1. From the following data, Calculate the standard enthalpy of sublimation of ice at -50°C. (in $J\,g^{-1}$). Mean heat capacity of ice = 1.975 $J K^{-1} g^{-1}$. Mean heat capacity of liquid water = 4.185 $J K^{-1} g^{-1}$. Mean heat capacity of water vapour = 1.860 $J K^{-1} g^{-1}$. Enthalpy of fusion of ice at 0°C = 333.5 $J g^{-1}$. Enthalpy of evaporation of water at 100°C = 2255.2 $J g^{-1}$. (6%)

2. An ideal monatomic gas initially at 298 K and a pressure of 5 atm is expanded to a final pressure of 1 atm: (a) isothermally and reversibly; (b) rapid isothermal expansion against a constant pressure of 1 atm. Calculate for each of these expansion (i) the work done, w (ii) q. (iii) ΔH. ((i) 4% (ii) 2% (iii) 2%)

3. pure benzene freezes at 5.40°C and a solution of 0.223 g of phenylacetic acid ($C_6H_5CH_2COOH$) in 4.4 g of benzene freezes at 4.47°C. The molal freezing point lowering constant of benzene is 5.12 K $molal^{-1}$. (a) Calculate the apparent relative molecular mass of phenylacetic acid. (6%) (b) Comment (註釋) on the result, the molecular mass of $C_6H_5CH_2COOH$ is 136. (2%)

4. For the equilibrium $NH_4Cl_{(s)} = HCl_{(g)} + NH_{3(g)}$. Estimate the temperature at which the pressure due to the dissociation of solid ammonium chloride reaches 1 atm, given the following values at 298 K: (8%)

	ΔH_f^o ($KJ\,mol^{-1}$)	ΔG_f^o ($KJ\,mol^{-1}$)
$NH_4Cl_{(s)}$	−315.4	−203.9
$HCl_{(g)}$	−92.3	−95.3
$NH_{3(g)}$	−46.2	−16.6

5. Given $U = NkT^2 \frac{\partial \ln Q}{\partial T}$ and $S = Nk\{\ln\frac{Q}{N} + T\frac{\partial \ln Q}{\partial T} + 1\}$, where Q is partition function. Show that $G = -NkT\ln\frac{Q}{N}$. (5%)

6. The microwave spectrum of HI gives a series of lines whose separation is 12.86 cm^{-1}. Calculate the moment of inertia and the internuclear distance of the molecule. (atomic mass: H = 1. I = 127) (6%)

7. (a) Construct the operator multiplication table for the point group C_{2h}. (4%) (b) Give the matrix representation of the C_{2h} group which transform a point $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ into $\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$. (4%)

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8. For a particle in a cubic box of length l on each side, (a) Calculate the first three energy levels. (b) what is the degeneracy for each level? (c) Write the wave-functions corresponding to these levels. (9%)

9. (a) Write the Hamiltonian operator for Li atom and draw the diagram to show r_i and r_{ij}. (b) Write the Slater's determinant type wavefunction for Li atom. and what are its eigenvalues M_L and M_S. (10%)

10. Diamond has a face-centered cubic structure with two atoms per lattice point. Calculate the length of the side of the unit cell. (density = 3.51 g/cm^3) (5%)

11. Derive the spacings corresponding to the (hkl) reflections that may appear on a powder diagram of a primitive cubic crystal. The length of the side of unit cell is a. (5%)

12. At 298°C, CH_3NNCH_3 decomposes mainly by

$$CH_3NNCH_3(g) \rightarrow C_2H_6(g) + N_2(g)$$

The first-order rate constant is $2.50\times10^{-4}\,s^{-1}$. What will be the partial pressures of CH_3NNCH_3 and N_2 when CH_3NNCH_3 initially at 200 torr decomposes for 30 min? (5%)

13. A proposed mechanism for a Br^--catalyzed reaction

$$H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow[H_2O]{Br^-} C_6H_5N_2^+ + 2H_2O$$ is given below

$$H^+ + HNO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2NO_2^+ \quad \text{(rapid equilibrium)}$$

$$H_2NO_2^+ + Br^- \xrightarrow{k_2} ONBr + H_2O \quad \text{(slow)}$$

$$ONBr + C_6H_5NH_2 \xrightarrow{k_3} C_6H_5N_2^+ + H_2O + Br^- \quad \text{(fast)}$$

Derive the rate law for this reaction. (6%)

14. For O_2 (radius = 0.120 nm) gas at one bar pressure at 25°C,

(a) Calculate the number of collisions per second undergone by a single O_2 molecule. (5%)

(b) What is the effect on number of collisions of doubling the absolute temperature at constant pressure? (3%)

(c) What is the mean free path? (3%)