THERMODYNAMICS II
(CHEN 2203)

Time Allotted : 3 hrs **Full Marks : 70**

Figures out of the right margin indicate full marks.

Candidates are required to answer Group A and any 5 (five) from Group B to E, taking at least one from each group.

Candidates are required to give answer in their own words as far as practicable.

Group – A
(Multiple Choice Type Questions)

1. Choose the correct alternative for the following: **10 × 1 = 10**

(i) An isentropic process is always
(a) reversible isothermal (b) reversible adiabatic
(c) irreversible isothermal (d) irreversible adiabatic

(ii) In a throttling process, the pressure of a ideal gas reduces by 50%. The specific volume will change by a factor of (γ is specific heat capacity ratio)
(a) 2 (b) $2^{1/\gamma}$ (c) $2^{(\gamma-1)/\gamma}$ (d) 0.5

(iii) As pressure approaches zero, fugacity coefficient value tends to
(a) pressure (b) unity (c) zero (d) infinity

(iv) Which of the following is true for excess property M^E? (M^{ig} thermodynamic property of ideal gas, M^{id} thermodynamic property of ideal solution)
(a) $M^E = M - \sum x_i M_i$ (b) $M^E = M - \sum x_i \overline{M_i}$
(c) $M^E = M - M^{ig}$ (d) $M^E = \Delta M - \Delta M^{id}$
(Symbols bear usual significance)

(v) For a binary system exhibiting VLLE, the degrees of freedom are
(a) 2 (b) 1 (c) 3 (d) 4

(vi) The intercepts at x_1=0 and x_1=1 in the plot of molar volume of a solution at various concentrations of component 1 in binary solution yield
(a) excess volume (b) partial molar volume
(c) volume change of mixing (d) volume of pure species 1

(vii) The intercept at x_1=0 in a plot of G^E/x_1x_2RT versus x_1 yields
(a) activity coefficient of species 1 at infinite dilution
(b) activity coefficient of pure species 2
(c) activity coefficient of species 2 at infinite dilution
(d) activity coefficient of pure species 1

(viii) The entropy change of mixing of a binary liquid system is
(a) negative (b) zero
(c) positive (d) depends on the system

(ix) The equilibrium constant of a reaction at 298 K is
(a) a function of composition of the reaction mixture
(b) calculated from standard Gibbs free energy change of reaction at 298 K
(c) always a constant
(d) independent of temperature

(x) Eutectic temperature is achieved at equilibrium between the following phases
(a) two liquids and one vapour phase
(b) one solid and one vapour phase
(c) two liquid phases
(d) two immiscible solids and one liquid phase

Group – B

2. (a) A rigid insulated tank contains an ideal gas (γ = specific heat capacity ratio) initially at temperature T_0 and pressure P_0. The gas continuously leaks out from the tank through a valve connected at its end. Applying control volume analysis, determine an expression of temperature of gas in the tank when the pressure reduces to P_f ($P_f < P_0$).

(b) A rigid evacuated cylinder is connected to a supply line through which an ideal gas (heat capacity ratio is γ) at temperature T and pressure P is flowing and the cylinder is filled with the gas till the pressure in the cylinder rises to P. Determine an expression of final temperature of the gas in the cylinder after filling it.

6 + 6 = 12

3. (a) Show that the relation between heat capacities of any real gas is given by $C_p - C_v = \frac{\alpha^2 VT}{\beta}$ where, α is isobaric thermal expansion coefficient, β is isothermal compressibility coefficient. Other symbols bear usual significance. From this relation also show that $C_p - C_v = R$ for ideal gas.

(b) From the following compressibility data for carbon dioxide gas at100^0C and 50 atm, determine the fugacity of carbon dioxide gas at 50 atm.

P (atm)	0	14	22	30	44	58	68
Z	1.00	0.95	0.92	0.89	0.84	0.79	0.76

6 + 6 = 12

Group – C

4. The excess Gibbs free energy of a binary solution is given by

$$\frac{G^E}{RT} = -3x_1x_2(0.4x_1 + 0.5x_2)$$

Find the expression for $\ln\gamma_1$ and $\ln\gamma_2$. Further show that the derived expression follows Gibbs-Duhem equation. (Symbols bear usual significance).

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5. (a) Prove that if Henry's law is obeyed by component 1 in a binary solution over certain concentration range, Lewis-Randall rule will be obeyed by component 2 over the same concentration range.

(b) The enthalpy at 300 K and 1 bar of a binary liquid mixture is
$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$
where H is in J/mol. For the stated temperature and pressure, determine
(i) Expressions for $\overline{H_1}$ and $\overline{H_2}$ in terms of x_1.
(ii) Values for the pure component enthalpies H_1 and H_2.
Values of partial molar enthalpies at infinite dilution $\overline{H_1^\infty}$ and $\overline{H_2^\infty}$

5 + (3 + 2 + 2) =12

Group – D

6. (a) Find parameter values of Margules equation that provide the best fit to the VLE data below, and prepare a P-x-y diagram that compares the experimental points with curves determined from the correlation. The following set of VLE data for the acetone (1)/methanol(2) system at 55^0C is given

P (kPa)	68.7	72.3	77.5	86.7	90.1	93.2	95.0	97.6	101.0	99.9	96.9
x_1	0	0.03	0.09	0.22	0.28	0.36	0.41	0.51	0.79	0.91	1
y_1	0	0.06	0.19	0.36	0.42	0.48	0.51	0.58	0.79	0.93	1

The Margules equation is given by $\frac{G^E}{x_1x_2RT} = (A_{21}x_1 + A_{12}x_2)$ and the activity coefficients derived from the equation are
$\ln\gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$, $\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$.

(b) Wilsons parameters for the system chloroform(1)-methanol(2) at $35^\circ C$ can be estimated from the data given as follows
$(\lambda_{12} - \lambda_{11}) = -1.522\ kJ/mol\ K$ $(\lambda_{12} - \lambda_{22}) = 7.559\ kJ/mol\ K$. Estimate the VLE data for the system (total pressure and equilibrium vapor composition) at $35^\circ C$ for x_1=0.3 if molar volume of pure chloroform and methanol are $80.67\times10^{-6}\ m^3/mol$ and $40.73\times10^{-6}\ m^3/mol$ respectively. The Wilson equation is given by

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2\Lambda_{12}) - x_2 \ln(x_2 + x_1\Lambda_{21})$$

where $\Lambda_{12} = \frac{v_2}{v_1}\exp\left[-\frac{\lambda_{12}-\lambda_{11}}{RT}\right]$ and $\Lambda_{21} = \frac{v_1}{v_2}\exp\left[-\frac{\lambda_{12}-\lambda_{22}}{RT}\right]$

The Antoinne equation is given as

$\log_{10} P^{sat} = A - \frac{B}{t+C}$, where Psat is saturation pressure in Torr, t is temperature in degree Celsius. The Antoinne constants of the components are given by

Component	A	B	C
Chloroform	6.95465	1170.966	226.232
Methanol	8.08097	1582.271	239.726

(c) Write the basic equation for vapour liquid equilibrium and explain each term. State the necessary assumptions and reduce the equation to a simple form for low pressure VLE.

7 + 3 + 2 = 12

7. (a) A single-effect evaporator operating at atmospheric pressure concentrates a 15% (by weight) LiCl solution to 40%. The feed enters the evaporator at the rate 2 kg/s at $25^{\circ}C$. The normal boiling point of 40% LiCl solution is $132^{\circ}C$ and its specific heat is 2.72 kJ/Kg $^{\circ}C$. What is the heat transfer rate in the evaporator? Given: Heat of solution data:

Moles H_2O/moles solute	Heat of solution kJ/mole solute
3.5	-23.2
6.1	-30
8	-32.2
13.3	-33.8

Enthalpy change of water during the process is 2652.2 kJ/kg.

(b) Pure liquid species 2 and 3 are immiscible in one another. Liquid species 1 is soluble in both liquid 2 and 3. One mole each of liquids 1,2 and 3 are shaken together to form an equilibrium mixture of two liquid phases: an α –phase containing species 1 and 2,and a β-phase containing species 1 and 3. What are the mole fractions of species 1 in the two phases if at the temperature of the experiment the excess Gibbs energies of the phases are given by

$$\frac{(G^E)^{\alpha}}{RT} = 0.4x_1^{\alpha}x_2^{\alpha} \text{ and } \frac{(G^E)^{\beta}}{RT} = 0.8x_1^{\beta}x_3^{\beta}.$$

(c) Write the general solid vapour phase equilibrium equation and reduce it to a simple form by making necessary assumptions. How is the vapour phase fugacity coefficient of the solute determined?

(d) How the enthalpy of a binary solution is determined using the enthalpy concentration diagram?

4 + 3 + 3 + 2 = 12

Group – E

8. (a) State the basic criterion of equilibrium for a chemically reacting system.

   (b) Derive the relation between standard Gibbs free energy change of reaction and equilibrium constant.

   (c) Explain what is meant by standard Gibbs free energy of formation of a compound. How is it related to the standard Gibbs free energy change of reaction?

   (d) Explain the significance of reaction coordinate. Develop expressions for mole fractions of reacting species as functions of reaction coordinates for a system initially containing 2 mol NH_3 and 5 mol O_2 and undergoing the reaction

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H2O(g)$$

2 + 3 + 2 + (1 + 4) = 12

9. (a) The following isomerisation reaction occurs in the liquid phase: $A \rightarrow B$ where A and B are miscible liquids for which $G^E/RT = 0.1x_Ax_B$ If , what is the equilibrium composition of the mixture at 25oC? How much error is introduced if one assumes that A and B form an ideal solution? Guess value of $x_A = 0.5$

   (b) Discuss the different types of ensembles. Derive the molar entropy of an ideal gas using statistical mechanics

4 + (5 + 3) = 12

Department & Section	Submission Link
CHE	https://classroom.google.com/c/MzEyNTE3MDYwNTEy/a/MzczNTE1ODE1MTAz/details