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 ($JK^{-1}g^{-1}$)	2.05	4.182	1.68

(atomic mass: H=1, O=16) (8%)

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

$$Ag^+(aq.) + Cl^-(aq.) = AgCl(s)$$

(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 AgCl(s) in water? (9%)

($Ag^+|Ag$ $E^\circ = 0.7992\,V$, $Cl^-|AgCl(s)|Ag$ $E^\circ = 0.2224\,V$)

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

5. Consider the reaction mechanism: $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + B$

$$X \xrightarrow{k_2} C + D$$

(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 $\frac{d[A]}{dt} = -k_{eff.}[A][B]$ and give an expression for $k_{eff.}$ in terms of k_1, k_{-1}, k_2 and [B]. Also, specify the $k_{eff.}$ as $[B] \to \infty$. (6%) (6%) 045

6. The compound $CH_3-O-N=O$ 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 $\Delta H^{\ddagger}$ 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 $\psi_n = (\frac{2}{a})^{\frac{1}{2}} \sin(\frac{n\pi x}{a})$. Evaluate and also write the meanings of the following integrals:

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

(c) $\frac{2}{a}\int_0^a x\sin^2(\frac{\pi x}{a})dx$ (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 $\frac{1}{2}A_2 + \frac{1}{2}B_2 \longrightarrow AB$ 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 $\Delta G = G_{mixture} - 0.5\mu^{\circ}_{A_2} - 0.5\mu^{\circ}_{B_2}$ 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 $P_n = [\exp(-\varepsilon_n/kT)]/q$, where $q = \sum_{n=0}^{\infty} \exp(-\varepsilon_n/kT)$ and $\varepsilon_n = nk\Theta$.

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

(c) calculate $\langle \varepsilon \rangle$ in the limit of $(\Theta/T) << 1$. (5%)

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