

- 1) Calculate the lowest possible energy for an electron (mass =  $9.1 \times 10^{-31}$  kg) confined in a cube of sides equal to (a) 10 pm ( $1 \text{ pm} = 10^{-12} \text{ m}$ ) and (b) 1 fm ( $1 \text{ fm} = 10^{-15} \text{ m}$ ). The latter cube is the order of magnitude of an atomic nucleus; what do you conclude from the energy you calculate about the probability of a free electron being present in a nucleus?

Note: Planck constant  $h = 6.626 \times 10^{-34} \text{ Js}$  (12%)

- 2) (a) Calculate the ionization energy of the hydrogen atom on the basis of the Bohr theory. (b) The first ionization energy of the Li atom is 5.39 eV. Estimate an effective nuclear charge  $Z_{\text{eff}}$  for the valence electron in the Li atom.

Note: Rydberg constant  $R = 1.0968 \times 10^7 \text{ m}^{-1} = \frac{e^2}{8\pi\epsilon_0 a_0 h c}$

The total energy is  $E = -\frac{Z^2 e^2}{8\pi\epsilon_0 n^2 a_0}$  (13%)

- 3) Explain why  $\text{Li}^+$  has a lower ionic conductivity than  $\text{Na}^+$  and why the value for  $\text{H}^+$  is so much higher than the values for both of these ions. (12%)

- 4) Compare the entropy changes for the system, surroundings and universe for the reversible isothermal expansion of one mole of an ideal gas from  $0.010 \text{ m}^3$  to  $0.100 \text{ m}^3$  at 298K to the entropy changes for the same expansion performed irreversibly against a constant external pressure of 0.100 atm. (14%)

- 5) If 1.585 g of nitrogen tetroxide gives a total pressure of 1.0133 bar when partially dissociated in a  $500\text{-cm}^3$  glass vessel at  $25^\circ\text{C}$ , what is the extent of reaction  $\xi$ ? What is the value of  $K_p$ ? What is the extent of reaction at a total pressure of 0.5 bar? (13%)

- 6) The two arms of a U-tube have radii of 0.05 cm and 0.10 cm. A liquid of density  $0.80 \text{ g cm}^{-3}$  is placed in the tube, and the height in the narrower arm is found to be 2.20 cm higher than that in the wider arm. Calculate the surface tension of the liquid, assuming contact angle  $\theta = 0^\circ$ . (12%)

- 7). The hydrolysis of ethyl acetate catalyzed by hydrochloric acid obeys the rate equation  $v = k[\text{ester}][\text{HCl}]$ , and the reaction essentially goes to completion. At  $25^\circ\text{C}$  the rate constant is  $2.80 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . What is the half-life of the reaction if  $[\text{ester}] = 0.1 \text{ M}$  and  $[\text{HCl}] = 0.01 \text{ M}$ ? (12%)
- 8). A first-order surface reaction is proceeding at a rate of  $1.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$  and a rate constant  $2.0 \times 10^{-3} \text{ s}^{-1}$ . What will be the rate and the rate constant if, (a) The surface area is increased by a factor of 10? (b) The amount of gas is increased tenfold at constant pressure and temperature? (12%)