

1. The vapor pressure of diethyl ether is  $0.247 \times 10^5$  Pa at  $0^\circ\text{C}$  and  $1.228 \times 10^5$  Pa at  $40^\circ\text{C}$ .  
 (a) Calculate the enthalpy of vaporization  
 (b) At what temperature would diethyl ether boil at  $1.013 \times 10^5$  Pa pressure? (8%)
2. Calculate the heat of formation of propane gas from its elements (a) at constant pressure  
 (b) at constant volume, given that at  $298\text{K}$  and one bar pressure:  
 heat of combustion of propane =  $-2220$  kJ/mol; heat of formation of liquid water =  $-286$  kJ/mol; heat of formation of carbon dioxide =  $-393.5$  kJ/mol. (8%)
3. From the following data, calculate (a) the standard Gibbs energy change, and (b) the equilibrium constant at  $298\text{K}$  for the reaction  $2\text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) = 2\text{H}_2\text{O}(\text{l}) + 3\text{S}(\text{s})$
- | substances  | $\text{H}_2\text{S}(\text{g})$ | $\text{SO}_2(\text{g})$ | $\text{H}_2\text{O}(\text{l})$ | $\text{S}(\text{s})$ |
|---|--------------------------------|-------------------------|--------------------------------|----------------------|
| $\Delta H_f^\circ, 298\text{K}$ (kJ/mol)                | -22.2                          | -296.6                  | -285.9                         | 0                    |
| $S_{298\text{K}}$ ( $\text{J K}^{-1} \text{mol}^{-1}$ ) | 205.6                          | 247.9                   | 70.1                           | 31.9                 |
- (8%)
4. (a) Given  $dH = TdS + VdP$ , show that  $dS = \frac{C_p}{T}dT - nR \frac{dP}{P}$  for ideal gas. (3%)  
 (b) Calculate the entropy change when 2 moles of nitrogen (as an ideal gas) initially at  $300\text{K}$  and one bar pressure is heated to  $600\text{K}$  (i) at constant pressure (3%) and (ii) at constant volume. (4%)  $C_p = 27 \text{ J K}^{-1} \text{mol}^{-1}$  for nitrogen.
5. Calculate the root-mean-square speed at  $25^\circ\text{C}$  for dust particles of mass  $1.00 \times 10^{-10}$  g/particle suspended in air, assuming that the particle can be considered as a giant molecule. (5%)
6. The radii of a  $\text{H}_2$  molecule and an  $\text{I}_2$  molecule are  $0.109\text{nm}$  and  $0.188\text{nm}$ , respectively. If  $[\text{H}_2] = [\text{I}_2] = 0.0100\text{M}$ , calculate the number of collisions per  $\text{dm}^3$  per second between a  $\text{H}_2$  molecule and an  $\text{I}_2$  molecule at  $25^\circ\text{C}$ . (At. Wt. H: 1.0079, I: 126.905) (6%)
7. The second-order rate constant for the reaction  $\text{CH}_3\text{CH}_2\text{NO}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CHNO}_2$  is  $39.1 \text{ M}^{-1} \text{min}^{-1}$  at  $0^\circ\text{C}$ . (a) Derive the integrated rate equation (6%) (b) If initially  $[\text{CH}_3\text{CH}_2\text{NO}_2]_0 = 4.00 \times 10^{-3}\text{M}$ ,  $[\text{NaOH}]_0 = 5.00 \times 10^{-3}\text{M}$ , how long will it take for 50% of  $\text{CH}_3\text{CH}_2\text{NO}_2$  to react? (4%)
8. A possible mechanism for the reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  is given below:  
 $2\text{NO} \xrightarrow{k_1} \text{N}_2\text{O}_2$ ,  $\text{N}_2\text{O}_2 \xrightarrow{k_2} 2\text{NO}$ ,  $\text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{k_3} 2\text{NO}_2$   
 (a) Write the rate equation for  $d[\text{N}_2\text{O}_2]/dt$ . (4%)  
 (b) Apply the steady-state approximation to  $\text{N}_2\text{O}_2$  to derive the rate law for  $d[\text{NO}_2]/dt$ . (4%)
9. At  $25^\circ\text{C}$ , the electric conductivity of pure water is  $5.50 \times 10^{-6} \text{ } \Omega^{-1} \text{ m}^{-1}$  and the electric mobility of  $\text{OH}^-$  ion is  $2.06 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Calculate the electric mobility of  $\text{H}^+$  ion at  $25^\circ\text{C}$ . (5%)

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10. Molecule  $\text{CH}_2\text{FCl}$  has its  $\text{CH}_2$  group on the plane  $\sigma(xy)$ ,  
(a) write the  $3 \times 3$  matrices for all symmetry operations  $\hat{R}$  and draw the diagram of  $\text{CH}_2\text{FCl}$  showing the directions of  $XYZ$  axes (4%)  
(b) Is this molecule optical active? why? (2%)  
(c) Is this molecule polar? why? (2%)  
(d) does  $\text{CH}_2\text{FCl}$  show pure rotational spectrum? why? (2%)
11. For the atoms He and Li, (a) write the operators of their kinetic energies  
(b) write the operators of their potential energies (6%)
12. For the rotational spectrum of the rigid molecules of diatomic type:  
write their (a) energy levels, (b) term values, (c) selection rules, (d) moment of inertia. (8%)
13. For  $\text{H}_2^+$  (or  $\text{H}_A\text{H}_B^+$ ) molecular ion, draw the following diagrams along the internuclear axis  $R$ :  
(a) MO  $\psi_g = \sigma_g 1s$ ; (b) MO  $\psi_u = \sigma_u 1s$ ; (c)  $\psi_g^2$  and  $\psi_u^2$ ; (d)  $1s_{\text{H}_A}$ ,  
(the  $1s$  AO around proton  $\text{H}_A$ ). (8%)
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