1. (12%) The equation of state for a van der Waals gas is $P = \frac{RT}{V - nb} - a\frac{n^2}{V^2}$. The gas is expanded isothermally from V_1 to V_2 at temperature T. Determine the change of Helmholtz energy ΔA for the process. Determine the change of internal energy ΔU for the process.

2. (6%) Over narrow ranges of temperature and pressure, the differential expression for the volume of a fluid as a function of temperature and pressure can be integrated to obtain $V = Ke^{\beta T}e^{-\kappa P}$. Here, β and κ are thermal expansion coefficient and isothermal compressibility, respectively, and K is a constant. Show that V is a state function.

3. (8%) The Rice-Herzfeld mechanism for the thermal decomposition of acetaldehyde (CH_3CHO (g)) is

$$CH_3CHO\ (g) \xrightarrow{k1} CH_3\bullet\ (g) + CHO\bullet\ (g)$$

$$CH_3\bullet\ (g) + CH_3CHO\ (g) \xrightarrow{k2} CH_4\ (g) + CH_2CHO\bullet\ (g)$$

$$CH_2CHO\bullet\ (g) \xrightarrow{k3} CO\ (g) + CH_3\bullet\ (g)$$

$$CH_3\bullet\ (g) + CH_3\bullet\ (g) \xrightarrow{k4} C_2H_6\ (g)$$

Using the steady-state approximation, determine the rate of methane (CH_4 (g)) formation. Elaborate the required conditions to apply the steady-state approximation in this mechanism.

4. (8%) Consider the collision-induced dissociation of $N_2O_5(g)$ via following mechanism:

$$N_2O_5(g) + N_2O_5(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_5(g)^* + N_2O_5(g)$$

$$N_2O_5(g)^* \xrightarrow{k_2} NO_2(g) + NO_3(g)$$

The asterisk (*) in the first reaction indicates that the reactant is activated through collision. Experimentally it is found that the reaction can be either first or second order in $N_2O_5(g)$ depending on the concentration of this species. Derive a rate law expression for this reaction consistent with this observation. And explain why the reaction can be either first or second order in $N_2O_5(g)$ experimentally and describe the assumptions in deriving the rate law.

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5. (8%) Give the number of independent intensive variables for the N_2, H_2, and NH_3 in a one-phase system, with each substance added separately and allowed to come to chemical equilibrium with catalyst. What degrees of freedom might be chosen for this equilibrium calculation?

6. (8%) (Multiple Choice) For a reversible first order reaction

$A \rightarrow B$, k_1,

$B \rightarrow A$, k_2,

$k_1 = 10^{-2}\ s^{-1}$ and $[B]_{eq}/[A]_{eq} = 4$. If the initial conditions, $[A]_0 = 0.01$ M and $[B]_0 = 0$, what will be the approximate ratio of concentrations $[B]/[A]_0$ after 30s?

(A) 0.25　(B) 0.50　(C) 0.75　(D) 1.00.

7. (14%) For (1) O_2, and (2) N_2H_4 hydrazine molecules, determine (A) the point group, (B) the term symbol of ground state, (C) whether it has permanent dipole moment, (D) whether it is optically active, (E) whether it is microwave spectrum active.

8. (14%) Particle in a box (PIAB) is the simplest system to be solved exactly for the Schrödinger equation.

(A) Solve the one-dimensional PIAB with the length of box l and mass of particle m.

(B) Extend the result of (A) into two- and three-dimensional PIAB systems.

(C) What are the applications of one-, two-, and three-dimensional PIAB.

9. (12%) Some simple quantum mechanical systems can be solved exactly, in addition to PIAB name three of them and for each (A) write the Schrödinger equation, (B) describe how it is applied to molecules, (C) describe the dependence of energy levels with its quantum number and the degeneracy of energy levels.

10. (10%) The partition function is the fundamental concept of statistical thermodynamics.

(2%) (1) For an ideal gas, define the molar partition function, Q, by partition function of one particle, q.

(5%) (2) What is the partition function of a molecule, q? Express it with degeneracy and energy level. (You do not have to do the summation or integration.)

(3%) (3) How do you apply partition functions to obtain thermodynamic data?

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