law which has not been proved) allows us to predict whether a reaction is feasible or not, even though the reaction has never been carried out.

[8 marks]

(v) Show how the Second Law of thermodynamics leads to (Gibbs) free energy.

[8 marks]

---

3. Answer both parts.

(i) What are the fundamental assumptions necessary in order to establish Boltzmann statistics?

[12 marks]

(ii) Calculate the molecular translational partition function,

$$\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

for H_2 in a volume of 1 cm^3 at 298 K.

[13 marks]

---

4. The data in the table are for the adsorption of a gas on 3.022g of charcoal at 273K. Confirm that they fit the Langmuir isotherm;

[8 marks]

find the relevant constant(s) of the equation

[8 marks]

and the surface area of the charcoal, assuming that each molecule of the sorbate occupies an area of 16.2×10^{-20} m^2.

[9 marks]

P/mm Hg	100	200	300	400	500	600	700
V/cm^3 stp	10.2	18.6	25.5	31.4	36.9	41.6	46.1

---

5. Answer (a) and (b).

(a) Describe the interfacial changes which occur when a copper electrode is initially immersed in a Cu^{2+} solution.

[12 marks]

(b) The data in the following table refer to the anodic current through a platinum electrode of area 2.0 cm^2 in contact with an Fe^{3+}, Fe^{2+} aqueous solution at 298K.

η/mV	**50**	**100**	**150**	**200**	**250**	**350**
I/mA	**8.8**	**25.0**	**58.0**	**131**	**298**	**300**

Estimate the exchange current density (i_0), the transfer coefficient (α) and the limiting current (i_L) for the electrode process.

[13 marks]

---

6. The energy of a particle of mass, m, confined to a region along the x-axis of zero potential energy between $x=0$ and $x=L$ is given by:

$$E_n = n^2h^2/8mL^2$$

Calculate the difference in energy between the levels (a) $n=2$ and $n=1$ and (b) $n=4$ and $n=3$ in joules of an electron in a box of length 1.0 nm.

[20 marks]

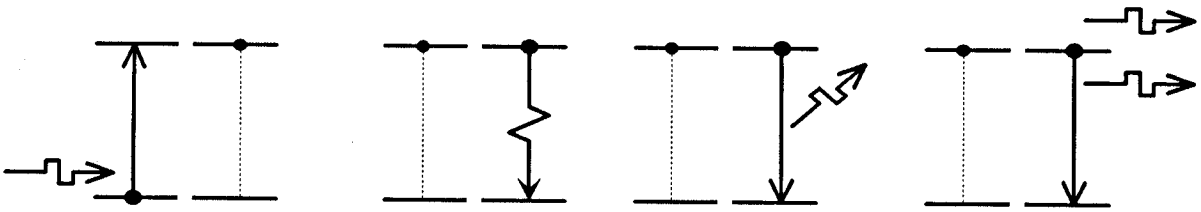
What are the most likely locations of a particle in a box of length L in the state $n=3$?

[5 marks]

---

7. **Answer (a), (b) and (c).**

(a) Provide an explanation for the following spectroscopic diagrams.



[12 marks]

(b) Write down an expression for the Law that governs the intensities of allowed transitions and discuss each term present.

[8 marks]

(c) How can it be used to measure temperature and under what circumstances would this be extremely useful?

[5 marks]

---

8. **Answer (a) and (b).**

(a) It is found that the rates of the majority of chemical reactions increase in a simple predictable manner with increasing temperature.
What is the name of the equation that represents this behaviour? Write down a *linear* form of the equation.

[10 marks]

(b) The rate constant for the atmospheric reaction:

$$NO + O_3 \rightarrow NO_2 + O_2$$

has been measured as a function of temperature with the following results:

T/K	200	250	300
k / cm^3 mol^{-1} s^{-1}	1.10×10^9	4.46×10^9	11.3×10^9

Calculate the activation energy for this reaction and estimate the A–factor.

[15 marks]
