Problem1(1)

(a) An ideal gas is compressed isothermally in a cylinder from 1 atm to 2 atm. Find the changes in
  (i) (1%) temperature
  (ii) (1%) internal energy,
  (iii) (1%) enthalpy of the gas; and
  (iv) (1%) heat exchange with the surrounding,
  (v) (1%) PV work required.

(b) An stream of ideal gas (Cp= 30 kJ/(kmol-K)) expand through an adiabatic valve from 2 atm to 1 atm steadily and continuously. Find the changes in
  (i) (1%) temperature,
  (ii) (1%) internal energy,
  (iii) (1%) enthalpy, and
  (iv) (1%) entropy of the gas.
  (v) (1%) Is the process reversible?

The constant pressure heat capacity of the ideal gas is Cp=30 kJ/(kmol-K).

The universal gas constant is R=8.314 kJ/(kmol-K).

Problem1 (2)

(a) (5%) Given an equation of state,

$$P = bT - a$$

where b and a are functions of molar volume $\underline{V}$ only. Find:

$$\left(\frac{\partial \underline{C}_V}{\partial \underline{V}}\right)_T$$

Hints

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

(b) When two fluids are mixed at 300 K to form a homogeneous binary solution of mole fraction 0.5, additional measurements was found that

$$\underline{\Delta H_{mix}} = -100 \frac{cal}{mol}$$

$$\underline{\Delta S_{mix}} = -0.5 \frac{cal}{mol \cdot K}$$

Find the values of the following excess properties:

(i) (1%) $\underline{\Delta H^{ex}_{mix}}$

(ii) (1%) $\underline{\Delta S^{ex}_{mix}}$

(iii) (1%) $\underline{\Delta G_{mix}}$

Is there any inconsistency among data ?(Yes or No, 1%, Why, 1%). Hints:

$$\ln(0.5) = -0.6931$$

Problem2

(1)

A binary *A-B* system is at atmospheric pressure. The normal melting points of *A* and *B* are at 962°C and 1085°C, respectively, and the stable crystalline structures of both of them are the face centered cubic structure. (a) What is the Gibbs free energy for a binary *A-B* liquid at a temperature *T* if the *A-B* liquid is an ideal solution? (b) There is a eutectic reaction, liquid=$\alpha+\beta$, at 779°C. The α and β phases are the terminal solid phases of *A* and *B* with limited solubilities of *B* and *A*, respectively. Draw a schematic phase diagram of the binary *A-B* system for the temperature ranges between 200°C and 1200°C. (c) Draw the schematic free energy curves of both the solid and liquid phases at 800°C. (10%)

(2)

In a closed system, one mole of component A is reacted in the liquid phase with one mole of component B at 25°C and atmospheric pressure to produce C and D according to the reaction: $A_{(\ell)} + B_{(\ell)} \rightarrow C_{(\ell)} + D_{(l)}$. The standard Gibbs free energy formation (at 25°C and atmospheric pressure), ΔG^o_{298}, for the liquid *A, B, C, D* are -389,900 J, -174,780 J, -332,200 J, and -237,129 J, respectively. (a) Is this reaction a spontaneous reaction? Why? (b) Draw a schematic diagram to illustrate the total Gibbs energy of this system in relation to the extent of reaction. (c) Estimate the mole fraction of product *C* in the reacting mixture at equilibrium.　　(10%)

Problem3

(1) Researchers examined the adsorption of the hexacyanoferrate(III) ion, $[Fe(CN)_6]^{-3}$, on γ-Al_2O_3 from aqueous solution. They modeled the adsorption with a modified Langmuir isotherm, obtaining the following values of K at pH=6.5:

T/K	283	298	308	318
$10^{-11}K$	2.642	2.078	1.286	1.085

(a) Determine the isosteric enthalpy of adsorption, $\Delta_{ads}H^\circ$, at this pH. (7%)

(b) The researchers also reported $\Delta_{ads}S^\circ$=+96 $Jmol^{-1}K^{-1}$ under these conditions. Please also determine $\Delta_{ads}G^\circ$. (3%)

(2) The excess Gibbs energy of a particular ternary liquid mixture is represented by the empirical expression, with parameters A_{12}, A_{13}, A_{23} functions of T and P only:

$$G^E/RT=A_{12}x_1x_2+A_{13}x_1x_3+A_{23}x_2x_3$$

(a) Determine the implied expressions for $\ln\gamma_1$ $\ln\gamma_2$ $\ln\gamma_3$. (7%)

(b) For species 1 determine expressions (or values) for $\ln\gamma_1$ for the limiting cases: $x_1=0$, $x_2=0$, and $x_3=0$. (3%)

Problem4

(1) For a chemical reaction, $Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^-$. Now, we employ a battery discharge process on an external electric circuit, R, to evaluate the thermal responses of this reaction. The thermal responses for R and the battery are measured through two independent calorimeters meanwhile the battery and R are placed in adiabatic vessels 1 and 2, respectively. We find that as R becomes larger, the heat from the circuit approaches -190 kJ/mol Zn and the heat from the battery approaches -43 kJ/mol Zn.

(a) What is ΔH° of this reaction (based on Zn in mole)? (4%)

(b) What is the energy efficiency of this electrochemical reaction? Why? (6%)

(2) An auto-catalytic reaction consists of the following elementary mechanism:

$$A + R \xrightarrow{k} 2R$$

where the rate of A disappearance: $-r_A = kC_AC_R$, k = 1.0 L/mol·min, the initial concentration of A (C_{A0}) = 0.99 mol/L, the initial concentration of R (C_{R0}) = 0.01 mol/L, the exit concentration of A (C_{Ae}) = 0.1 mol/L and the exit concentration of R (C_{Re}) = 0.9 mol/L. Please determine the space time of (a) a single PFR (3%), (b) a single CSTR (3%), and (c) two reactors in series (one PFR and one CSTR) with the shortest space time (4%).

Problem5

(1) **Residence time distribution**

Consider isothermal operation of a plug-flow reactor with mean residence time τ_p and an ideal, perfectly mixed batch reactor with mean residence time τ_m.

(a) What is the overall residence time distribution if the two are arranged in series such that the plug flow reactor is followed by perfectly mixed reactor (Case 1)? What would be the overall residence time distribution if the order of arrangement is reversed (Case 2)? (4%)

(b) For a 1st-order reaction $r_A \equiv -dC_A/dt = k_1 C_A$, find the fractional conversion $\alpha \equiv 1 - C_A/C_{A0}$ at the exit for both Cases 1 and 2. (4%)

(c) For a 2nd-order reaction $r_A \equiv -dC_A/dt = k_2 C_A^2$, find the fractional conversion $\alpha \equiv 1 - C_A/C_{A0}$ at the exit for both Cases 1 and 2. (6%)

(2) **Nonisothermal reactor**

For a first-order exothermic liquid-phase reaction A→P in a perfectly mixed batch reactor, energy balance dictates that the rate of temperature change is governed by $\rho c_p\, dT/dt = (-\Delta H_{rxn})\, r_A - qa$ where ρ and c_p are respectively the density and the heat capacity of the reaction mixture, ΔH_{rxn} the heat of reaction, a the area of cooling coils, the flux of heat removal $q = h\,(T-T_0)$ with h the heat transfer coefficient and T_0 the cooling water temperature, and $r_A \equiv -dC_A/dt = k_1 C_A = A_1 \exp(-E_1/RT)\, C_A$ with A_1 the pre-exponential factor, E_1 the activation energy, R the gas constant. Plug in expression for q and r_A and reduce the governing equation into dimensionless form. Find dimensionless groups affecting the temperature stability of the reactor; assign each its proper physical meaning. (6%)