

說明： 1. 請儘量依序作答、並標明題號，但不必抄題。  
2.  $R=8.314 \text{ J K}^{-1}\text{mol}^{-1}$ ,  $h=6.626 \times 10^{-34} \text{ J s}$ ,  $k=1.38 \times 10^{-23} \text{ J K}^{-1}$

1. "The larger the heat liberated by a chemical reaction, the faster the rate of this reaction." Is this statement correct? Why? (4%)
2. Calculate the work done when 0.171 mol of methane expands reversibly and isothermally from 1.55L to 3.55L. The van der Waals constants of methane are  $a=2.28 \text{ L}^2 \text{ bar mol}^{-2}$  and  $b=0.0428 \text{ L mol}^{-1}$ . (6%)
3. Prove that the final temperature ( $T_2$ ) of  $n$  moles of an ideal gas that expanded (or compressed) adiabatically and reversibly from a volume  $V_1$  and temperature  $T_1$  to a final volume  $V_2$  is given by  $T_2=T_1(V_1/V_2)^{\gamma}$  ( $C_v$ : heat capacity at constant volume) (6%)
4. Predict the effect of a two-fold increase of pressure on the value of  $K_y$  ( $y$ : mole fraction) of the ammonia synthesis at equilibrium. ( $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$ ) (6%)
5. Estimate the solubility of  $\text{O}_2(\text{g})$  in water at  $25^\circ\text{C}$  and a partial pressure of 190 torr. (Henry's law constant of  $\text{O}_2(\text{g})$  is  $3.30 \times 10^7 \text{ torr}$ ) (6%)
6. One mole of an ideal gas at 298K expands freely and isothermally from a pressure of 10 bar to 1 bar. Calculate (a)  $w$ , (b)  $\Delta H$ , (c)  $\Delta S$  and (d)  $\Delta G$  (8%)
7. For  $\text{O}_2(\text{g})$  at  $25^\circ\text{C}$  and a pressure of 1 bar, the number of collision  $Z_{11}$  is  $1.26 \times 10^8 \text{ mol L}^{-1} \text{ s}^{-1}$ . Estimate the collision diameter of  $\text{O}_2$  molecules. (8%)
8. For the three parallel reactions  $\text{A} \xrightarrow{k_1} \text{B}$ ,  $\text{A} \xrightarrow{k_2} \text{C}$ , and  $\text{A} \xrightarrow{k_3} \text{D}$ , derive the activation energy  $E_a$  for the disappearance of A in terms of the activation energies  $E_1$ ,  $E_2$ , and  $E_3$  for these three paths. (8%)
9. The dissociation reaction of ozone  $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$  follows the rate law  $-d[\text{O}_3]/dt = k[\text{O}_3]^2/[\text{O}_2]$ . It is observed that oxygen atoms are the intermediate species in this reaction. Suggest the mechanism that leads to the above rate law. (8%)
10. Use diagrams to explain the following terms. (6%)  
(a) Franck-Condon principle (b) predissociation

11. Name the point groups (Schoenflies) of the following molecules. (6%)  
(a)  $C_6H_6$  (b)  $C_6H_3Cl_3$  (1,3,5-trichlorobenzene) (c)  $C_3H_4$  ( $H_2C=C=CH_2$ )
12. Which vibrational level and which rotational level are the maximum populated levels in diatomic molecules with the vibrational frequency  $\nu$  (in Hz) and with the rotational constant  $B$  (in  $cm^{-1}$ ) in the room temperature? Explain your answers. (6%)
13. The wavefunction for a particle moving only between 0 and  $a$  in a one-dimension box is  $\Psi = (2/a)^{1/2}\sin(n\pi x)$ . Calculate the probability that the particle can be found in the first third (i.e. between  $x=0$  and  $x=a/3$ ) and middle third (i.e. between  $x=a/3$  and  $x=2a/3$ ) of the box for  $n=2$ ? ( $\int \sin^2(ax)dx = (x/2) - (1/4a)\sin(2ax)$ ) (6%)
14. How many spectral lines of the  $H_\alpha$  line ( $n=3 \rightarrow n=2$ ) in the atomic hydrogen spectra by (a) a low-resolution spectroscopy and (b) a high-resolution spectroscopy? (6%)
15. Explain in a diatomic system (a) why the vibrational spacing is becoming smaller when increasing the vibrational quantum number  $v$ , and (b) why the rotational spacing is becoming larger when increasing the rotational quantum number  $J$ ? (6%)
16. The pure rotational spectrum of  $^1H^{131}I$  consists of a series of lines separated by  $13.10\text{ cm}^{-1}$ . Calculate (a) the moment of inertia, and (b) the internuclear distance. (4%)