

CPSS 4273

## FIRST PUBLIC EXAMINATION

Trinity Term 1997

Preliminary Examination in Physical Sciences

SUBJECT 3. CHEMISTRY 3: PHYSICAL CHEMISTRY

also

Preliminary Examination in Biochemistry

Monday 9 June 2.30 p.m. – 5.00 p.m.

Time allowed: 2½ hours

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*Candidates should answer FOUR questions only*

*The numbers in the margin indicate the approximate weight the Moderators expect to assign to each part of the question*

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$$

$$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.6261 \times 10^{-34} \text{ J s}$$

$$c = 2.9979 \times 10^8 \text{ m s}^{-1}$$

$$F = 9.6485 \times 10^4 \text{ C mol}^{-1}$$

$$1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

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You must not open this paper until instructed to do so by an invigilator.

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1 (a) Explain what is meant by a *phase diagram* and the *phase boundaries* that appear in it. [5]

(b) From the expression  $dG = V dp - S dT$ , derive a form of the Clausius–Clapeyron equation that describes the variation of the vapour pressure of a solid with temperature. Be careful to specify and justify all the approximations involved in the derivation. [10]

(c) The vapour pressures of two crystalline forms of tungsten tetrachloride were found to fit the following expressions:

$$\text{WCl}_4(s, \alpha) \quad \ln(p/\text{Pa}) = 20.124 - 9200/(T/\text{K})$$

$$\text{WCl}_4(s, \beta) \quad \ln(p/\text{Pa}) = 18.235 - 8260/(T/\text{K})$$

(i) Calculate the enthalpy and temperature of transition between the two crystalline forms. [7]

(ii) Which of the two forms is the more stable below the transition temperature? [3]

2 (a) Write notes on the following topics: [4 × 2]

(i) Principal quantum number,  $n$ .

(ii) Orbital angular momentum quantum number,  $l$ .

(iii) Spin quantum number,  $s$ .

(iv) Magnetic quantum number,  $m_l$ .

(b) The wavefunction for a  $2p_z$ -electron in a hydrogenic atom of atomic number  $Z$  is

$$\psi = Nr \cos \theta e^{-Zr/2a_0}$$

where  $a_0$  is the Bohr radius and  $N$  is a normalization constant.

(i) Normalize this wavefunction. For this step, you will need the integrals [8]

$$\int_0^{\infty} r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}} \quad \int_0^{\pi} \cos^2 \theta \sin \theta d\theta = \frac{2}{3} \quad \int_0^{2\pi} d\phi = 2\pi$$

(ii) Evaluate the most probable distance of the electron from the nucleus. [5]

(iii) Identify the most probable location of the electron in terms of  $r$  and  $\theta$ . [4]

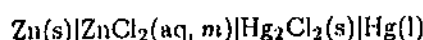
3 (a) The relation between the reaction Gibbs energy and the standard reaction Gibbs energy is

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

where  $Q$  is the reaction quotient. Define, as precisely as you can, all the terms in this expression. [5]

(b) Use the equation in part (a) to derive the Nernst equation for the zero-current cell potential (the emf of a cell). [4]

(c) Consider the following electrochemical cell:



where  $m$  is the molality of  $\text{ZnCl}_2$  in the solution.

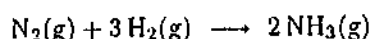
(i) Write down the overall cell reaction. [3]

(ii) Write the Nernst equation for the cell potential. [3]

(iii) Given that  $E^\ominus(\text{Zn}^{2+}, \text{Zn}) = -0.7628 \text{ V}$  and  $E^\ominus(\text{Hg}, \text{Hg}_2\text{Cl}_2, \text{Cl}^-) = +0.2676 \text{ V}$ , evaluate  $E^\ominus$  for the cell and  $\Delta_r G^\ominus$  and  $K$  for the cell reaction at 298.15 K. [5]

(iv) It is found that the slope of a plot of standard cell potential against temperature is  $-0.452 \text{ mV K}^{-1}$ . Derive an expression for the standard reaction enthalpy of the cell reaction, and deduce its value. [5]

4 In the Haber process, ammonia is produced by passing a mixture of nitrogen and hydrogen over a catalyst:



The standard enthalpies of formation, standard entropies, and heat capacities are given in the table below for each of the three species at 298 K:

	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	$S_m^\ominus / (\text{J K}^{-1} \text{mol}^{-1})$	$C_{p,m} / (\text{J K}^{-1} \text{mol}^{-1})$
$\text{N}_2(\text{g})$	0	192	29.1
$\text{H}_2(\text{g})$	0	131	28.8
$\text{NH}_3(\text{g})$	-46.2	193	35.7

(a) Calculate  $\Delta_r H^\ominus$ ,  $\Delta_r S^\ominus$ ,  $\Delta_r G^\ominus$ , and  $K$  for the reaction at 298 K. [8]

(b) An industrial reactor operates at 600 K. Calculate  $K$  at this temperature, assuming heat capacities to be independent of temperature. [10]

(c) The gas flowing into the reactor has the composition ratio 3 mol  $\text{H}_2$  : 1 mol  $\text{N}_2$ . If the mole fraction of ammonia in the exhaust gas from the reactor is 0.35, what is the total pressure in the reactor? (Assume that equilibrium is established in the reactor at 600 K.) [7]

Turn over

4

5 (a) Show, by using Raoult's law, that the chemical potential of a component J in an ideal solution can be written

$$\mu_J = \mu_J^* + RT \ln x_J$$

where  $x_J$  is the mole fraction of the component. [5]

(b) Give one example of two liquids that form an ideal solution and one example of two that form a non-ideal solution. [2 × 2]

(c) (i) From the expression in (a), derive expressions for the ideal Gibbs energy of mixing,  $\Delta_{\text{mix}}G$ , and entropy of mixing,  $\Delta_{\text{mix}}S$ , for a binary (two-component) system. [8]

(ii) For this ideal binary mixture, make sketches illustrating the variation of  $\Delta_{\text{mix}}G$ ,  $\Delta_{\text{mix}}S$ , and  $\Delta_{\text{mix}}H$  with mole fraction. [3 × 1]

(iii) The vapour pressures of the pure liquids A and B are 47.3 kPa and 11.4 kPa, respectively. Assuming ideal behaviour of the liquid phase and perfect behaviour for the vapour, calculate the total vapour pressure and the equilibrium composition of the vapour phase above a liquid of composition  $x_A = 0.35$ . [5]

6 (a) Explain the terms [5 × 2]

- (i) Integrated rate law
- (ii) Steady-state approximation
- (iii) Autocatalysis
- (iv) Chain reaction
- (v) Half-life of a reactant

(b) The rate law of a certain reaction  $A \rightarrow P$  is

$$\frac{d[P]}{dt} = k[A][P]$$

(i) Set up the rate law in terms of the initial concentrations of A and P, which are  $[A]_0$  and  $[P]_0$ , respectively. [4]

(ii) Solve this rate law for the concentration of P as a function of time. You will need the relation [8]

$$\frac{1}{(a-x)(b+x)} = \frac{1}{a+b} \left\{ \frac{1}{a-x} + \frac{1}{b+x} \right\}$$

Comment on the behaviour of the concentration of P. [3]

7 (a) Sketch the energy level (Grotrian) diagram for a hydrogen atom. Use it to explain the atomic spectrum that is observed for hydrogen. [6]

(b) What is meant by the term *radial distribution function* when discussing atomic orbitals? Sketch the radial distribution functions of the  $2s$  and  $2p$  orbitals of lithium. [6]

(c) The principal series of lines in the emission spectrum of atomic lithium arise from the  $np \rightarrow 2s$  transitions, where  $n$  is the principal quantum number. The first five lines in the series are observed at the following wavenumbers:

$$14\,908, 30\,935, 36\,479, 39\,024, 40\,399 \text{ cm}^{-1}$$

Use a graphical method to estimate the ionisation energy (expressed as a wavenumber, in  $\text{cm}^{-1}$ ) of the  $2s$  electron in lithium. [8]

(d) In fact, under higher resolution, the  $2p \rightarrow 2s$  transition in (b) is split into a doublet separated by  $0.3 \text{ cm}^{-1}$ . Explain this observation. [5]