| | Utech |
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| Name: | |
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| Invigilator's Signature : | |

THERMODYNAMICS & KINETICS

Time Allotted: 3 Hours Full Marks: 70

The figures in the margin indicate full marks.

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

GROUP - A

(Multiple Choice Type Questions)

- 1. Choose the correct alternatives for any *ten* of the following : $10 \times 1 = 10$
 - i) A closed system can exchange
 - a) energy with surrounding
 - b) mass with surrounding
 - c) both energy & mass with surrounding
 - d) none of these.
 - ii) Which of the following is a state function?
 - a) Internal energy
- b) Enthalpy
- c) Entropy
- d) All of these.

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iii) Mathematical expression for enthalpy is

a) H = U + PV

b) H = U PV Example Part Control

c) H = Q - PV

d) none of these.

iv) At triple point the degrees of freedom is

a) 1

b) 2

c) 0

d) 3.

- v) An isothermal process is a process of
 - a) no heat exchange between system & surrounding
 - b) constant volume
 - c) constant temperature
 - d) constant pressure.
- vi) The dimensionless ratio fugacity coefficient is represented by

a) f_i / P

b) f_i / T

c) f_i

d) $f_i P$.

- vii) The first law of thermodynamics is concerned with the
 - a) direction of energy transfer
 - b) reversible process only
 - c) irreversible process only
 - d) none of these.





a) K^{-1}

b) bar -

c) °C

d) bar.

ix) Hydrolysis of ethyl acetate follows the

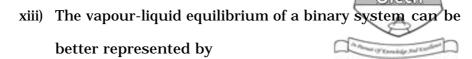
- a) 1st order reaction kinetics
- b) 2nd order reaction kinetics
- c) zero order reaction kinetics
- d) pseudo 1st order reaction kinetics.
- x) Throttling (Joule-Thomson effect) process is a constant process of
 - a) entropy
- b) enthalpy
- c) pressure
- d) volume.

xi) Which one is true?

- a) dG = TdS + VdP
- b) dG = VdP SdT
- c) dG = PdV TdS
- d) dG = SdT + PdV.

xii) For sparingly soluble gases, Henry's law constant is

- a) very high
- b) very low
- c) moderate
- d) all of these.



- a) T X Y diagram
- b) P X Y diagram
- c) P T diagram
- d) all of these.

xiv) As the time is passing entropy of the universe

- a) is decreasing
- b) remains constant
- c) is increasing
- d) insufficient data for prediction.

xv) Recirculation fraction for Lindey liquefaction process is

a) zero

- b) less than one
- c) greater than one
- d) none of these.

GROUP - B (Short Answer Type Questions)

Answer any *three* of the following. $3 \times 5 = 15$

- 2. Write down Gibbs phase rule. What do you mean by critical point? 2+3
- 3. Show P-T diagram of pure substance & comment on it.

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- 4. Write short note on any one of the following:
 - a) Heat Engine
 - b) Heat Pump.
- 5. Prove that enthalpy change of mixing for ideal gas is zero. Give the expression for chemical potential in terms of Gibbs energy. 3+2
- 6. Derive the working equation for liquid-liquid equilibria.

GROUP - C (Long Answer Type Questions)

Answer any *three* of the following. $3 \times 15 = 45$

- 7. a) Prove that $RT \ln \phi = G_i^R$ where the symbols have their usual meaning in thermodynamics.
 - b) What is 'Ton of refrigeration'? Calculate the amount of heat removed for one ton of refrigeration. 1+4
 - c) Show that for an ideal gas $\mu_{\pi}=0$, where μ_{π} is the Joule-Thomson coefficient.
- 8. With very neat diagram explain the steps involved in absorption refrigeration system by using ammonia. 6 + 9

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9. Write the two forms of the virial equation. Define volume expansibility & isothermal compressibility. For acetone at 293.15 K (20°C) and 1 bar,

$$B = 1.487 \times 10^{-3} \text{ K}^{-1}$$

$$K = 62 \times 10^{-6} bar^{-1}$$

$$V = 1.287 \times 10^{-3} \text{ m}^{3} \text{ kg}^{-1}$$

Find:

- a) the value of $(\delta P/\delta T) v$
- b) the pressure generated when acetone is heated at constant volume from $293.15K(20^{\circ}C)$ & 1 bar to $303.15K(30^{\circ}C)$.
- c) the volume change when acetone is changed from 293.15K (20°C) & 1 bar to 273.15K (0°C) & 10 bar.

$$2 + 3 + 10$$

- 10. a) Show that half value period for first order kinetics is not dependent on initial concentration of reactant. State Duhem's theorem. 3+2
 - b) In an isomerisation process, the following first order constants are found:

| Temp (°C) | 120 | 130 | 140 |
|---------------|-----|------|------|
| K (sec - 1) | 5.0 | 11.5 | 26.4 |

Calculate (i) the activation energy (ii) frequency factor of the process.

- 11. a) Define COP value of a refrigerator. Temperature of a refrigerator space is 10°C and that of surrounding is 30°C. Calculate the COP value of that refrigerator.
 Derive an expression for the amount of heat absorbed by the refrigerator.
 - b) Define fugacity and fugacity coefficient. How can you evaluate fugacity coefficient using second virial coefficient? Prove that for multiple phases at the same temperature & pressure in equilibrium the chemical potential of each species is the same in all phases.

2 + 3 + 3

12. a) Explain with the help of examples the kinetic properties of unimolecular, bimolecular and pseudomolecular reactions. Name the controlling factors of reaction rate.

4 + 2

- b) A certain substance R_1 is mixed with equal moles of another substance R_2 . At the end of 30 seconds, R_1 is 25% reacted. How much of R_1 and R_2 be left untreated at the end of 35 seconds, if the reaction is
 - i) first order in R_1 and independent of R_2
 - ii) first order in both R_1 and R_2 . 4+5