

1. (a) Which symmetry operations and symmetry elements the molecules H_2CO has? What symmetry group H_2CO belong to?
(b) Write the matrix representations of these symmetry operations of H_2CO .
(c) Is this matrix representation reducible? If not, please reduce it into irreducible representations, and write down the characters of these irreducible representation. (10%)

2. (a) For three dimensional rotation of a particle of mass m , write the classical rotation energy and its quantum operator.
(b) Write the definition of the moment of inertia for a polyatomic molecule rotating around z -axis.
(c) Write the quantum energy levels for the following types of molecules: (i) spherical top; (ii) linear molecule. What is the difference between them?
(d) Give some examples of spherical top and linear molecules. (15%)

3. (a) Draw the normal modes of vibrations for the molecules CO_2 and H_2CO .
(b) Assign the proper symmetry species for these normal mode vibrations.
(c) Compare the magnitudes of the frequencies of these normal mode vibrations. (10%)

4. An ideal gas mixture consists of N , N_2 , and N_2O , which is linear. As the temperature is high enough such that all various molecular motions are highly excited, the translational, vibrational, and rotational motion contribution to heat capacity of the mixture, C_v , is found to be $9R$, $7R$, and $4R$, respectively. Find the mole fraction of N_2 and N_2O . (8%)

5. A possible equation of state for a liquid is

$$V = V_0(1 + \alpha T - \beta(P-1))$$

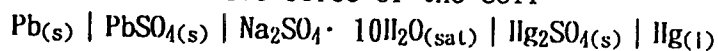
in which P is the pressure in atmospheres, T is the temperature in centigrade ($^{\circ}\text{C}$), V_0 is the volume at 0°C and 1 atm, and α and β are constants.

Prove that (a) $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$, (b) $\left(\frac{\partial H}{\partial P}\right)_T = V_0[1 - 273\alpha - \beta(P-1)]$.

Calculate ΔS and ΔH in cal/deg and cal when 1 mole of water is compressed at 20°C from 1 to 25 atm.

(for water near 20°C and 1 atm, $\alpha = 2.1 \times 10^{-4} \text{ deg}^{-1}$ and $\beta = 49 \times 10^{-6} \text{ atm}^{-1}$) (16%)

6. The electromotive force of the cell



is 0.9647 V at 25°C . The temperature coefficient is $1.74 \times 10^{-4} \text{ VK}^{-1}$.

(a) What is the cell reaction?

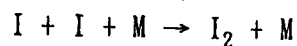
(b) What are values of $\Delta_r G$, $\Delta_r H$? (11%)

7. (a) Opposite to the behavior of a liquid, a gas becomes more viscous (higher viscosity) when the temperature is raised. Explain.

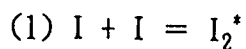
(b) Explain the differences between ΔG^{\ddagger} (activation free energy and E_a (energy of activation) of reaction.

(c) Explain why interfacial tensions between two liquid phases are generally smaller in magnitude than surface tensions between liquid and vapor phases. (15%)

8. The gas-phase recombination of iodine atoms proceeds in the presence of a second substance, M :



Two mechanisms are proposed. The first is



where I_2^* represents a high-energy molecule. The second mechanism is

- (1) $I + M + M \rightarrow IM + M$
- (2) $IM + I \rightarrow I_2 + M$

where IM represents a loosely bound molecules that is not necessarily capable of permanent existence.

- (a) Find the rate differential for each mechanism, using the rate-limiting step approximation and assuming that the second step in each mechanism is rate-limiting.
- (b) It is found that the activation energy for the overall reaction is negative. If M is argon, $k=8.3 \times 10^{33} \text{ cm}^6\text{s}^{-1}$ at 300 K, and $k=1.3 \times 10^{33} \text{ cm}^6\text{s}^{-1}$ at 1300 K. Find the value of the activation energy.
- (c) Explain the fact that the activation energy is negative. (15%)