1. (10%) Nitryl chloride (NO_2Cl) decomposes to nitrogen dioxide (NO_2) and chlorine gas (Cl_2) according to the following mechanism. Please determine the overall rate law expression.

$$(1)\ 2NO_2Cl(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClO_2(g) + N_2O(g) + ClO(g) \quad \text{(fast)}$$

$$(2)\ N_2O(g) + ClO_2(g) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO_2(g) + NOCl(g) \quad \text{(fast)}$$

$$(3)\ NOCl(g) + ClO(g) \xrightarrow{k_3} NO_2(g) + Cl_2(g) \quad \text{(slow)}$$

2. Human blood contains an enzyme (carbonic anhydrase) that catalyzes the formation of HCO_3^- and the hydration of CO_2 according to the following reaction:

$$CO_2 + 2H_2O \xrightarrow{\text{Carbonic anhydrase}} HCO_3^- + H_3O^+$$

When catalyzed by carbonic anhydrase, the reaction obeys Michaelis-Menten kinetics, and all elementary steps are shown here:

$$E + CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ECO_2 \qquad ECO_2 + 2H_2O \xrightarrow{k_2} E + HCO_3^- + H_3O^+$$

Its Michaelis-Menten constants are $K_M = 8\times10^{-5}$ mol/L and $k_2 = 6\times10^5$ s^{-1}.
(a) (5%) If the concentration of dissolved CO_2 (non-hydrated) is 0.5 M. What is the reaction order of non-hydrated CO_2?
(b) (5%) Calculate the maximum reaction rate of CO_2 if the total enzyme concentration is 5×10^{-6} M.
(c) (5%) Calculate the concentration of CO_2 at which the reaction rate reaches 30% of its maximum value calculated in part (b) where the total enzyme concentration is 5×10^{-6} M.

3. (10%) Determine the order of the reaction (a and b) in the rate equation, rate $= kC_A^aC_B^b$, given the following table:

Rate (mol/L·s)	0.04	0.12	0.36	1.08
$C_{A,0}$ (mol/L)	0.5	0.5	1	1
$C_{B,0}$ (mol/L)	0.5	1	0.5	1

4. (5%) The activation energy for the isomerization of cyclopropane to propene is 274 kJ/mol. By what factor does the rate of reaction increase as the temperature rises from 500 °C to 550 °C, assuming all else remains constant? (R = 8.314 J/mol·K).

5. (5%) Determine the average velocity of a H_2 molecule at 273 K if the average velocity of an O_2 molecule at this temperature is 500 ms^{-1}.

6. (5%) A mixture of 5.000×10^{-3} mol of H_2 and 1.000×10^{-2} mol of I_2 is placed in a 5.000 L container at 448 °C, and allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M. Calculate equilibrium constant (K_c) at 448 °C for the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

7. (9%) Consider an ideal refrigerator operating between 0 °C and 25 °C. The refrigerator is to cool the water initially at 25 °C and then produce 1.0 g of ice each second at 0 °C. How much work must be done? The molar heat of fusion of water is 6.0095 kJ/mol and the molar heat capacity is 75.3 J/K·mol.

8. (8%) Assume that graphite can be changed to diamond at 298 K by increasing the pressure to 1.5×10^4 bar. Given ΔH_m = 1895 J/mol and the volume change $\Delta V_m = -1.92 \times 10^{-3}$ L/mol for this process, determine the temperature at which graphite can be changed to diamond at 1 bar.

9. (8%) What is the entropy change for the system for producing 1-mol sample of artificial air consisting of 79% N_2 and 21% O_2?

10. (8%) The standard reduction potential for Ni^{2+}(aq) is -0.250 V. What is the half-cell potential at 25 °C if the activity of Ni^{2+} is 0.015?

11. (9%) Assume that C_6H_6 and $C_6H_5CH_3$ form ideal solutions, calculate ΔG, ΔH, and ΔS at 25 °C for the addition of 1.00 mol of C_6H_6 to an infinitely large amount sample of solution with the mole faction of C_6H_6 equal to 0.35. The vapor pressure of C_6H_6 at 25 °C is 0.153 bar.

12. (8%) A glass filter with a uniform pore diameter of 0.20 μm is filled with water at 20 °C. Estimate the pressure that would be necessary to blow the capillary water out of the pores of the filter. The surface tension of water at 20 °C is 72.75 dyne/cm.

試題隨卷繳回