

$$R = 0.082 \frac{\text{atm l}}{\text{mol K}} = 8.314 \frac{\text{J}}{\text{mol K}} \quad , \quad F = 96500 \frac{\text{C}}{\text{mol}} \quad , \quad H = 1.0 \quad , \quad C = 12.0 \quad , \quad N = 14.0 \quad , \quad O = 16.0 \quad , \quad \text{Cu} = 63.5$$

1. Suppose that a gas obeys the van der Waals equation  $(p + \frac{a}{\bar{V}^2})(\bar{V} - b) = RT$ , where  $a$  and  $b$

are constants not equal to zero. (a) Prove that  $\left(\frac{\partial U}{\partial \bar{V}}\right)_T = \frac{a}{\bar{V}^2}$  (b) Express the critical constants

in terms of  $a$  and  $b$ . (c) Express the coefficient of thermal expansion (d) One mole of a  $\text{CO}_2$  gas at 300K is compressed isothermally and reversibly from an initial volume of  $10 \text{ dm}^3$  to a final volume of  $0.2 \text{ dm}^3$ . The constants of van der Waals are  $a = 3.64 \times 10^{-1} \text{ Pa m}^6 \text{ mole}^{-2}$  and  $b = 0.427 \times 10^{-4} \text{ m}^3 \text{ mole}^{-1}$ . Calculate the work done on the system. (40%)

2. 56 g of nitrogen gas at 400 K is expand adiabatically at against a constant pressure of 1.0 bar from 3.8 bar to 1.0 bar. Calculate the  $w$ 、 $q$ 、 $\Delta U$  and  $\Delta H$  for the system. Assume the nitrogen gas to be ideal with  $C_p = 28.40 + 0.22 \times 10^{-2} T$ , where the unit is  $C_p(\frac{\text{J}}{\text{mol K}})$  and  $T(\text{K})$ . (15%)

3. The voltage required to electrolyze certain solutions changes as the electrolysis proceeds because the concentration in the solution are changing. In an experiment, one litre of a 0.050 M solution of copper (II) bromide was electrolyzed until 2.858 g Cu was deposited. The theoretical minimum voltage  $E$  required 0.843 V to sustain the electrolysis reaction at the beginning of the experiment. Calculate the theoretical minimum voltage at the end of the experiment. (15%)

4. In organic chemistry it is a common procedure to separate a mixture of an organic liquid in water by adding a solvent to it. This is known as “extracting out.” The ternary system acetone-water-methyl isobutyl ketone (MIK) is shown in Fig. 5. A mixture containing 40 weight percent acetone and 60 weight percent water is contacted with an equal amount of MIK. What fraction of the acetone could be extracted if the mixture remains at equilibrium. (10%)

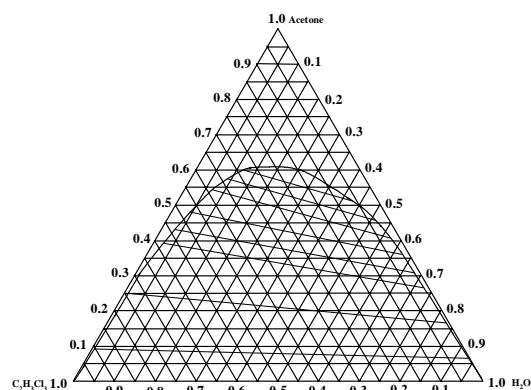
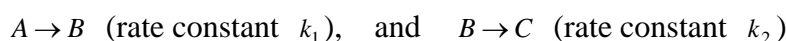


Figure 5

5. Consider the consecutive of first order irreversible reactions.



The initial concentration of  $A$  is  $C_{A0}$ . Neither  $B$  nor  $C$  is present initially.

(a) Derive the expressions for the variations of  $C_A$ ,  $C_B$  and  $C_C$  with time.

(b) At what time does the concentration of  $B$  reach a maximum? (20%)