R_H (Rydberg constant for H atom) = 109677 cm⁻¹
R(gas constant) = 8.314 J K⁻¹ mol⁻¹

\[ RT \ln 10 / F = 59.16 \text{meV} \] (R is gas constant, T=25°C, and F is Faraday constant)

Properties of gases and Thermodynamics

I (5%) Consider a gas that obey the equation of state

\[ P = \frac{R T e^{-\frac{\nu R T}{V_m}}}{V_m^a - b} \]

where \( a \) and \( b \) are constant and \( V_m \) is the molar volume. Determine the second and third virial coefficients for this gas as a function of \( a, b, R \) and \( T \).

II (15%) One mole of a non-ideal gas obeys the equation of state

\[ V_m = RT \left( \frac{1}{P} + \frac{a}{P^2} \right) \]

where \( a \) is a function of temperature only. If the gas is compressed from pressure \( P_1 \) to pressure \( P_2 \) isothermally, obtain an expression giving the entropy change for the process in terms of \( P_1, P_2, a \) and \( da/dT \).

(Hint: Prove first the equation \( T dS = C_P dT - T \left( \frac{\partial V}{\partial T} \right)_P dP \).)

Chemical equilibrium and Electrochemistry

III In the gas-phase reaction \( 2A + B \rightarrow 3C + 2D \), it was found that when 1.0 mole of A, 2.0 mole of B, and 1.0 mole of C were mixed and allowed to come to equilibrium at 25°C, the resulting mixture contained 0.5 mole of D at a total pressure of 1.0 bar.

(A)(5%) What is the standard reaction Gibb energy?

(B)(5%) If the equilibrium constant of the reaction is doubled when the temperature is increased by 10 °C at 25 °C, what is the standard reaction enthalpy?

Express your answer in terms of \( R \) (gas constant)

IV Consider the cell \( \text{Pt}|\text{H}_2(\text{g})|\text{HCl}(\text{aq})|\text{AgCl(s)}|\text{Ag(s)} \), for the cell reaction is

\[ \text{AgCl(s)} + 0.5 \text{H}_2(\text{g}) \rightarrow \text{Ag(s)} + \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \]

(A) (5%) At 25°C and a molality of HCl of 0.01 mol kg⁻¹, the cell potential is 0.4658 V.

What is the standard potential for the half reaction \( \text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq}) \).

(B) (5%) Use the value obtained in (A) to estimate the pH of the electrolyte solution as the zero-current potential of the cell is 0.32 V at 25°C.
Kinetics of chemical reactions

V (10%) Compound A simultaneously undergoes a pseudo first-order reaction and a second-order reaction, so that the mechanism is

$$ A \rightarrow P_1 \quad \text{and} \quad A + A \rightarrow P_2 $$

The rate constants for the formation of $P_1$ and $P_2$ are $k_1$ and $k_2$, respectively.

Obtain the integrated rate expression of [A] as a function of time.

VI (10%) Derive the rate law for the decomposition of ozone in the reaction

$$ 2O_3(g) \rightarrow 3O_2(g) $$
on the basis of the following mechanism:

1. $$ O_3 \rightarrow O_2 + O \quad k_1 $$
2. $$ O_2 + O \rightarrow O_3 \quad k'_1 $$
3. $$ O + O_3 \rightarrow 2O_2 \quad k_2 $$

Atomic structure and Spectroscopy

VII If the mass of the electron becomes double and both charges of electron and proton become one half of their values,

(A)(5%) What is the ground state energy of the "hydrogen" atom?
(B)(5%) What is the average radius of the atom in the ground state?
(C)(10%) What is the wavelength of the emitted radiation as the electron decays from the first excited state?

Statistical thermodynamics

VIII If a heteronuclear diatomic molecule can be considered as a linear rigid rotor whose Hamiltonian is expressed as

$$ H_{rot} = \frac{\tilde{J}^2}{2I}, $$

where $\tilde{J}$ and $I$ are the angular momentum and the moment of inertia of the rotor, respectively.

(A) (5%) What is the rotational partition function in quantum mechanism?
(B) (5%) What is the expression for the average rotational energy of the diatomic molecule at temperature $T$?
(C) (5%) What is the average rotational energy at the high-temperature limit?
(D) (5%) What is the rotational entropy at sufficiently high temperatures?