

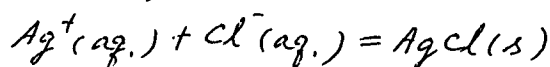
1. The coefficient of cubic expansion α is defined by $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ and the isothermal compressibility K is defined by $K = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ calculate these quantities for a gas for which $P(V-b) = RT$ (8%)

2. Compute the entropy difference between 1 mole of solid ice at -10°C , and 1 mole of water vapor at 120°C and 1.01325 bar. The heat of fusion is 330 J g^{-1} , and heat of vaporization is 2259 J g^{-1}

	ice	water	steam
average specific heat ($\text{JK}^{-1} \text{g}^{-1}$)	2.05	4.182	1.68

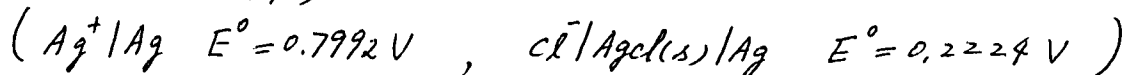
(atomic mass: $\text{H}=1, \text{O}=16$) (8%)

3. Devise (設計) a cell for which the reaction is



(a) What is the standard electromotive force of the cell at 25°C ?

(b) Calculate ΔG° for the cell reaction. (c) What is the equilibrium constant for the reaction? (d) what is the solubility of $\text{AgCl}(\text{s})$ in water? (9%)



4. In what proportion of binary collisions does the kinetic energy along the line of centers exceed 100 kJ at 300°K , 600°K , 1200°K (5%)

5. Consider the reaction mechanism: $A + B \xrightleftharpoons[k_{-1}]{k_1} X + B$
 $X \xrightarrow{k_2} C + D$

(a) Write chemical rate equation for $[A]$ and $[X]$ (4%)

(b) Employing the steady-state approximation, show that an effective rate equation for $[A]$ is $\frac{d[A]}{dt} = -k_{\text{eff}} [A][B]$ and give an expression for k_{eff} in

terms of k_1, k_{-1}, k_2 and $[B]$. Also, specify the k_{eff} as $[B] \rightarrow \infty$. (6%)

6. The compound $\text{CH}_3\text{-O-N=O}$ undergoes a cis-trans isomerization by internal rotation about the O-N bond. The half-life of the first-order conversion of the cis form was measured by NMR

techniques as 10^{-6} s at 298°K . Assuming $\Delta S^\ddagger = 0$ for this reaction, calculate ΔH^\ddagger and the height of the barrier to rotation. (10%)

7. If \hat{S} is the spin operator of the electron (a) write the eigen-value equations for the operators \hat{S}^2 and \hat{S}_z (3%) (b) find the eigen-values and eigen-functions of \hat{S}^2 and \hat{S}_z (3%). (c) find the expectation value $\langle \hat{S}^2 \rangle$ for any eigen-function. (3%)

8. The particle in a one-dimensional box of length a has the wavefunctions $\Psi_n = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)$. Evaluate and also write the meanings of the following integrals:

(a) $\frac{2}{a} \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx$ (2%) (b) $\frac{2}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{3\pi x}{a}\right) dx$ (2%)

(c) $\frac{2}{a} \int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx$ (2%)

9. Molecules CHClBr , CH_2FCl , CH_2Cl_2 (a) write all symmetry operators they have and what kinds of symmetry groups they belong? (use Schoenflies notation) (5%) (b) which molecule is optical active and which one is polar? (5%)

10. The gaseous reaction $\frac{1}{2}A_2 + \frac{1}{2}B_2 \rightarrow AB$ consists initially of 0.5 mole of A_2 and 0.5 mol of B_2 at 500°K and a total pressure of 1 atm. (a) express $\Delta G = G_{\text{mixture}} - 0.5\mu_{A_2}^\circ - 0.5\mu_{B_2}^\circ$ as a function of number of moles of AB , n_{AB} . Here, μ_i is the chemical potential of component i , and G is free energy. (7%)

(b) minimize ΔG to obtain the equilibrium value of n_{AB} . (4%)

11. The probability that a single molecule is in the n -th energy state is given by $P_n = \frac{\exp(-E_n/kT)}{q}$, where

$$q = \sum_{n=0}^{\infty} \exp(-E_n/kT) \text{ and } E_n = n k \alpha.$$

(a) Derive q as a function of α and T . (3%) (b) Express the average energy $\langle E \rangle$ in terms of $\left(\frac{\partial \ln q}{\partial T}\right)$ (3%)

(c) calculate $\langle E \rangle$ in the limit of $(\alpha/T) \ll 1$. (5%)

(d) What fraction of molecule is in the $n=2$ state at $T = \frac{\alpha}{2}$? (3%)