

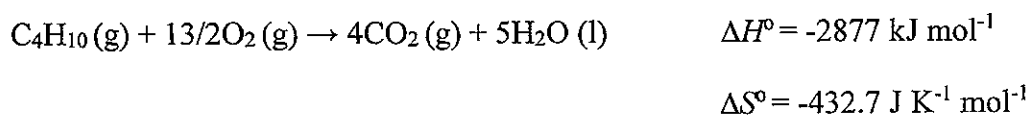
※ 考生請注意：本試題可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

1. Answer each of the following questions with Y (Yes) or N (No). (14%)

- (a) The internal energy of an isolated system is constant whether it undergoes a reversible or an irreversible process.
- (b) The entropy is conservative for any cyclic process whether it undergoes a reversible or an irreversible process.
- (c) Most substances contract on freezing, and for them the slope for the melting line is positive.
- (d) The dissolution of sodium chloride in water always causes an increase in entropy.
- (e) In a dilute solution, the activity coefficient of an ion species is increased with increasing the ionic strength.
- (f) The activation energy of a reaction is always positive.
- (g) Due to mixing, a simple gas reaction never goes to completion.

2. Two moles of a monatomic ideal gas is expanded isothermally and reversibly at 25 °C from 5 to 1 bar. Calculate  $q$ ,  $w$ ,  $\Delta H$ ,  $\Delta U$ ,  $\Delta G$ ,  $\Delta A$ , and  $\Delta S$  for the gas. (14%)

3. The following thermodynamic data apply to the complete oxidation of butane at 25 °C.



Suppose that a completely efficient fuel cell could be set up utilizing this reaction. Calculate (a) the maximum electrical work and (b) the standard emf of the cell. (14%)

4. Oxygen at pressures that are not too high obeys the van der Waals' equation

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT.$$

The constants  $a$  and  $b$  are  $0.1378 \text{ Pa m}^6 \text{ mol}^{-1}$ , and  $0.0318 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ , respectively.

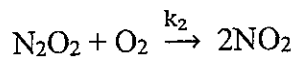
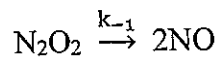
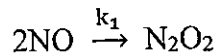
(a) Show that the fugacity  $f$  can be expressed as  $f = P \exp\left[\frac{P}{RT}\left(b - \frac{a}{RT}\right)\right]$  starting from

$$RT \ln \frac{f}{P} = \int_0^P \left(V_m - \frac{RT}{P}\right) dP. \quad (8\%)$$

(b) Calculate  $\Delta G$  at 25°C if the pressure is raised from 1 bar to 5 bar. (6%)

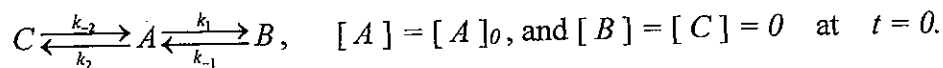
5. The standard Gibbs energy of formation of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are  $51.31$  and  $97.89 \text{ kJ mol}^{-1}$ , respectively, at  $298.15 \text{ K}$ . For the reaction  $\text{N}_2\text{O}_4(\text{g}) = 2\text{NO}_2(\text{g})$ , calculate the equilibrium constant  $K_P$  and Gibbs energy change  $\Delta G^\circ$ . If only one mole of  $\text{NO}_2$  exists in the reaction system initially, and the total pressure is  $2 \text{ bar}$ , what is the extent of reaction in equilibrium? (15%)

6. The reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  is believed to occur by the mechanism:



Assume  $\text{N}_2\text{O}_2$  to be in a steady state and derive the rate equation. Under what conditions does the rate equation reduce to second-order kinetics in  $\text{NO}$  and first-order kinetics in  $\text{O}_2$ ? (15%)

7. For the parallel reversible first-order reactions



The equilibrium constants for the formation of  $B$  and  $C$  from  $A$  are given by

$$K_1 = \frac{k_1}{k_{-1}} \quad \text{and} \quad K_2 = \frac{k_2}{k_{-2}}.$$

(a) Derive the equilibrium concentrations of  $A$ ,  $B$ , and  $C$ . (6%)

(b) If  $k_1 = 1$ ,  $k_{-1} = 0.01$ ,  $k_2 = 0.1$ , and  $k_{-2} = 0.0005 \text{ s}^{-1}$ , show that  $B$  is formed initially 10 times faster than  $C$  (i.e.,  $[B] = 10[C]$ ) and,  $C$  is twice of  $B$  (i.e.,  $[C] = 2[B]$ ) at infinite time. (8%)