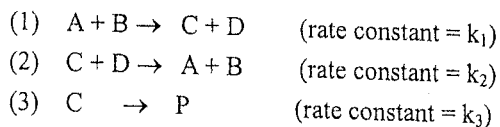


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1. (a) Draw a plot of chemical potential versus temperature of the solid, liquid, and gas phases for a pure substance. (2pts)
 - (b) What is the meaning of the slope in plot (a) of each phase. (1 pt)
 - (c) What criterion is used in deciding where a phase transition will take place? (1 pt)
 - (d) For an aqueous solution, why the boiling point increases and the melting point decreases. Please use the plot (a) to answer the question and give your reason. (2 pts)
 - (e) Use plot (a) to explain what will the melting points change for (1) water and (2) CO₂ if a higher pressure is applied, respectively? (hint: $(\frac{\partial \mu}{\partial P})_T = V_m$) (2 pts)
 - (f) Draw the diagram of pressure vs. temperature for (1) water and (2) CO₂ and use Clapeyron equation to provide thermodynamic explanations for the observations in (d). (4 pts)
- (hint: Clapeyron equation, $\frac{dP}{dT} = \frac{\Delta H_{fus}}{T\Delta V_m}$)

2. Consider the following complex mechanism:



- (a) Write down differential rate equations for species A, C, and D. (3 pts)
- (b) Determine the overall reaction by ignoring the equilibrium step (i.e., equation (2)) (1 pt)
- (c) Using a stationary-state approximation for the intermediate, show that the rate of production of product P is first order with respect to both A and B, provided that $k_3 \gg k_2[D]$ (3 pts)

3. Assume one mole of oxygen gas can be described by the state equation:

$$PV(1 - \beta P) = RT,$$

where β is a function of temperature only. Answer the following questions:

- (a) Derive an expression for the compression factor $Z = 1 + aP + bP^2 + \dots$, i.e., Virial series in terms of pressure, assuming βP is very small ($\ll 1$). What is the value of a and b, respectively. (2 pts)
- (b) Obtain the analytic function of fugacity as a function of β and P.

(hint: $\ln f = \ln P + \frac{1}{RT} \int_0^P [V_m - \frac{RT}{P}] dP$) (4 pts)

- (c) Initially at 373 K 1 mole of oxygen undergoes Joule-Thomson expansion from 100 atm to 1 atm. Given that $C_{p,m} = 5R/2$, Joule-Thomson coefficient $\mu = 0.21 \text{ K atm}^{-1}$, $\beta = -0.5$, and that these are constants over the temperature range involved, calculate ΔT and ΔS for the oxygen gas. (7 pts)

(hint: $(\frac{\partial T}{\partial P})_H = \mu$, $(\frac{\partial S}{\partial T})_P = \frac{C_p}{T}$, $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$, $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$, $\ln(352.2/373) = -0.06$, $\ln(1/100) = -4.6$, $\ln(51/1.5) = 3.53$)

4. The L_+ and L_- are raising and lowering operators for angular momentum, respectively, and are defined by $L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$, where L_x and L_y are the x and y components of angular momentum operator,

注：背面有試題

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respectively. If the eigenstate of the system is denoted $|l, m\rangle$, calculate the following based on

$$L_z|l, m\rangle = m\hbar|l, m\rangle, L^2|l, m\rangle = l(l+1)\hbar^2|l, m\rangle, [L_x, L_y] = i\hbar L_z, [L_y, L_z] = i\hbar L_x, \text{ and } [L_z, L_x] = i\hbar L_y$$

(a) show $[L_+, L_z] = aL_+$, what is the value of a ? (2 pts)

(b) show $[L_+, L_-] = bL_z$, what is the value of b ? (4 pts)

5. The operator e^A has a meaning if it is expanded as a power series:

$$e^A = \sum_n \left(\frac{1}{n!}\right) A^n.$$

If the following relation is valid:

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!}[A, [A, B]] + \frac{1}{3!}[A, [A, [A, B]]] + \dots$$

where A and B are two operators, and $[A, B]$ is the commutator between the operators A and B .

(a) If $\exp(-i\omega L_z) L_x \exp(i\omega L_z) = C$, where ω is a constant and L_z is an operator, what is C ? Give your reason. (2 pts)

(b) Express $\exp(-i\omega L_z) L_y \exp(i\omega L_z)$ as a combination of cosine and sine functions, where L_z and L_y are angular momentum operators as defined above. (4 pts)

(hint: $\sin\theta = \theta - \theta^3/3! + \theta^5/5! - \theta^7/7! + \dots$; $\cos\theta = 1 - \theta^2/2! + \theta^4/4! - \theta^6/6! + \dots$)

6. (a) Prove that the spin function:

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

, where 1 and 2 represent the electrons, is anti-symmetric with respect to electron exchange. (2 pts)

(b) For the $1s2s$ configuration of He, two spatial functions can be constructed from the products: $1s(1)2s(2)$ and $2s(1)1s(2)$. To account for the Pauli principle, what will be the wavefunctions (including both spatial functions and spin functions) for singlet and triplet states? (4 pts)

7. Define following terms: (each 4 pts) (total 20 pts)

- Surrogate and internal standard
- Student's t-test and F-test in data comparison
- Alkalinity and acidity
- Junction potential
- Nernst equation

8. For a reversed-phase separation, predict and explain the order of elution of n -hexane, n -hexanol and benzene. (10 pts)

9. Describe electron-impact ionization and chemical ionization in ion sources of mass spectrometer, and how do the mass spectra differ from each other? (10 pts)

10. What is electroosmosis? And explain how neutral molecules can be separated by micellar electrokinetic chromatography (MEKC). (10 pts)