科目：物理化學(1004)

校系所組：中央大學化學學系
交通大學應用化學系（甲組）
清華大學化學系
清華大學材料科學工程學系（丙組）

1. (15 %) Calculate the work, heat, energy, enthalpy, entropy, and Gibbs free energy of one mole ideal gas that undergoes reversible isothermal compression from V to V/2.

2. (10 %) Starting with the virial equation for a real gas in the following form

$$PV_m = RT \times (1 + \frac{B(T)}{V_m})$$

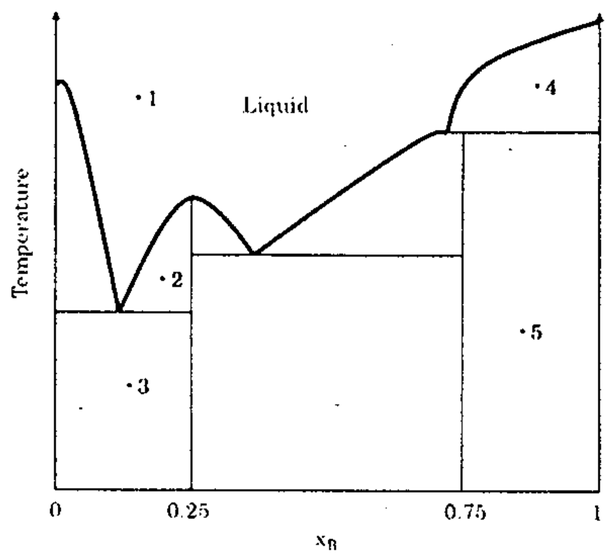
V_m and B(T) represent the molar volume and temperature–dependent virial coefficient, respectively. If the sample undergoes isothermal expansion from V to 2V,

(1) Derive "X" and "Y" for $\left(\frac{\partial H}{\partial V}\right)_T = X\left(\frac{\partial P}{\partial V}\right)_T + Y\left(\frac{\partial P}{\partial T}\right)_V$. (4 %)

(2) Derive $\left(\frac{\partial H}{\partial V}\right)_T$ in terms of B, T, V, R, and $\frac{\partial B}{\partial T}$. (3 %)

(3) Derive the molar enthalpy change (ΔH_m). (3 %)

3. (9 %) A phase diagram for the binary alloy A+B is shown below.



x_B represents the molar fraction of component B. Please answer the questions (a)-(c).

Point	Composition
1	Liquid
2	(a)
3	(b)
4	(c)
5	Pure $B_{(s)}$ + $AB_{3(s)}$

注意：背面有試題

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4. (8%) A hypothetical chain reaction leads to a complicated rate law.

$$A_2 + B_2 \rightarrow 2\,AB \qquad \frac{d[AB]}{dt} = \frac{k_1[A_2][B_2]^{3/2}}{[B_2]+k_2[AB]}$$

The reaction mechanism is defined as a proposed set of elementary steps:

Initiation: $B_2 + M \xrightarrow{k_a} B + B + M \quad \frac{1}{2}\frac{d[B]}{dt} = k_a[M][B_2]$

Propagation: $B + A_2 \xrightarrow{k_b} AB + A \quad \frac{d[AB]}{dt} = k_b[A_2][B]$

$A + B_2 \xrightarrow{k_c} AB + B \quad \frac{d[AB]}{dt} = k_c[A][B_2]$

Inhibition: $A + AB \xrightarrow{k_d} A_2 + B \quad \frac{d[AB]}{dt} = -k_d[A][AB]$

Termination: $B + B + M \xrightarrow{k_e} B_2 + M \quad \frac{1}{2}\frac{d[B]}{dt} = -k_e[B]^2[M]$

Derive k_1 and k_2 in terms of k_a, k_b, k_c, k_d, and k_e when applying the steady-state approximation on d[A]/dt and d[B]/dt.

5. (8%) A reversible reaction is expressed in the following form

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B.$$

The initial concentrations of A and B are $[A]_0$ and 0, respectively. k_f and k_r represent the first-order rate coefficients of the forward and backward reactions, respectively.

(1) Derive the time dependence of [A] and [B]. (4 %)

(2) Derive the concentrations of [A] and [B] at equilibrium. (4%)

6. (10%) Explain the method of using half-life times to derive the order of a chemical reaction for the 0-, 1st-, and 2nd-order reaction. Please write down the proper equation to describe your method.

7. (5%) For the gas-phase reaction $H_2 + Br_2 \rightarrow 2HBr$ at 373.15 K, the rate constant is equal to 8.75×10^{-15} L mol^{-1}s^{-1}. At 473.15 K it is equal to 9.53×10^{-15} L mol^{-1}s^{-1}. Show all the details for how to find the value of the activation energy and of the preexponential factor.

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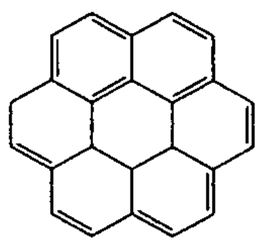
8. (7 %) For (1) B_2, and (2)H_2O_2 molecules, determine (a) the point group, (b) the term symbol of ground state, (c) whether it has a permanent dipole moment, (d) whether it is optically active, (e) whether it is microwave spectrum active.

9. (20%) The partition function is the fundamental concept of statistical thermodynamics.
   (1) For an ideal gas, define the molar partition function, Q, by partition function of one partical, q.
   (2) The Hamiltonian of an individual molecule can be simplified based on Born-Oppenheimer approximation. What is the Born-Oppenheimer approximation?
   (3) Describe the result of the simplified Hamiltonian based on Born-Oppenheimer approximation.
   (4) For each part of (3) state a proper model to botain the eigenvalues, *i.e.*, energy levles.
   (5) 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.)

10. (8%) The molecule cocronen



is quite often used as a very simple modle of graphene. Show how you will calcualte the frequency of the π electron transition.The carbon-carbon distance is 1.33Å.