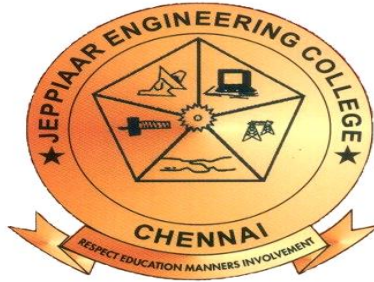# JEPPIAAR ENGINEERING COLLEGE



## B.TECH – BIOTECHNOLOGY (R- 2017)

## BT 8302 APPLIED THERMODYNAMICS FOR BIOTECHNOLOGISTS

## II YEAR & III SEM

## BATCH: 2017-2021

# QUESTION BANK

## PREPARED BY

## A.MUTHULAKSHMI

| VISION OF THE INSTITUTION |
|---|

❖ To build Jeppiaar Engineering College as an institution of academic excellence in technological and management education to become a world class University

| MISSION OF THE INSTITUTION |
|---|

❖ To excel in teaching and **learning, research and innovation** by promoting the principles of scientific analysis and creative thinking.

❖ To participate in the production, **development and dissemination of knowledge** and interact with **national and international communities.**

❖ To equip students with **values, ethics and life skills n**eeded to enrich their lives and enable them to meaningfully contribute to the **progress of society.**

❖ To prepare students for **higher studies and lifelong learning,** enrich them with the **practical and entrepreneurial skills** necessary to excel as future professionals and contribute to **Nation's economy**

| PROGRAM OUTCOMES (PO) | |
|---|---|
| PO 1 | **Engineering knowledge**: **Apply** the knowledge of mathematics, science, engineering fundamentals, and an engineering specialization to the solution of complex engineering problems. |
| PO 2 | **Problem analysis**: **Identify, formulate, review** research literature, and **analyze** complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences, and engineering sciences. |
| PO 3 | **Design/development of solutions**: **Design solutions** for complex engineering problems and **design** system components or processes that meet the specified needs with appropriate consideration for the public health and safety, and the cultural, societal, and environmental considerations |
| PO 4 | **Conduct investigations of complex problems**: **Use** research-based knowledge and research methods including **design** of experiments, **analysis** and **interpretation** of data, and **synthesis** of the information to provide valid conclusions. |
| PO 5 | **Modern tool usage**: **Create**, **select**, and **apply** appropriate techniques, resources, and modern engineering and IT tools including prediction and modeling to complex engineering activities with an understanding of the limitations. |
| PO 6 | **The engineer and society**: **Apply** reasoning informed by the contextual knowledge to assess societal, health, safety, legal and cultural issues and the consequent responsibilities relevant to the professional engineering practice. |
| PO 7 | **Environment and sustainability**: **Understand** the impact of the professional engineering solutions in societal and environmental contexts, and **demonstrate** the knowledge of, and need for sustainable development. |
| PO 8 | **Ethics**: **Apply** ethical principles and commit to professional ethics and responsibilities and norms of the engineering practice. |
| PO 9 | **Individual and team work**: **Function effectively** as an individual, and as a member or leader in diverse teams, and in multidisciplinary settings. |
| PO 10 | **Communication**: **Communicate effectively** on complex engineering activities with the engineering community and with society at large, such as, being able **to comprehend** and **write** effective reports and **design** documentation, **make** effective presentations, and **give** and **receive** clear instructions. |
| PO 11 | **Project management and finance**: **Demonstrate** knowledge and understanding of the engineering and management principles and **apply** these to one's own work, as a member and leader in a team, to **manage** projects and in multidisciplinary environments. |
| PO 12 | **Life-long learning**: **Recognize** the need for, and have the preparation and ability to **engage** in independent and life-long learning in the broadest context of technological change. |

| | VISION OF THE DEPARTMENT |
|---|---|
| | To pursue excellence in producing bioengineers coupled with research attributes. |

| | MISSION OF THE DEPARTMENT |
|---|---|
| **M1** | To **impart** quality education and **transform** technical knowledge into career opportunities. |
| **M2** | To **establish** a bridge between the **program and society** by **fostering** technical education. |
| **M3** | To **generate societal conscious technocrats** towards **community development** |
| **M4** | To **facilitate higher studies** and research in order to have an **effective career / entrepreneurship.** |

| | PROGRAM EDUCATIONAL OBJECTIVES (PEOS) |
|---|---|
| **PEO - 1** | To impart knowledge and produce competent graduates in the field of biotechnology |
| **PEO - 2** | To inculcate professional attributes and ability to integrate engineering issues to broader social contexts. |
| **PEO - 3** | To connect the program and community by fostering technical education. |
| **PEO - 4** | To provide a wide technical exposure to work in an interdisciplinary environment |
| **PEO - 5** | To prepare the students to have a professional career and motivation towards higher education. |

| | PROGRAM SPECIFIC OUTCOMES (PSOS) |
|---|---|
| **PSO 1** | **Professional Skills:**  This programme will provide students with a solid foundation in the field of Biological Sciences and Chemical engineering enabling them to work on engineering platforms and applications in Biotechnology as per the requirement of Industries, and facilitating the students to pursue higher studies |
| **PSO 2** | **Problem-solving skills:** This programme will assist the students to acquire fundamental and problem solving knowledge on subjects relevant to Biotechnology thereby encouraging them to understand emerging and advanced concepts in modern biology |
| **PSO 3** | **Successful Career and Entrepreneurship:** Graduates of the program will have a strong successful career and entrepreneurial ability with the blend of inputs from basic science, engineering and technology, thereby enabling them to translate the technology and tools in various industries and/or institutes |

# BT8302 APPLIED THERMODYNAMICS FOR BIOTECHNOLOGISTS

**UNIT I -THERMODYNAMIC LAW AND PROPERTIES OF FLUIDS(9)**
First Law of thermodynamics, a generalized balance equation and conserved quantities, Volumetric properties of fluids exhibiting non ideal behavior; residual properties; estimation of thermodynamic properties using equations of state; calculations involving actual property exchanges; Maxwell's relations and applications.

**UNIT II - SOLUTION THERMODYNAMICS (9)**
Partial molar properties; concepts of chemical potential and fugacity; ideal and non-ideal solutions; concepts and applications of excess properties of mixtures; activity coefficient; composition models; Gibbs Duhem equation.

**UNIT III - PHASE EQUILIBRIA(9)**
Criteria for phase equilibria; VLE calculations for binary and multi component systems; liquid- liquid equilibria and solid-solid equilibria.

**UNIT IV- CHEMICAL REACTION EQUILIBRIA (9)**
Equilibrium criteria for homogeneous chemical reactions; evaluation of equilibrium constant; effect of temperature and pressure on equilibrium constant; calculation of equilibrium conversion and yields for single and multiple reactions.

**UNIT V -THERMODYNAMIC DESCRIPTION OF MICROBIALGROWTH AND PRODUCT FORMATION (9)**
Thermodynamics of microbial growth stoichiometry thermodynamics of maintenance, Calculation of the Operational Stoichiometry of a growth process at Different growth rates, Including Heat using the Herbert –Pirt Relation for Electron Donor, thermodynamics and stoichiometry of Product Formation.

### TEXT BOOKS:
1. Smith J.M., Van Ness H.C., and Abbot M.M. "Introduction to Chemical Engineering Thermodynamics", 6th Edition. Tata McGraw-Hill, 2003.
2. Narayanan K.V. "A Text Book of Chemical Engineering Thermodynamics", PHI,2003.
3. Christiana D. Smolke, " The Metabolic Pathway Engineering Handbook Fundamentals",CRC Press Taylor & Francis Group, 2010.

**REFERENCE:**
1. Sandler S.I. "Chemical and Engineering Thermodynamics", John Wiley,1989.

| BT 8302 APPLIED THERMODYNAMICS FOR BIOTECHNOLOGISTS | |
| --- | --- |
| **CO NO.** | **COURSE OUTCOMES** |
| **C211.1** | **Able to describe the knowledge** on thermodynamic law and properties of fluids |
| C211.2 | **Able to understand** the concept of solution thermodynamics |
| C211.3 | **Able to understand** the phase equilibria in liquid liquid and solid –solid equilibria |
| C211.4 | **understand the concept of** chemical reaction equilibria |
| C211.5 | **Ability to apply** the thermodynamic description of microbial    growth and product formation |

# BT8302 APPLIED THERMODYNAMICS FOR BIOTECHNOLOGISTS

| S. No. | Title | Reference Book | Page No. |
|---|---|---|---|
| UNIT I -THERMODYNAMIC LAW AND PROPERTIES OF FLUIDS (9) | | | |
| 1. | First Law of thermodynamics | Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" (CET) | 23-30 |
| 2. | A generalized balance equation and conserved quantities | Narayanan K.V (CET) | 31-32 |
| 3. | Volumetric properties of fluids exhibiting non ideal behavior; | Narayanan K.V (CET) | 188-191 |
| 4. | Residual properties | Narayanan K.V (CET) | 237-240 |
| 5. | Estimation of thermodynamic properties using equations of state | Narayanan K.V (CET) | 191-216 |
| 6. | Calculations involving actual property exchanges | Narayanan K.V (CET) | 288-291 |
| 7. | Maxwell's relations and applications. | Narayanan K.V (CET) | 192-195 |
| UNIT II - SOLUTION THERMODYNAMICS (9) | | | |
| 1. | Partial molar properties | Narayanan K.V (CET) | 257-262 |
| 2. | Concepts of chemical potential and fugacity | Narayanan K.V (CET) | 265-273 |
| 3. | Ideal and non-ideal solutions | Narayanan K.V (CET) | 273-275 |
| 4. | Concepts and applications of excess properties of mixtures. | Narayanan K.V (CET) | 298-300 |
| 5. | Activity coefficient | Narayanan K.V (CET) | 278-282 |
| 6. | Composition models | Narayanan K.V (CET) | 288-294 |
| 7. | Gibbs Duhem equation | Narayanan K.V (CET) | 283-285 |
| UNIT III - PHASE EQUILIBRIA (9) | | | |
| 1. | Criteria for phase equilibria | Narayanan K.V (CET) | 310-312 |
| 2. | VLE calculations for binary and multi component systems | Narayanan K.V (CET) | 315-380 |
| 3. | Liquid- liquid equilibria and | Narayanan K.V (CET) | 381-383 |
| 4. | Solid-solid equilibria. | Narayanan K.V (CET) | REF.PAPER |
| UNIT IV- CHEMICAL REACTION EQUILIBRIA (9) | | | |
| 1. | Equilibrium criteria for homogeneous chemical reactions | Narayanan K.V (CET) | 398-404 |
| 2. | Evaluation of equilibrium constant | Narayanan K.V (CET) | 404-408 |
| 3. | Effect of temperature and pressure on equilibrium constant | Narayanan K.V (CET) | 409-421 |
| 4. | Calculation of equilibrium conversion and yields for single and multiple reactions. | Narayanan K.V (CET) | 422-439 |
| UNIT V -THERMODYNAMIC DESCRIPTION OF MICROBIAL   GROWTH AND PRODUCT FORMATION (9) | | | |
| 1. | Thermodynamics of microbial growth stoichiometry thermodynamics of maintenance | Christiana D. Smolke, " The Metabolic Pathway Engineering Handbook Fundamentals" | 11-2, 11-13 |
| 2. | Calculation of the Operational Stoichiometry of a growth process at Different growth rates, Including Heat using the Herbert –Pirt Relation for Electron Donor | Christiana D. Smolke | 11-14 |
| 3. | Thermodynamics and stoichiometry of Product Formation. | Christiana D. Smolke | 11-17 |

**BT8302 APPLIED THERMODYNAMICS FOR BIOTECHNOLOGISTS**
**UNIT I -THERMODYNAMIC LAW AND PROPERTIES OF FLUIDS**
**PART A**

1. What are the limitations of first law of thermodynamics? (Apr/May 2017)

    (i) The first law of thermodynamics is a law of conservation of energy. It does not specify the direction of the process. All spontaneous processes processed in one direction only.
    (ii) The first law of thermodynamics does not specify the feasibility of a process reversing itself.
    (iii) This Law is silent about its % of conversion of energy from one form to another form. Work can be converted into equivalent amount of heat but heat cannot be converted into equivalent amount of work.
    (iv) Mathematically first law of thermodynamics is dU = dQ-dW. Thus first law gives the term of internal energy 'U'.

2. What is 'equation of state'? (Apr/May 2017)

    An equation of state is a functional relationship between state variables P, T and V.
    Ideal gas equation of state is PV = RT.
    This equation was established from the postulates of the kinetic theory of gases by Maxwell with the following assumptions:
    (1) There is little or no attraction between the molecules of the gas
    (2) Volume occupied by the molecules is negligibly small compared to the volume of gas
    Applicability: Ideal gas equation of state is applicable to gas with very small pressure or very high temperature.

3. Discuss on volume expansivity. (May/June 2016)

    It is a parameter that is used to measure the volume expansivity of pure substances and is defined at constant pressure, P. In the field of materials science, the property of linear coefficient of thermal expansion is an important consideration in materials selection and design of products. This property is used to account for the change in volume when the temperature of the material is changed.

    $$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

4. Define the principle of corresponding states. (May/June 2016)

    All gases when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor and all deviate from the ideal behavior to the same extent. $Z = f(T_r, P_r)$

5. Distinguish between internal energy, kinetic energy and potential energy of a system.(Apr/May 2015)

| S.No. | Internal Energy | Kinetic Energy | Potential Energy |
|---|---|---|---|
| 1 | The system possesses by virtue of the molecular configuration and motion of molecules. Unit of energy is joule. | The energy possessed by the body by virtue of its motion is called its kinetic energy. (KE) | The energy possessed by the system due to its position above some arbitrary reference plane is referred to as its potential energy. (PE) |
| 2 | $1J = 1\ Nm = 1kg\ m^2/s^2$ | $KE = \frac{1}{2}\ mv^2$ | $PE = mgz$ |
| 3 | Internal energy is a thermodynamic property of the system. | Kinetic Energy is not a thermodynamic property of the system. It doesn't change with change in the temperature or pressure of the body. | Potential Energy is not a thermodynamic property of the system. It doesn't change with change in the temperature or pressure of the body. |

6. What are the Maxwell's equations and what is their importance in establishing relationships between thermodynamic properties? (Apr/May 2015)

Maxwell's equations are helpful in replacing unmeasurable quantities appearing in thermodynamic equations by measurable quantities. Using these relations, the partial derivatives of entropy with respect to pressure and volume are expressed as derivatives possessing easily identifiable physical meaning. Each of the four Maxwell's equations is derived from the exact differential equations of the four energy properties.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \rightarrow 1$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \rightarrow 2$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \rightarrow 3$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \rightarrow 4$$

7. Distinguish between state and path function. (May/June 2014) (May/June 2007)

| State Function | Path Function |
|---|---|
| Depends only on the state at the moment and independent of path taken to establish property or value. | Dependent on path taken to establish property or value. |
| Can integrate using final and initial values. | Need multiple integrals and limits of integration in order to integrate. |
| Multiple steps result in same value. | Multiple steps result in different value. |
| Based on established state of system (temperature, pressure, amount, and internal energy). | Based on how state of system was established. (heat and work) |

8. Define $C_P$ and $C_v$. (May/June 2014)

At constant volume (isometric), $C_V$ = molar specific heat at constant V
At constant pressure (isobaric), $\mathbf{Q_P} = n\ \mathbf{C_P}\ \Delta T$, $C_P$ = molar specific heat at constant P
$C_P$ = Specific heat capacity at constant pressure, i.e. $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

$C_V$ = Specific heat capacity at constant volume, i.e. $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

It can be shown that for a perfect gas: $C_P - C_V = R,$ where R is the gas constant.
The ratio, $C_p/C_v = \gamma$

7

9. Give two examples of properties. (May/June 2013)
   Temperature, volume, entropy – Examples of reference properties.
   Internal energy, enthalpy – Examples of energy properties.

10. Define Helmholtz energy. (May/June 2013,2012)
    Helmholtz free energy (A) of a system is defined as **A = U – TS**
    Where, U - Internal energy, T- Temperature, S –Entropy of the system. Since, U, T and S are characteristic of the system and depend only on its thermodynamic state, Helmholtz free energy is a state function. Since U and S are both extensive, A also is an extensive property.

11. What are residual properties? (May/June 2012) (Apr/May 2010)
    The residual properties are defined as the difference between the thermodynamic property at the specified temperature and pressure and the property that the substance would have exhibited at the same temperature and pressure (ideal gas condition).
    Properties in the ideal state represented with the superscript *id*, the residual enthalpy ($H^R$) and residual entropy ($S^R$) are defined as
    $$H^R = H - H^{id}$$
    $$S^R = S - S^{id}$$

12. What are fundamental property relations? (May/June 2013) (Apr/May 2010)
    The differentials of energy properties form the basis for the derivation of a large number of equations relating thermodynamic properties. These are developed for systems of constant mass and composition in which the only external force is the pressure and the process occurring is reversible.

    **Fundamental property relations**
    i) **Internal Energy**, $dU = dQ - dW = TdS - PdV$
    $$dU = TdS - PdV \rightarrow (1)$$
    ii) **Enthalpy,** $H = U + PV, dH = dU + d(PV), dH = (TdS - PdV) + PdV + VdP$
    $$dH = TdS + VdP \rightarrow (2)$$
    iii) **Helmholtz Free Energy,** $A = U - TS, dA = dU - d(TS) = dU - SdT - TdS$
    $$dA = TdS - PdV - SdT - TdS$$
    $$dA = -PdV - SdT \rightarrow (3)$$
    iv) **Gibbs Free energy**, $G = H - TS, dG = dH - d(TS) = TdS + VdP - TdS - SdT$
    $$dG = VdP - SdT \rightarrow (4)$$

13. What are three means by which the second virial coefficient can be determined? (Apr/May 2010)
    The second virial coefficient can be determined by,
        (i)      Kinetic theory
        (ii)     Equations of state
        (iii)    Physical interpretation.

14. Define-volume expansivity and isothermal compressibility. (Apr/May 2011)
    The volume coefficient of expansion (β) and coefficient of isothermal compressibility (κ) are two other measurable quantities like heat capacities at constant pressure and constant volume. They are defined as

    $$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad , \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

By introducing wherever possible, volume coefficient of expansion ($\beta$) and coefficient of isothermal compressibility ($\kappa$), the resulting relationships get fully expressed in terms of measurable quantities.

15. How do you relate the Van der Waals constants to the critical properties? (May/June 2009) (Apr/May 2011)

Van der waals equation is used to explain the P-V-T behavior of real gases.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Where a and b are called van der waals constants.

This equation is cubic in volume and below the critical temperature, there are three real roots. The largest is the vapour volume and the smallest the liquid volume. The intermediate root has no physical significance. When P is the saturation pressure, the smallest and the largest roots correspond to molar volumes of saturated liquid and saturated vapour respectively.

$$V_C = 3b \; ; \quad T_C = \frac{8a}{27Rb} \; ; \quad P_C = \frac{RT_C}{2b} - \frac{a}{9b^2}$$

Van der waals constant is expressed in terms of critical properties

$$a = \frac{27R^2T_C^2}{64P_C} \; ; \quad b = \frac{RT_C}{8P_C}$$

16. Define system.(Nov/Dec 2009)

A system is a region in which the process occurs. (eg) reaction vessel, distillation column.

17. Define system and surroundings. (Nov/Dec 2009)

The part of the universe outside the system and separated from the system by boundaries is called surroundings.

18. What is physical significance of virial coefficients? (Apr/May 2008)
   - Virial coefficients are functions of temperature only (for a given gas).
   - virial coefficients can be given physical interpretation.
   - The virial coefficients account for the molecular interactions.

The two sets of virial coefficients are related as:

$$B' = \frac{B}{RT}, \qquad C' = \frac{C - B^2}{RT^2}$$

19. What is compressibility factor? (Apr/May 2008)

Compressibility factor (Z) is defined as the ratio of the volume of a real gas (V) to the volume if the gas behaved ideally at the stated temperature and pressure (RT/P). Virial equations express the compressibility factor of a gas or vapor as a power series expansion in P or 1/V.

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + ....$$

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + .....$$

20. State the law of corresponding states and explain its significance. (Nov/Dec 2008)

**Law of corresponding states**: All gases when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor and all deviate from the ideal behavior to the same extent. $Z = f(T_r, P_r)$

**Significance**: generalized compressibility charts are made correlating the P-V-T behavior of all fluids, based on the principle of corresponding states.

21. What is control volume? (Nov/Dec 2008)

For a control volume, the law of conservation of mass may be written as:

$$\begin{pmatrix} \text{Rate of accumulati on of mass} \\ \text{Within the control volume} \end{pmatrix} + \begin{pmatrix} \text{Net rate of mass out} \\ \text{by the flowing streams} \end{pmatrix} = 0$$

$$\frac{dm}{dt} + \Delta(\rho u A) = 0$$

For steady –state flow process, there is no accumulation of mass within the control volume, hence dm/dt=0 then above equation becomes, $\Delta(\rho u A) = 0$

22. Show that the Joule –Thomson coefficient is zero for ideal gases. (May/June 2007)

For ideal gases: $PV = RT \Rightarrow V = \dfrac{RT}{P}$, Differentiate w.r.to temperature at constant pressure

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Joule Thomson coefficient: $\mu C_p = T\left(\dfrac{\partial V}{\partial T}\right)_P - V$

Substitute $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P}$ in above equation which gives

$$\mu C_p = T\left(\frac{R}{P}\right) - V$$

$$\mu C_p = \frac{TR}{P} - \frac{RT}{P} \Rightarrow 0$$

$$\mu = 0$$

Hence, Joule Thomson coefficient is zero for ideal gases.

23. State first law of thermodynamics. (May/June 2006)

The law states that change in internal energy (dU) in any system is equal to the heat added to the system (dQ) minus the work done by the system (dW).

$$dU = dQ - dW$$

24. State second law of thermodynamics. (May/June 2006)

The change in entropy (dS) during any change in a system is equal to the heat entering the syatem (when the change is performed reversibly) divided by the absolute temperature, T.

$$dS = \frac{dQ_{rev}}{T}$$

Entropy of an isolated system always increases (dS > 0).

The statements for the first and second laws of thermodynamics can be combined: *The energy of the universe is conserved whereas the entropy is increasing.*

25. Define a closed system with one example. (Nov/Dec 2003)

Systems that can exchange energy with the surroundings but which cannot transfer matter across the boundaries are known as closed systems. (eg) batch reactor, power and refrigeration cycles

26. Define an open system with one example.(Nov/Dec 2003)

Systems that can exchange both energy and matter with their environment. (eg) compressor, pump and heat exchanger.

27. Define Clausius inequality.

In a cyclic operation, the sum of the dQ/T terms around a complete cycle is less than or equal to zero depending on whether the process is irreversible or reversible.

$$\oint \frac{dQ}{T} \leq 0$$

28. Define the term: Intensive property.

An intensive property is independent of the size of the system. (eg) pressure, temperature and density are intensive properties.

29. Define the term: Extensive property.

Extensive properties depend on the quantity (or extent) of matter specified in the system. (eg) Mass and volume are extensive properties.

30. State the commonly used equation for equations of state.
    (i)     Van der waals equation
    (ii)    Redlich –Kwong equation
    (iii)   Redlich-Kwong-Soave equation
    (iv)    Peng-Robinson equation
    (v)     Benedict –Webb-Rubin equation
    (vi)    Virial equation

31. Define equilibrium state.

A system is said to be in a state of equilibrium if the properties are uniform throughout and they do not vary with time. A system is in
    (i)     Thermal equilibrium: when no heat exchange occurs within the system & temperature is uniform throughout.
    (ii)    Mechanical equilibrium: pressure is uniform.

32. Define triple point of water.

The temperature at which the solid, liquid and vapor phases of water coexist in equilibrium and it is assigned as value of 273.15 K.

33. State Avogadro's hypothesis.

Avogadro's hypothesis states that gases containing the same number of molecules occupy the same volume at same temperature. That is, the number of molecules in one mole of any substance is constant and it is called the Avogadro Number ($N_A$)

$N_A = 6.022 \times 10^{23}$ per mole

34. Mention the application of equation of state?

Equation of state is applicable to gas with very small pressure or very high temperature. With increase in pressure the intermolecular force of attraction and repulsion increases, and also the volume of the molecules becomes appreciable compared to the gas volume. Under such condition real gas equations are to be used.

35. State Hess's law.

The net heat evolved or absorbed in a chemical reaction is the same whether the reaction takes place in a single step or in a series of steps.

## PART B

1. Derive Maxwell equations and also mention the applications. (13)(APR/MAY 2017,2010,12,13,14) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No. 192-194)

2. Derive the residual property equation for Gibbs energy, volume, enthalpy and entropy. (13) (MAY 2010,12,13) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No. 237-240)

3. (i) Show that ideal gases $C_p - C_v = R$ (4) (MAY 2007) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No. 208)

(ii) Prove that $[dc_p/dp]_T = -T [d^2v / dT^2]_P$ (6) )(MAY 2008,09) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No. 210-211)

4. Calculate the pressure developed by 1 kmol of gaseous ammonia contained in a vessel of $0.6m^3$ capacity at a constant temperature of 473 K by the following methods:

    (i)      Using the ideal gas equation

    (ii)    Using the vander Waals equation given that

            a= 0.4233 $Nm^4/mol^2$;

            b=3.73 x $10^{-5}$ $m^3/mol$

    (iii)   Using the Redlich – Kwong equation given that Pc=112.8 bar; Tc=405.5K (Apr/May 2010) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.73 )

5. Show that

(i) $\quad T\left(\dfrac{\partial P}{\partial T}\right)_v - P = \left(\dfrac{\partial U}{\partial V}\right)_T$ (May/June 2009)

(ii) $\quad \left(\dfrac{\partial C_P}{\partial P}\right)_T = -T\left(\dfrac{\partial^2 V}{\partial T^2}\right)_P$ (Nov/Dec 2009,2008)(Apr/May 2011)

(iii) $\quad \left(\dfrac{\partial C_V}{\partial V}\right)_T = T\left(\dfrac{\partial^2 P}{\partial T^2}\right)_V$ (Nov/Dec 2008) (Apr/May 2011)

(Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.210-211)

6. How is Joule-Thomson coefficient evaluated from P-V-T information? And show that the Joule-Thomson coefficient is zero for ideal gases. (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.214-216)


## PART-C

1. Deduce from fundamentals, the first law of thermodynamics for flow process. (Apr/May 2017) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No. 30-32)
2. What are different types of thermodynamic diagrams? Explain the method of construction of any two thermodynamic diagrams. (May/June 2014) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No. 240-245)
3. Derive the relationship between entropy and heat capacity. (MAY 2009) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.197-199)
4. Develop equations for evaluating the change in internal energy and change in enthalpy for process involving ideal gases. (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.200-201)

# UNIT II - SOLUTION THERMODYNAMICS
## PART A

1. What is mass and molar concentration? (Apr/May 2017)

   Mass concentration is defined as the mass of a constituent divided by the volume of the mixture. The mass concentration of a component in a mixture can be called the density of a component in a mixture. Molar concentration is defined as the amount of a constituent (usually measured in moles ) divided by the volume of the mixture.

2. Define chemical potential. What is its physical significance? (Apr/May 2017, 2015) (May/June 2013,2012,2009,2007)(Nov/Dec 2010)

   Chemical potential is used as an index of chemical equilibrium in the same manner as temperature and pressure are used as indices of thermal and mechanical equilibrium. The chemical potential $\mu_i$ of component I in a solution is same as its partial molar free energy in the solution, $G_i$. That is, chemical potential of a component i in a solution can be defined as,

   $$\mu_i = \overline{G}_i = \left( \frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j}$$

3. Differentiate between Clapeyron and Clausius-Clapeyron equations. (May/June 2016) (Apr/May 2011,2010)

   **Clapeyron equation:** The Clapeyron equation predicts the dependence of equilibrium pressure on temperature when two phases of a given substance coexist. It is given by

   $$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

   Where $\Delta H$ and $\Delta V$ are the enthalpy and volume change accompanying a phase change.

   **Clausius-Clapeyron equation**: If the temperature is not too near the critical point, the volume of the liquid is small in comparison with the volume of vapour. The volume change accompanying vapourization $\Delta V = V_G - V_L$ is therefore approximately equal to $V_G$, the molar volume of vapour.

   $$\frac{dP}{dT} = \frac{\Delta H}{TV_G}$$

   The vapour pressure in regions well below the critical point is relatively small so that the vapor can be assumed to behave as an ideal gas. The molar volume, $V_G$, can now be replaced by $RT/P^S$

   So the above equation becomes

   $$\frac{dP^S}{dT} = P^S \frac{\Delta H}{RT^2} \quad \text{or} \quad \frac{d \ln P^S}{dT} = \frac{\Delta H}{RT^2}$$

   This equation is known as Clausius-Clapeyron equation.

4. What is meant by partial molar property?(May/June 2016) (Apr/May 2011,2008)(Nov/Dec 2010,2009)

   Partial molar property of a particular component in a mixture measures the contribution of that component to the mixture property. The partial molar property $\overline{M}_i$ of the component $i$ in the solution is defined as

   $$\overline{M}_i = \left( \frac{\partial nM}{\partial n_i} \right)_{T,P,n_{j\neq i}} = \left( \frac{\partial M^t}{\partial n_i} \right)_{T,P,n_{j\neq i}}$$

14

$M^t$ is the total value of any extensive thermodynamic property of a solution, n is the total number of moles and M is the molar property of the solution. $n_i$ denotes the number of moles of component *i* in the solution.

5. Distinguish between molar volume and partial molar volume. Does the partial molar volume of a substance vary with concentration of the substance in the solution? (Apr/May 2015)
   **Molar volume**: consider an open beaker containing a huge volume of water. Assume that one mole of water is added to it. The volume increases by $18 \times 10^{-6} \, m^3$, which is the molar volume of pure water.
   **Partial Molar volume**: if the same amount of water is added to a large amount of pure ethanol taken in a beaker, the increase in volume will be approximately $14 \times 10^{-6} \, m^3$, which is the partial molar volume of water in pure ethanol.
   The difference in the increase in volumes can be explained thus: the volume occupied by a given number of water molecules depends on the molecules surrounding them. When water is mixed with a large volume of alcohol, there is so much alcohol present that each water molecule is surrounded by pure ethanol.
   Yes. The partial molar volume of a substance varies with concentration of the substance in the solution.

6. State Raoult's law, show that it is a simplified form of Lewis Randell rule. (May/June 2014)
   **Raoult's law** states that the partial pressure of a component in vapor phase is equal to the product of liquid phase mole fraction and pure component vapor pressure.
   $$\bar{p_i} = x_i P_i^S$$
   **Lewis Randall rule** is applicable to ideal liquid solutions which states that fugacity ($f_i$) of each constituent is directly proportional to the number of moles of the constituent in the solution.
   $$\bar{f_i} = x_i f_i$$

7. What are excess properties and give its significance? (May/June 2014)(Nov/Dec 2009)
   For real liquid solutions, the molar excess property is the departure function which quantifies the deviation from ideal solution property.
   The excess property, $M^E$, is defined as the difference between an actual property and the property that would be calculated for the same temperature, pressure and composition by the equations for an ideal solution.
   $$M^E = M - M^{id}$$
   M- molar property of the solution
   $M^{id}$ – property of an ideal solution under the same conditions.
   $M^E$ – excess property

8. State Gibbs Duhem equation.(Nov/Dec 2013) (May/June 2006)
   At constant temperature and pressure, the property Mt of the solution is the sum of the partial molar properties of the constituents, each weighted according to the number of moles of the respective constituents.
   $$M^t = \Sigma n_i \bar{M}_i$$

9. How is the activity coefficient related to the excess free energy? (May/June 2012,2007) (Apr/May 2011)
   The most useful excess property is the partial molar excess Gibbs free energy ($G^E$) which can be directly related to the activity coefficients.
   $$G^E = RT \sum x_i \ln \gamma_i$$

$$\ln \gamma_i = \left[ \frac{\partial (nG^E / RT)}{\partial n_i} \right]_{T,P,n_j}$$

10. What do you mean by acentric factor? (Apr/May 2011)

For simple fluids, temperature equal to 7/10 of the critical temperature, the reduced vapor pressure closely follows the following empirical result:

$$\frac{P^S}{P_C} = \frac{1}{10} \; at \; \frac{T}{T_C} = 0.7$$

Where $P^S$ is the vapor pressure. Pitzer defined the acentric factor in terms of the reduced vapour pressure at a reduced temperature of 0.7 as

$$\omega = -1.00 - \log \left( \frac{P^S}{P_C} \right)_{T_R = 0.7}$$

For simple fluids, the acentric factor = 0; for more complex fluids, the acentric factor > 0.

11. What are the characteristics of an ideal solution? (Apr/May 2011,2008)
    (i)     There is no volume change when the components are mixed together to form an ideal solution.
    (ii)    If a mixture of two liquids is to behave ideally, theoretical considerations reveal that the two types of molecules must be similar.

12. State Gibb's theorem. (Apr/May 2010)

Except for volume all other partial molar property of a species in an ideal gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at a temperature same as that of the mixture, but at a pressure equal to its partial pressure in the mixture.

13. Define fugacity coefficient. (Apr/May 2010)

The ratio of fugacity to pressure is referred to as fugacity coefficient and is denoted by $\phi$. It is dimensionless and depends on nature of the gas, the pressure, and the temperature.

$$\phi = \frac{f}{P}$$

14. How is entropy change in an irreversible process determined? (Apr/May 2010)

The entropy change in an irreversible process occurring between any two states would be the same as the entropy change in a reversible process occurring between them. Thus, the entropy change in any irreversible process can be evaluated by devising an imaginary reversible process for accomplishing the same change and calculating the entropy change in the latter.

15. Define the term activity coefficient. (Apr/May 2011) (May/June 2006)

Activity coefficients measure the extent to which the real solution departs from ideality. Activity coefficient of the component i in the solution is denoted by $\gamma_i$ and is defined by the following relationship.

$$\bar{f}_i = \gamma_i x_i f_i^0$$

Where $f_i^0$ is the fugacity in the standard state. For ideal solutions $\gamma_i = 1$.

16. What is the effect of temperature on the activity coefficient of a component in a solution? (May/June 2009)

Effect of temperature on activity coefficient is given by

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_P = \frac{H_i - \overline{H}_i}{RT^2}$$

The term ($H_i - \overline{H}_i$) is the partial heat of mixing of component $i$ from its pure state to the solution of given composition both in the same state of aggregation and pressure. For gaseous mixtures, this term is negligible at low pressures.

17. What is the effect of pressure on the activity coefficient of a component in a solution? (May/June 2009)

Effect of pressure on activity coefficient is given by

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_T = \frac{\overline{V}_i - V_i}{RT}$$

The molar volumes $\overline{V}_i$ and $V_i$ correspond to the particular phase under consideration. For liquid solutions, the effect of pressure on activity coefficients is negligible at pressures below atmospheric. For gaseous mixtures, activity coefficients are nearly unity at reduced pressures below 0.8.

18. What is a heat pump? (Nov/Dec 2009)

A heat pump is a thermodynamic system operating in a cycle that removes heat from a low temperature body and delivers it to a high temperature body. External energy in the form of work is necessary to accomplish this.
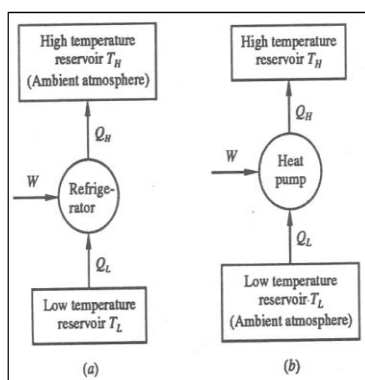


19. Define fugacity for a real gas. (Apr/May 2008)(Nov/Dec 2008)

Fugacity is used in the study of phase and chemical reaction equilibria involving gases at high pressures. For real gas, pressure is replaced by an 'effective pressure' or fugacity $f$ of the gas.

$$dG = RTd(\ln f)$$

20. Define fugacity coefficient for a real gas. (Apr/May 2008)(Nov/Dec 2008)

Fugacity coefficient for a real gas is given by the following relation,

$$G = G^0 + RT \ln \frac{P}{P^0} + RT \ln \phi$$

Free energy of a real gas=free energy of an ideal gas $+ RT \ln \phi$. The quantity $RT \ln \phi$, therefore, expresses the entire effect of intermolecular interaction.

17

21. What is an inversion point? (Nov/Dec 2008)

    At any given pressure, the joule-Thomson coefficient is positive only within a temperature range that is between the upper and lower inversion temperatures. Only within these temperatures a gas cools on throttling.

22. Define COP of refrigerator. (Nov/Dec 2008)

    The coefficient of performance (COP) is defined as the ratio of heat transferred from low temperature reservoir ($Q_2$) to the work-input (W). For refrigerator,

    $$\eta = \frac{Q_2}{W}$$

23. Define COP of pump. (Nov/Dec 2008)

    The COP is defined as the ratio of heat rejected ($Q_1$) to the work-input (W).
    For heat pump,

    $$\eta = \frac{Q_1}{W}$$

24. Define the term activity.

    Activity or relative fugacity is defined as the ratio of fugacity to fugacity in the standard state. It finds wide application in the study of homogeneous chemical reaction equilibria involving solids and liquids. Activity is denoted by 'a'.

    $$a = \frac{f}{f^0}$$

25. What are ideal solutions?

    A solution in which the partial molar volumes of the components are the same as their molar volumes in the pure state is called an ideal solution.

26. State Lewis fugacity rule. (Nov/Dec 2013)

    It states that the fugacity of a component in an ideal solution is directly proportional to the mole fraction of the component in the solution.

    $$\bar{f}_i = y_i f_i$$

    Lewis fugacity rule is valid for systems where the intermolecular forces in the mixture are similar to those in the pure state.

27. State Henry's law.

    Partial pressure or fugacity is directly proportional to the concentration in the liquid or its mole fraction, the proportionality constant.

    $$\bar{p}_i = x_i k_i \ \text{Or} \ \bar{f}_i = x_i k_i$$

    $\bar{p}_i$ - Partial pressure of the solute

    $x_i$ - Mole fraction in the solution

    $k_i$ - Proportionality constant (or) Henry's law constant

28. Define non -ideal solution.

A solution, any of whose components does not obey Raoult's law is known as non-ideal solution. Even non –ideal solutions exhibit a common form of ideal behavior over a limited concentration range where the fugacity (or, the partial pressure) is directly proportional to the concentration in the liquid.

29. State lewis Randall rule.

Lewis Randall rule is applicable to ideal liquid solutions which states that fugacity ($f_i$) of each constituent is directly proportional to the number of moles of the constituent in the solution.

$$\bar{f_i} = x_i f_i$$

30. Define partial molar volume.

**Partial Molar volume**: if the same amount of water is added to a large amount of pure ethanol taken in a beaker, the increase in volume will be approximately $14 \times 10^{-6}$ m$^3$, which is the partial molar volume of water in pure ethanol.

The difference in the increase in volumes can be explained thus: the volume occupied by a given number of water molecules depends on the molecules surrounding them. When water is mixed with a large volume of alcohol, there is so much alcohol present that each water molecule is surrounded by pure ethanol.

31. Mention the application of Gibbs Duhem equation.

Gibbs-Duhem equation can be used for the calculation of

(i) a partial molar quantity of a binary mixture from measurements of the composition dependence of the corresponding total molar quantity,

(ii) the partial molar quantity of a component, say 1, of a binary mixture from measurements of the composition dependence of the corresponding partial molar quantity of component 2, and

(iii) the partial vapor pressures from measurements of the liquid-phase composition dependence of the total vapor pressure.

32. Define Clausius-Clapeyron equations.

**Clausius-Clapeyron equation**: If the temperature is not too near the critical point, the volume of the liquid is small in comparison with the volume of vapour. The volume change accompanying vapourization $\Delta V = V_G - V_L$ is therefore approximately equal to $V_G$, the molar volume of vapour.

$$\frac{dP}{dT} = \frac{\Delta H}{T V_G}$$

The vapour pressure in regions well below the critical point is relatively small so that the vapor can be assumed to behave as an ideal gas. The molar volume, $V_G$, can now be replaced by RT/P$^S$

So the above equation becomes

$$\frac{dP^S}{dT} = P^S \frac{\Delta H}{RT^2} \quad \text{or} \quad \frac{d \ln P^S}{dT} = \frac{\Delta H}{RT^2}$$

This equation is known as Clausius-Clapeyron equation.

33. State the Characteristics of Entropy.

1. It increases when the heat is supplied irrespective of the fact whether temperature changes or not.
2. Whether temperature changes or not the entropy decreases when heat is rejected.
3. In all the adiabatic processes, the entropy remains constant.

34. State conditions of Lewis fugacity rule.

Lewis fugacity rule is valid
(i)     At low pressures when the gas phase behaves ideally
(ii)    At any pressure if the component is present in excess
(iii)   If the physical properties of the components are nearly the same
(iv)    At moderate and high pressures, the Lewis-Randall rule will give incorrect results if the molecular properties of the components are widely different and the component under consideration is not present in excess.

## PART B

1. Derive an expression for fugacity and fugacity coefficient of pure species.(APR/MAY 2017,2007)  (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.225 – 228)

2. Discuss the importance of Gibbs-Duhem equation and explain its various forms. Explain the applications of Gibbs-Duhem equation. (MAY  2017, 2010,12,13,14)  (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.283-285)

3. Derive the Lewis / Randell rule as applicable to ideal solutions. (MAY 2010)   (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.271-272)

4. At 300 K and 1 bar, the volumetric data fo r a liquid mixture of benzene and cyclohexane are represented by $V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6}\,x - 2.64 \times 10^{-6}x^2$, where x is the mole fraction of benzene and V has the units of $m^3\ /\ mol$. Find the expressions for the partial molar volumes of benzene and cyclohexane. (May/June 2014,2013)  (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.262-263)

5. Derive the expressions for the effect of temperature and pressure on activity coefficient. (Nov/Dec 2013) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.236 - 237)

6. The enthalpy of a binary liquid mixture containing components 1 and 2 at 298 K and 1.0 bar is given by

    $H = 400x_1 + 600x_2 + x_1x_2(40x_1 + x_2)$

where H is in J/mol, Determine
(i)     Pure component enthalpies
(ii)    Partial molar enthalpies        (Apr/May 2015,2011) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.263-264)

## PART-C

**1.** Explain the methods by which fugacity for a pure component is calculated. (MAY 2010,12)(Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" PageNo.228-234)
**2.** Derive the expressions for the effect of temperature and pressure on fugacity coefficient. (Nov/Dec 2013) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.227-228)
**3.** Find the van Laar constants for the binary system benzene (1) – ethanol (2) using the following data:

| $x_1$ | 0.1 | 0.3 | 0.45 | 0.7 | 0.9 |
|---|---|---|---|---|---|
| $P_1^S$ kPa | 73.31 | 68.64 | 63.98 | 67.98 | 81.31 |
| $P_2^S$ kPa | 75.98 | 69.64 | 67.98 | 69.31 | 79.98 |

(May/June 2016)
(Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.389)
**4.** Two substances A and B are known to form ideal liquid solutions. A vapour mixture containing 50% (mol) A and 50% (mol) B is at 311 K and 101.3 kPa. This mixture is compresses isothermally until condensation occurs. At what pressure, does condensation occurs and what is the composition of the liquid that forms? The vapour pressures of A and B are 142 kPa and 122 kPa respectively. (May/June 2016) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.386)

# UNIT III - PHASE EQUILIBRIA
## PART A

1. Define the term Phase equilibria. (Apr/May 2017)

   The equilibrium state of a closed system is that state for which the total Gibbs energy is a minimum with respect to all possible changes at the given T and P.

   $$\left[dG^t\right]_{T,P} = 0$$

2. In liquid –liquid equilibrium curve, define plait point with neat sketch. (Apr/May 2017)

   The Plait Point P is the intersection of the raffinate-phase and extract-phase boundary curves. At this **point**, the equilibrium phases become coincident and no separation can be made at that **point**.
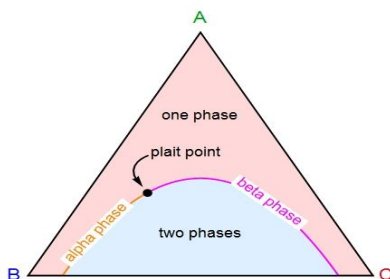
   

3. Distinguish between bubble point and dew point temperature. (May/June 2016, 2012) (Apr/May 2011,2008)

   | S.No | Bubble point temperature | Dew point temperature |
   |------|--------------------------|-----------------------|
   | 1 | The first bubble of vapour is produced from the liquid on heating at a constant pressure. | The first drop of condensate is formed on cooling a vapour at constant pressure. |
   | 2 | At the bubble point the liquid has the same composition as the original mixture. | The vapour in equilibrium with the liquid at the dew point has the same composition as the original mixture. |
   | 3 | At bubble point, $\sum y_i = \sum k_i x_i = 1$ | At dew point, $\sum x_i = \sum y_i / k_i = 1$ |

4. What is an azeotrope? Under what conditions do azeotropes generally form? (May/June 2016, 2014)

   An **azeotrope** is a mixture of two or more liquids whose proportions cannot be altered by simple distillation. This happens because, when an azeotrope is boiled, the vapor has the same proportions of constituents as the unboiled mixture. Because their composition is unchanged by distillation, **azeotropes** are also called **constant boiling mixtures.**

5. What is critical solution temperature? (Apr/May 2015) (May/June 2012)
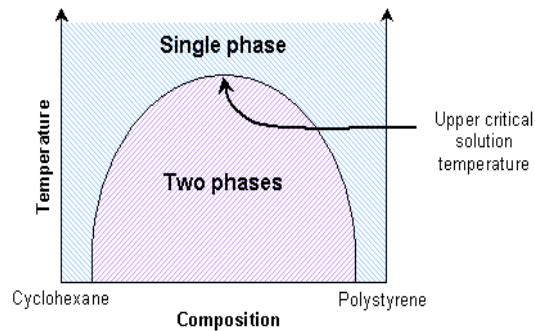


The point P gives the critical solution temperature. This point represents the last of the tie lines where the A-rich and B-rich phases become identical.

6. Write down the equation for solving general VLE problem. (Apr/May 2015)(Nov/Dec 2008)
Vapour liquid equilibrium (VLE) data are essential for many engineering calculations, especially in the design and analysis of separation operations such as distillation, absorption, etc. The fundamental relationship in the study of vapor liquid equilibrium is given by,
$$y_i \bar{\phi}_i P = \gamma_i x_i f_i^o.$$

7. What is Poynting correction? (May/June 2014)
For a pure fluid in vapor–liquid equilibrium, the vapor phase fugacity is equal to the liquid phase fugacity. The fundamental relationship in the study of vapour-liquid equilibrium is $y_i \bar{\phi}_i P = \gamma_i x_i f_i^o$. At pressures above the saturation pressure, the liquid phase fugacity is $f_i^o = \phi_i^S P_i^S exp\left[\frac{V_i(P-P_i^S)}{RT}\right]$. When this equation is substituted in the first equation, we get, $y_i \bar{\phi}_i P = \gamma_i x_i \phi_i^S P_i^S exp\left[\frac{V_i(P-P_i^S)}{RT}\right]$. The exponential term represents the Poynting correction factor and is usually near 1.0 unless pressures are very high.

8. What is the general criteria for phase equilibrium for heterogeneous multicomponent system?(Nov/Dec 2013) (May/June 2013)
When a system consisting of several components distributed between various phases is in thermodynamic equilibrium at a definite temperature and pressure, the chemical potential of each component is the same in all the phases.
If they are different, the component for which such a difference exists will show a tendency to pass from the region of higher to the region of lower chemical potential.
Thus the equality of chemical potential along with the requirement of uniformity of temperature and pressure serves as the general criterion of thermodynamic equilibrium in a heterogeneous multicomponent system.

$$\boxed{\begin{array}{l} T = \text{constant}; \qquad P = \text{constant} \\ \mu_i^\alpha = \mu_i^\beta = ... = \mu_i^\pi \quad \text{for} \quad i = 1,2,3,.....C \end{array}}$$

9. What are bubble point and dew point temperatures? (May/June 2013)
   **Bubble point temperature**: Bubble point temperature is the one at which the first bubble of vapour is produced from the liquid on heating at a constant pressure.
   **Dew point temperature**: Dew point temperature is one at which the first drop of condensate is formed on cooling a vapour at constant pressure.

10. What is the fugacity criterion for phase equilibrium? (Apr/May 2011) (Apr/May 2010)
    General fugacity criterion for phase equilibrium is given by

$$\boxed{\begin{array}{c} T = \text{constant}; \qquad P = \text{constant} \\ \bar{f}_i^{\alpha} = \bar{f}_i^{\beta} = .... = \bar{f}_i^{\pi} \quad \text{for} \quad i = 1,2,3,.....C \end{array}}$$

    Fugacity is a more useful property than chemical potential for defining equilibrium since it can be expressed in absolute values, whereas chemical potential can be expressed only relative to some arbitrary reference state. This equation is widely used for the solution of phase equilibrium problems.

11. Brief on bubble point and dew point pressures. (Apr/May 2011) (Nov/Dec 2008)
    To find the bubble point pressure, assume various values of pressure and get the $k_i$ values at this pressure. Calculate $y_i = k_i x_i$. if the assumed pressure is correct then $\sum y_i = \sum k_i x_i = 1$
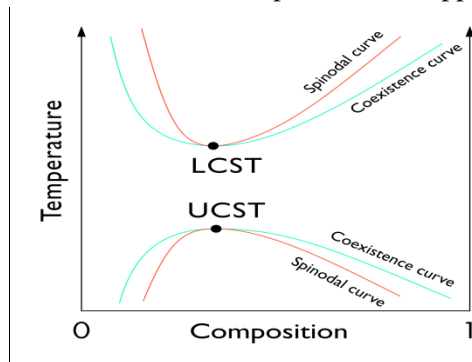    To find the dew point pressure, pressure is assumed arbitrarily and $k_i$ is determined. Then, $x_i = y_i/k_i$
    At the dew point, $\sum x_i = \sum y_i / k_i = 1$.

12. What is the criterion for liquid-liquid equilibrium? (Apr/May 2010)

    $\hat{f}_i^{\alpha} = \hat{f}_i^{\beta}$ for all i=1,2,.......n, α and β are two liquid phases.

13. Define lower critical solution temperature and upper critical solution temperature. (Apr/May 2010)



    The curves FC and GD eventually merge to a single point and the two liquid phases become identical. The temperature at which this occurs is known as the upper critical solution temperature (UCST). For pressures above this critical condition, the three phase equilibrium conditions do not exist.

14. What is meant by positive and negative deviations from Raoult's law? (Apr/May 2010)
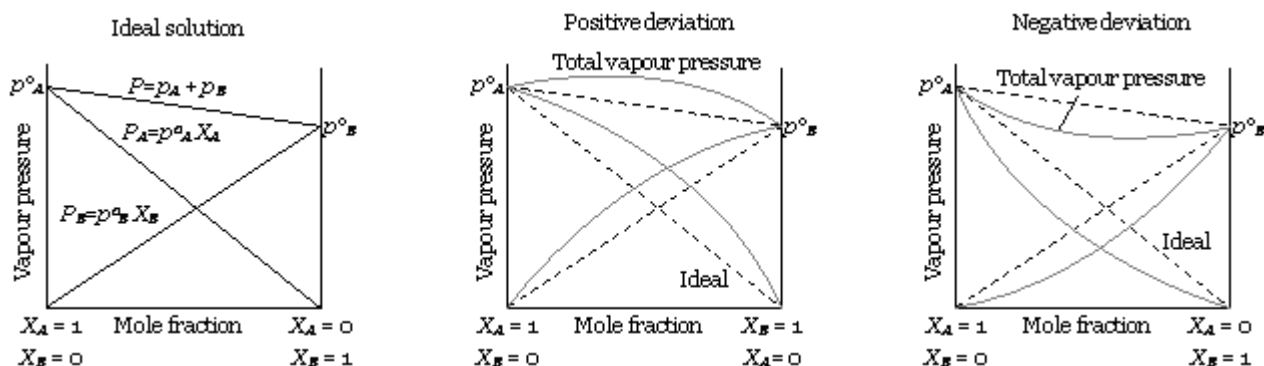


Positive deviation from ideality results when the actual partial pressure of each constituent is greater than it should be if Raoult's law were obeyed. It is present in solutions in which intermolecular forces between like molecules are stronger than those between unlike molecules.
(eg) benzene-cyclohexane, water-ethanol, $O_2$-$N_2$.
**Negative deviation from ideality** results when the partial pressures are less than those given by Raoult's law. At molecular level, negative deviation reflects stronger intermolecular forces between unlike molecules than between like pairs of molecules.
(eg) chloroform-acetone, HCL-water, chloroform-benzene.

15. How does one mathematically express the molar change in enthalpy (dh) for a multicomponent system? (Apr/May 2010)

$$dh = T\Delta V \frac{dP}{dT}$$

Where

$\Delta V$ - volume change accompanying phase rule
dP- change in pressure
dT-change in temperature

16. State Gibb's phase rule. (Nov/Dec 2010)

$F = C - \pi + 2$. This equation is known as Gibbs phase rule.
F-Number of degrees of freedom
$\pi$ -The number of phases in equilibrium
C- Number of components constituting the system.

17. List the criteria for phase equilibrium. (Nov/Dec 2010)
The criteria of internal thermal and mechanical equilibrium are that the temperature and pressure be uniform throughout the system.
(i)     Constant U and V :   $dS_{U,V} \geq 0$

(ii)    Constant T and V:   $dA_{T,V} \leq 0$

(iii)    Constant P and T:    $dG_{T,P} \leq 0$

18. How do you predict the low pressure VLE data for a binary system using the excess Gibbs free energy models? (May/June 2009)

Redlich-kister method is used to test the consistency of experimental data when the activity coefficient value over the entire concentration range is available. It is based on the excess free energy of mixing which is the difference between the free energy of mixing of a real solution and that of an ideal solution.

$$\Delta G^E = RT \sum x_i \ln \gamma_i$$

For a binary solution, it can be written as

$$\Delta G^E = RT \sum \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right)$$

19. What is an azeotrope? (May/June 2009)

An **azeotrope** is a mixture of two or more liquids whose proportions cannot be altered by simple distillation. This happens because, when an azeotrope is boiled, the vapor has the same proportions of constituents as the unboiled mixture. Because their composition is unchanged by distillation, **azeotropes** are also called **constant boiling mixtures.**

20. How many types of azeotropes are there? (May/June 2009)

There are two types of azeotropes.

(i)    Minimum boiling azeotropes

(ii)    Maximum boiling azeotropes.

21. Define equilibrium in terms of chemical potential. (Nov/Dec 2009)

For the system to be in equilibrium with respect to mass transfer, the driving force for mass transfer –the chemical potential- must have uniform values for each component in all phases.

$$\sum \mu_i dn_i = 0 \text{ (At constant temperature and pressure)}$$

22. Define isochoric process. (Nov/Dec 2009)

The relationship between pressure and volume is assumed to be $PV^n = cons \tan t$, where n is a constant. If $n = \infty$, the process is isochoric (constant volume).

23. Why does immiscibility occur in liquid solutions? (May/June 2009)

The equilibrium state of the system is two phases of a fixed composition corresponding to a temperature. The compositions of two such phases, however, change with temperature.

24. Define coexistence equation and its applications. (May/June 2009)

The coexistence equation can be used for testing the consistency of vapor-liquid equilibrium data.

$$\frac{dP}{dy_1} = \frac{P(y_1 - x_1)}{y_1(1 - y_1)}$$

The above equation is known as the coexistence equation.

25. Write the applications of coexistence equation. (May/June 2009)

Applications:

(i) It can be used to calculate any one of the three variables P, x or y if experimentally measured values of the other two variables are available.

(ii) If all the three variables are experimentally determined, then coexistence equation can be used to test the consistency of the measured data.

26. State Duhem's theorem.

For any closed system formed initially from the given masses prescribed chemical species, the equilibrium state is completely determined when any two independent variables are fixed.

27. Explain about consistency test.

Thermodynamic provides tests for consistency of experimental VLE data, as the VLE measurements are prone to accuracies.

All the tests are based on Gibbs-Duhem equation written in terms of activity coefficients.

$$x_1 \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 \left( \frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P}$$

28. Name the different types of consistency tests for VLE data.

(i) Using slope of lnγ curves

(ii) Using data at the Mid-point

(iii) Redlich-kister method (or) zero order method

(iv) Using the coexistence equation

(v) Using the partial pressure data.

29. Define criterion of stability.

At constant temperature and pressure, the free energy change on mixing ΔG, its first and second derivatives are all continuous functions of the concentration x and

$$\frac{d^2 \Delta G}{dx_1^2} > 0 \text{ at constant T \& P.}$$

30. Define system at equilibrium.

System at equilibrium is defined as one in which there are no driving forces for energy or mass transfer. That is for a system in a state of equilibrium, all forces are in exact balance.

31. What are the two types of phase equilibrium problems?

(i) The determination of composition of phases which exist in equilibrium at a known temperature and pressure

(ii) The determination of conditions of temperature and pressure required to obtain equilibrium between phases of specified compositions.

32. What are the advantages of NRTL equation?

NRTL equation is applicable to partially miscible as well as totally miscible systems. This equation is also applicable for non ideal solutions and especially partially miscible systems.

33. What is bubble point temperature?

Bubble point temperature is the one at which the first bubble of vapour is produced from the liquid on heating at a constant pressure.

34. What is dew point temperature?

Dew point temperature is one at which the first drop of condensate is formed on cooling a vapour at constant pressure.

35. Define zero order method.

This method is used to test the consistency of experimental data when the activity coefficient value over the entire concentration range is available. It is based on the excess free energy of mixing which is the difference between the free energy of mixing of a real solution and that of an ideal solution.

## PART B

1. Construct the P-x-y diagram for the cyclohexane(1)-benzene (2) system at 313 K the vapour pressures are $P_1^S$ =24.62 kPa and $P_2^S$ = 24.41 kPa. The liquid-phase activity coeffiients are given by $\ln \gamma_1 = 0.458x_2^2$, $\ln \gamma_2 = 0.458x_1^2$. (Apr/May 2017, 2015) (May/June 2012) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.356)

2. Explain the phase equilibria in single component systems. (May/June 2013) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.315-316)

3. (i) Describe the methods used for testing the thermodynamic consistency of experimentally determined vapor-liquid equilibrium data for binary systems. (MAY 2007,11) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.367-372)

   (ii) Compare Dew point and bubble point temperature. (4) (Apr/May 2007,11) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.328)

4. Explain the liquid/liquid solubility diagram for liquid liquid equilibrium (10) (MAY 2007,11) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.381-383)

5. A binary system, (i) benzene (ii) ethyl benzene obeys the Raoult's law and at vapour pressures are given by the Antoine equations

$$\ln P_1^S = 13.8858 - \frac{2788.51}{T - 52.41}$$
$$\ln P_2^S = 14.0045 - \frac{3279.47}{T - 60.00}$$

   where P is in kPa and T is in K. Construct the p-x-y at 373K and T-x-y at 101.3 kPa. (May/June 2014) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.337)

6. Ethanol-water mixture forms an azeotrope boiling at 351.4K under a pressure of 101.3kPa and its composition is 89.4% (mol) ethanol. The vapour pressures of ethanol and water at 351.4K are 100 kPa and 44 kPa respectively. Using Van Laar method and assuming that the ratio of vapour pressures remains constant. Calculate the composition of the vapor in equilibrium with a liquid containing 80% ethanol. (May/June 2013) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.390)

## PART C

1. At 750 mm Hg pressure, the A-B azeotrope boils at 65°C and contains 35 mole% of A. The vapor pressure of A and B are 1000 mm and 800 mm of Hg respectively at 65°C. Calculate the composition of vapour at this temperature in equilibrium with liquid analyzing 10 mole% of A. what is the total pressure at this condition? (Apr/May 2017) (class notes)

2. Discuss in detail about Vapour – Liquid Equilibria (VLE) at low pressures. (Narayanan K.V "A Text Book of Chemical Engineering Thermodynamics" Page No.347-352)

3. Explain in detail about the methods available for calculation of Vapour Liquid Equilibria involving high pressures. (Narayanan K.V "A Text Book of Chemical Engineering Thermodynamics" Page No.362-364)

4. A vapour mixture containing 18% ethane, 17% propane, 62% isobutene and the rest n-butane is subjected to partial condensation so that 75% of the vapour is condensed. If the condenser temperature is 300 K, determine the pressure.(May/June 2016) (Narayanan K.V "A Text Book of Chemical Engineering Thermodynamics" Page No. 391)

# UNIT IV- CHEMICAL REACTION EQUILIBRIA
## PART A

1. When the chemical reaction attains equilibrium? (Apr/May 2017)

   The chemical equilibrium state describes concentrations of reactants and products in a reaction taking place in a closed system, which no longer change with time. In other words, the rate of the forward reaction equals the rate of the reverse reaction, such that the concentrations of reactants and products remain fairly stable, in a chemical reaction. Equilibrium is denoted in a chemical equation by the $\rightleftharpoons$ symbol.
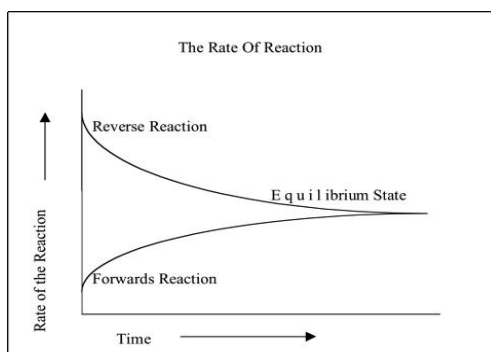
   

2. For the gas phase reaction $C_2H_4 + H_2O \rightarrow C_2H_5OH$ the equilibrium constant at 145°C and 1 bar is K= $6.8 \times 10^{-2}$, how would you calculate the equilibrium constant at 10 atm pressure? (Apr/May 2017)

   Solution:

   Given data: T =145°C, P= 1 bar, K= $6.8 \times 10^{-2}$

   Equilibrium constant k =? At P = 10 atm.

3. Define equilibrium constant $K_e$ of a chemical reaction. How is it related to $K_f$ and $K_p$? (May/June 2016) (Apr/May 2011)(May/June 2007)

   Consider the chemical reaction $aA + bB \rightarrow lL + mM$

   The equilibrium constant $K_e$ for this reaction is defined in terms of the activities of the reactants and the products as

   $$K_e = \frac{a_L^l a_M^m}{a_A^a a_B^b} = \Pi a_i^{v_i}$$

   Where $a_i$ is the activity of component i in the reaction mixture and $v_i$ is the stoichiometric number of i.

   Equilibrium constant in terms of fugacity is given by

   $$K_e = \Pi\left(\bar{f_i}\right)^{v_i} = K_f$$

   Equilibrium constant in terms of partial pressures is given by

   $$K_e = \Pi\left(\bar{p_i}\right)^{v_i}$$

   For gaseous systems, the relationship between equilibrium constants is given by $K = K_f = K_p$.

4. What is reaction coordinate? What is its significance in chemical reaction? (Apr/May 2015)

   Reaction coordinate measures the progress of a reaction. It is defined as the degree to which a reaction has advanced. Reaction coordinate is otherwise known as extent of reaction.

   The extent of reaction and number of moles taking part in the reaction are related as,

$$\frac{dn_i}{v_i} = d\varepsilon$$

For the initial state of the system, (ie) before the reaction, the value of ε is zero.

5. What is the effect of pressure on equilibrium conversion of a gas-phase chemical reaction? (Apr/May 2015) (Apr/May 2008)

In the case of reaction equilibrium for $N_2 + 3H_2 \rightarrow 2NH_3$ formation of ammonia will be favored by an increase in pressure as there is a reduction in the number of moles due to this reaction. When the composition of the system changes in this manner in response to increase or decrease in pressure, it does so without changing the equilibrium constant.

6. What is the phase rule for reacting systems? (May/June 2014) (Nov/Dec 2013)

The number of degrees of freedom will be reduced by one for each independent chemical reaction. If $r$ independent reactions occur in the system, then the phase rule becomes
$$F = C - \pi - r + 2$$

7. What is meant by extent of reaction? (May/June 2014)(May/June 2013)(Nov/Dec 2010)

The extent of the reaction measures the progress of the reaction and it is defined as the degree to which a reaction has advanced. It is denoted byε. It is also known as the reaction coordinate. It has the advantage that the change in the change in the extent of reaction dε is the same for each component, whereas the change in the number of moles is different for different species taking part in the reaction.
$$\frac{dn_i}{v_i} = d\varepsilon$$

8. List the criterion for chemical reaction equilibria. (May/June 2013,2012)

At constant temperature and pressure, the transfer of materials from one phase to another under equilibrium is found to occur with no change in the free energy.
$$dG_{T,P}^t = 0$$

The criterion of equilibrium for chemical reaction is given by
$$\sum \mu_i v_i = 0$$

9. How the equilibrium is constant related to the standard free energy change? (May/June 2012)

The standard free energy change $\Delta G^0$, accompanying the reaction when each of the reactants and the products is in its standard state.
$$\Delta G^0 = -RT \ln K$$

The equilibrium constant is determined by the standard free energy change and the temperature.
The standard free energy change depends on the temperature, the specification of standard state for each component and the number of moles involved in the stoichiometric equation under consideration.

10. Explain the concept of entropy and enthalpy departures. (Apr/May 2011)

The departure functions are defined as the difference between the thermodynamic property at the specified temperature and pressure and the property that the substance would have exhibited at the same temperature and pressure (ideal gas condition).
Properties in the ideal state represented with the superscript *id*, the residual enthalpy ($H^R$) and residual entropy ($S^R$) are defined as

$$H^R = H - H^{id}$$
$$S^R = S - S^{id}$$

$H^R$ and $S^R$ are known as **enthalpy departure** and **entropy departure**. These represent hypothetical property changes because a gas cannot be both real and ideal at a given P and T.

11. What is standard Gibbs free energy change of a chemical reaction and how is it related to the equilibrium constant? (Apr/May 2011)(Nov/Dec 2010,2008) (May/June 2009)

The standard free energy change depends on the temperature, the specification of standard state for each component and the number of moles involved in the stoichiometric equation under consideration. It is independent of pressure at equilibrium. Temperature in the standard state is the same as that in the equilibrium state.

$$\sum \mu_i^0 v_i = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b}$$

The left hand side gives the standard free energy change $\Delta G^0$, accompanying the reaction when each of the reactants and the products is in its standard state.

$$\Delta G^0 = -RT \ln K$$

12. Define van't Hoff equation. (Apr/May 2011) (May/June 2007)

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2}$$

This equation is known as van't Hoff equation, predicts the effect of temperature on the equilibrium constant and hence on the equilibrium yield.

$\Delta H^0$ - Standard heat of reaction. If $\Delta H^0$ is negative, ie. if the reaction is exothermic, the equilibrium constant decrease as the reaction temperature increases. If $\Delta H^0$ is positive, i.e. if the reaction is an endothermic reaction, the equilibrium constant will increase with increase in temperature.

13. State the effect of temperature of Equilibrium constant. (Apr/May 2010)

An increase in temperature will shift the equilibrium state in the direction of absorption of heat. That is, the equilibrium will shift in the endothermic direction if the temperature is raised, for then, energy is absorbed as heat.

Similarly, equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, for then the reduction in temperature is opposed. Thus, an endothermic reaction is favored by an increase in temperature and an exothermic reaction is favoured by a decrease in temperature.

The effect of temperature on equilibrium constant is quantitatively expressed by van't Hoff equation.

14. How does the standard heat of reaction related to standard Gibbs-energy change of reaction? (Apr/May 2010)

The standard free energy of the reaction and standard heat of reaction are related to the free energy and enthalpy of individual species respectively as given below.

$$\Delta G^0 = \Sigma v_i G_i^0, \qquad \Delta H^0 = \Sigma v_i H_i^0$$

The relationship between standard heat of reaction and standard Gibbs-energy change of reaction is given by

$$\left( \frac{d\left( \Delta G^0 / RT \right)}{dT} \right) = - \frac{\Delta H^0}{RT^2}$$

15. List down the causes of entropy change in chemical systems. (Apr/May 2010)

In an irreversible process, a decrease in entropy may occur either in the system or in the surroundings. These statements require only that the sum of the entropy changes of the system and the surroundings together be positive in an irreversible process like the isothermal expansion of a gas. If the same expansion were carried out reversibly, the increase in the entropy of the gas will be compensated by a decrease in the entropy of the surroundings that results because of the withdrawal of heat. If this heat exchange also were accomplished reversibly, the net change in entropy would be zero.

16. What do you understand by the number of independent reactions in a chemically reacting system? (Apr/May 2010)

The number of independent reactions that must be considered as the least number that includes every reactant and product present to an appreciable extent in all phases of the equilibrium system, and accounts for the formation of each product from the original reactants.

17. How does the dilution of a reaction mixture with an inert gas effect the degree of conversion in a gas phase reaction? (May/June 2009)

Diluting the reaction mixture with an inert material will increase total number of moles in the reaction mixture (N). This will result in an increased conversion, if v is positive. That is, if the reaction proceeds with an increase in the number of moles, presence of inerts in the system will increase the equilibrium yield.

18. What do you understand by the term "available energy"? (Nov/Dec 2009)

Available energy is the greatest amount of mechanical work that can be obtained from a system or body, with a given quantity of substance, in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition. In this definition, the initial state of the body is supposed to be such that the body can be made to pass from it to states of dissipated energy by reversible processes.

19. Is the Gibbs free energy change of a chemical reaction related to the work done by the system? Give an example. (Apr/May 2008)

Yes. The value of ΔG in any process is quite definite, no matter under what conditions the process is carried out, but only the temperature and pressure are constant the free energy change would represent the maximum net work available from the given change in state.

(eg) The maximum electrical work that could be done by the system undergoing a given change in state is less than the maximum work, - ΔA, by the expansion work and is measured by the decrease in the Gibbs free energy, - ΔG.

20. How the number of independent reactions in a chemically reacting system is determined?
    (i)     For each chemical compound present in the system, an equation for its formation reaction from
            its elements is written.  ($F = C - \pi - r + 2$)
    (ii)    The elements that are not present in the system are eliminated by properly combining the
            equations written in step (i).
            The number of equations, r that results from the above procedure is equal to the number of
            independent chemical reactions occurring.

21. What do you understand by the principle of increase in entropy? (Apr/May 2008)
    The principle of increase in entropy with reference to an isolated system means that the only processes
    that can occur in an isolated system are those that have an increase in entropy associated with them. The
    universe is a perfect example of an isolated system and all naturally occurring processes in the universe
    are accompanied by an increase in entropy and are irreversible. Hence we can say that the entropy of the
    universe goes on increasing.

22. Give an explanation of the effect of the pressure on a first order reaction. (May/June 2006)
    Increasing the pressure on a reaction involving reacting gases increases the rate of reaction. Changing
    the pressure on a reaction which involves only solids or liquids has no effect on the rate.

23. Give an explanation of the effect of the temperature on a first order reaction. (May/June 2006)
    The fraction of molecules whose kinetic energy exceeds the activation energy increases quite rapidly as
    the temperature is raised. This is the reason, all chemical reaction proceed more rapidly at higher
    temperature.

24. What reaction conditions affect the equilibrium conversion in chemical reactions?
    Temperature, pressure, excess amount of reactants, initial amount of products and inert substances.

25. What is the significance of free energy calculations in the thermodynamic analysis of chemical
    reactions?
    To find the equilibrium compositions, from free energy calculations, we can find the feasibility of a
    reaction.
    (i)     $\Delta G^0 < 0$, the reaction is promising.
    (ii)    $0 < \Delta G^0 < 40{,}000$ kJ/kmol, the reaction may or may not be possible and needs further study.
    (iii)   $\Delta G^0 > 40{,}000$ kJ/kmol, the reaction is very unfavorable.
            These guides may be useful as an approximate criterion for ascertaining the feasibility of
            chemical reactions.

26. What is quasistatic process? (May/June 2006)
    Consider the special case of an interaction of the system A with its surroundings which is carried out so
    slowly that A remains arbitrarily close to equilibrium at all times. Such a process is said to be quasistatic
    for the system.
    dQ=dE +dW
     dQ- infinitesimal heat
     dE- infinitesimal work
     dW – environment

27. How you evaluate the entropy changes accompanying chemical reactions?

The entropy changes accompanying chemical reactions are evaluated through the use of absolute entropies of the various components taking part in the reaction. Let $S_P$ denote the sum of the entropies of the reactants and $S_R$ denotes that of the products. Then the entropy change accompanying the reaction by

$$\Delta S = S_P - S_R$$

28. What are Giauque functions?

Data for calculation of standard free energy of reactions are sometimes tabulated as Giauque functions. These are Gibbs free energy functions that vary very slowly with temperature. Two such functions are in general use – the first is referred to 0 K and the second referred to 298 K. These are written as

$$\phi_0 = \frac{G_T^0 - H_0^0}{T}, \quad \phi_{298} = \frac{G_T^0 - H_{298}^0}{T}$$

29. What will happen if the system is not in chemical equilibrium?

If the system is not in chemical equilibrium, the reaction occurring must be irreversible and the total Gibbs free energy must decrease at constant temperature and pressure.

30. Define heterogeneous reaction equilibria.

In the study of heterogeneous reaction equilibria, we are concerned with a gas phase that is in equilibrium with a liquid or a solid phase. When the heterogeneous system is in equilibrium we would have to consider the equilibrium with respect to chemical reactions in the gas phase as well as the phase equilibria between the components in the gas phase and the liquid or the solid phase as the case may be.

31. What is the effect of presence of inert materials?

Diluting the reaction mixture with an inert material will increase the total number of moles in the reaction mixture. This will result in an increased conversion if v is positive. That is, if the reaction proceeds with an increase in the number of moles, presence of inerts in the system will increase the equilibrium yield. The presence of inerts will decrease conversion if the reaction is accompanied by a decrease in the number of moles, and the inerts present in the system will have no influence on the degree of completion if v is zero, if there is no change in the number of moles during a reaction.

32. What is effect of presence of excess of reactants?

When the reactants are not present in stoichiometric proportions, increasing the number of moles of the excess reactant will result in increase in the number of moles of the products and improved conversion of the limiting reactant at equilibrium.

33. What is the effect of addition of inert gas at constant volume?

When an inert gas is added to the system in equilibrium at constant volume, the total pressure will increase. But the concentrations of the products and reactants (i.e. ratio of their moles to the volume of the container) will not change.

34. What is the effect of addition of inert gas at constant pressure?

When an inert gas is added to the system in equilibrium at constant pressure, then the total volume will increase. Hence, the number of moles per unit volume of various reactants and products will decrease. Hence, the equilibrium will shift towards the direction in which there is increase in number of moles of gases.

35. What is the effect of presence of products?

If the initial reaction mixture contained any of the products of the reaction, then the number of moles of that product formed by the reaction so as to establish equilibrium will decrease. Therefore, the addition of the products to the original reactant stream decreases the equilibrium conversion.


## PART B

1. Methanol is produced by the following reaction: $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$. The standard heat of formation of $CO(g)$ and $CH_3OH(g)$ at 298 K are -110,500 J/mol and -200,700 J/mol respectively. The standard free energies of formation are -137,200 J/mol and -162,000 J/mol respectively. Calculate the standard free energy change and determine whether the reaction is feasible at 298K. Determine the equilibrium constant at 400 K assuming that the heat of reaction is constant. (May/June 2015, 2012,13) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.442)

2. Derive the effect of pressure and temperature on the equilibrium constants. (May/June 2012,13)(Nov/Dec 2008) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.419-421)

3. (i) Derive the equilibrium criteria for homogeneous chemical reactions. (8) (Nov 2009,10) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.402-404)

    (ii) Explain the factors affecting equilibrium conversion (8) (Nov 2009,10) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.422-423)

4. Prove that Ka = Kf = Kp with example. (Nov/Dec 2013) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.404-407)

5. A gaseous mixture containing 30% CO, 50% $H_2$ and the rest inert gas is sent to a reaction chamber for methanol synthesis. The following reaction occurs at 635 K and 310 bar.

    $$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$
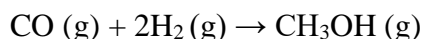
    Assuming that the gas mixture behaves as an ideal solution, calculate the percent conversion of CO given that $K_f = 5X\ 10^{-5}$ and $K\varphi = 0.35$. (May/June 2009) (Apr/May 2008)
    (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.444)

6. The standard heat of formation and standard free energy of formation of $NH_3$ at 328 K are
    -46,100 J/mol & 13,650 J/mol respectively. Calculate the equilibrium constant for the reaction. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ at 500 K assuming that the standard heat of reaction is constant in the temperature range of 328 K to 500 K. (Apr/May 2017)
    (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.417)


## PART – C

1. Explain how the equilibrium constants expressed for gas and liquid phase reactions. (Apr/May2017) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.404-407)

2. The gases from the pyrites burner of a contact sulphuric acid plant have the following composition: $SO_2 = 7.8\%$, $O_2 = 10.8\%$ and $N_2 = 81.4\%$. This is then passed into a converter where the $SO_2$ is converted to $SO_3$. The temperature and pressure in the converter are 775 K and 1 bar. The equilibrium constant for the reaction $SO_2 + 1/2\ O_2 \rightarrow SO_3$ may be taken as

Ke =85. Calculate the composition of gases leaving the converter. (May/Jun 2016) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.445)

3. What is the influence of temperature on equilibrium constant and derive Van't Hoff's equation.(Nov/Dec 2013) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.409-413)

4. (i) Describe the effect of reaction conditions on chemical equilibrium conversion.(Apr/May 2014) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.422-423)

   (ii) Derive the equation relating equilibrium constant and standard free energy change. (Apr/May 2014, 2010) (Narayanan K.V"A Text Book of Chemical Engineering Thermodynamics" Page No.413-415)

# UNIT V -THERMODYNAMIC DESCRIPTION OF MICROBIAL GROWTH AND PRODUCT FORMATION

## PART A

1. Mention the expression for Gibbs energy for thermodynamics of maintenance. (Apr/May 2017)

The expression for Gibbs energy for thermodynamics of maintenance is given by

$$\mu = \left[\frac{\left(-q_S^{max}\right)C_S}{K_S + C_S} - \left(-m_S\right)\right]Y_{SX}^{max}$$

- $C_S = 0$, $\mu = m_S Y_{SX}^{max} = -k_d$
- $C_S >>>$, $\mu = [-q_S^{max} - (m_S)]Y_{SX}^{max} = \mu^{max}$
- $\mu = 0$, $(-q_S) = (-m_S)$, which occurs at $C_S = C_S^{min}$.

2. Define specific growth rate. (Apr/May 2017)

It is defined as the rate of increase of biomass of a cell population per unit of biomass concentration. It can be calculated in batch cultures, since during a defined period of time, the rate of increase in biomass per unit of biomass concentration is constant and measurable.

3. What do you understand by Basal Metabolic rate? (May/June 2016)

Basal metabolic rate is the rate at which food is converted into heat transfer and work done while the body is at complete rest. The body adjusts its basal metabolic rate to compensate (partially) for over-eating or under-eating. The body will decrease the metabolic rate rather than eliminate its own fat to replace lost food intake.

4. Brief on Herbert-Pirt equation. (May/June 2016)

$$(-q_S) = \frac{\mu}{Y_{SX}^{max}} + (-m_S)$$

It means the substrates taken into cells are used for growth and maintenance only. Both $m_S$ and $Y_{SX}^{max}$ are model parameters.

### Herbert-Pirt relation for substrate

$$(-q_S) = \frac{\mu}{Y_{SX}^{max}} + (-m_S)$$

It means the substrate taken into cells are used for growth and maintenance only. Both $m_S$ and $Y_{SX}^{max}$ are model parameters.



Herbert-Pirt linear plot for substrate, non-catabolic product is absent
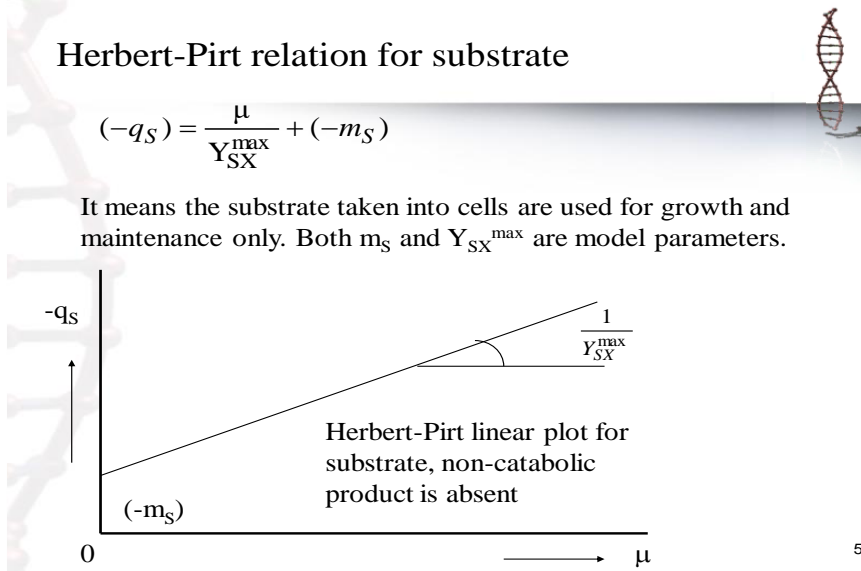
Combination of the $q_S$ equation with Herbert-Pirt relation

$$\mu = \left[\frac{\left(-q_S^{max}\right)C_S}{K_S + C_S} - \left(-m_S\right)\right]Y_{SX}^{max}$$

38

- $C_S = 0$ , $\mu = m_S Y_{SX}^{max} = -k_d$
- $C_S >>>$, $\mu = [-q_S^{max}-(m_S)]Y_{SX}^{max} = \mu^{max}$
- $\mu = 0$, $(-q_S) = (-m_S)$, which occurs at $C_S = C_S^{min}$.

  The specific growth rate equation based on single substrate is then:

  $$\mu = \mu^{max}\frac{C_S - C_S^{min}}{K_S + C_S}$$

5. Name the important parameters which describe growth of organism.

   Growth of organisms is usually described by four parameters which belong to the hyperbolic substrate uptake relation ($\mu^{max}$, $k_s$) and the Herbert-Pirt relation ($Y^{max}_{sx}$, $m_s$). The values of these four parameters are essential to design processes in which growing organisms are used.

6. Define heterotrophic growth.

   The biomass composition formula $C_1H_{1.8}O_{0.5}N_{0.2}$ shows that synthesis of biomass requires a carbon source and an N-Source. In addition there is a need for an electron donor (D). When growth uses an organic compound as substrate, then the substrate is both carbon and electron donor. This is called heterotrophic growth.

7. Define autotrophic growth.

   When growth uses $CO_2$ as C-Source, then there is a need for a separate electron donor to reduce $CO_2$ to biomass. This is called autotrophic growth.

8. Define operational yield.

   The operational yield $Y_{DX}$ (Cmol X/mol electron donor) is defined as the ratio of $\mu$ and $(-q_D)$:

   $$Y_{DX} = \frac{\mu}{-q_D} = Y_{DX}^{max}\left[\frac{\mu}{\mu+(-m_D Y_{DX}^{max})}\right]$$

9. Write the significance of operational biomass yield.

   The operational biomass yield $Y_{DX}$ is a hyperbolic function in $\mu$.

   At high $\mu$ : ($\mu >> (-m_D Y^{max}_{DX})$) the operational biomass yield approaches asymptotically the maximum yield.

   At low $\mu$ : ($\mu >> (-m_D Y^{max}_{DX})$) the operational biomass yield $Y_{DX}$ drops to zero.

   $$Y_{DX} = \frac{\mu}{-q_D} = Y_{DX}^{max}\left[\frac{\mu}{\mu+(-m_D Y_{DX}^{max})}\right]$$

10. Define Gibbs energy based coupling of catabolism to anabolism.

    In catabolism, an electron acceptor performs a redox reaction with an electron donor leading to the production of energy. This energy is coupled to anabolism to derive the anabolic reaction.

**Catabolism**

**Anabolism**
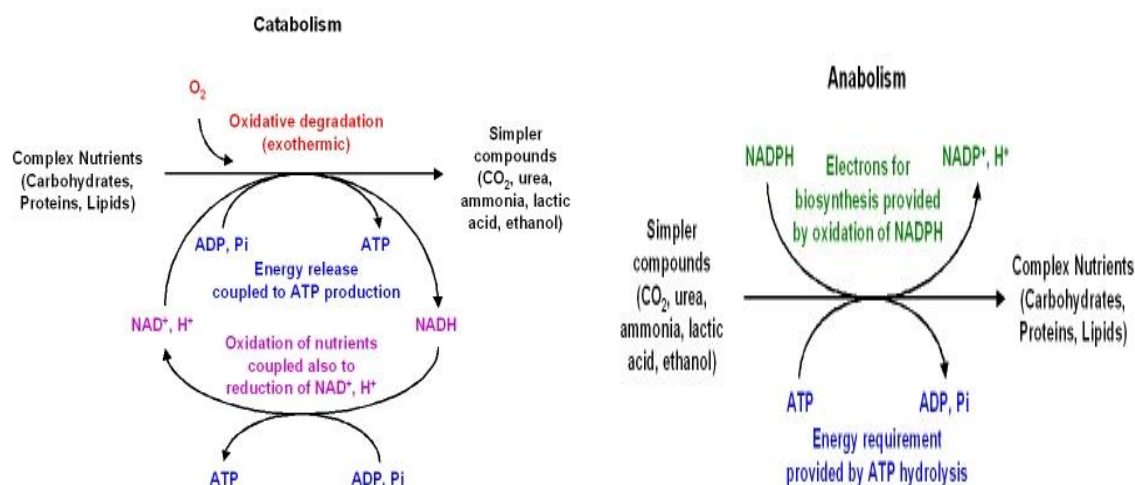
11. How Gibbs energy of a catabolic reaction is obtained?

The Gibbs energy of a catabolic reaction is obtained by first calculating the correct stoichiometry of the complete catabolic reaction for the consumption of 1 mol electron donor, after which are calculates $-\Delta G_R^{01} = \Delta G_{cat}^{01}$ (which is the produced catabolic energy under biochemical standard conditions.

12. Define biochemical standard conditions.

Biochemical standard conditions, indicated with superscript 01, (ie) 298 K, 1 bar, 1 mol/l, and pH 7 ($H^+$ concentration of $10^{-7}$ mol/l).

13. Write the equation for Heterotrophic growth.

a electron donor / C –source + b N- source + c$H^+$ + d$H_2O$ +e $CO_2$ + 1 $C_1H_{1.8}O_{0.5}N_{0.2}$ = 0

14. Write the equation for Autotrophic growth.

f $CO_2$ +a electron donor / C –source + b N- source + c$H^+$ + d$H_2O$ +e Oxidized electron donor + 1 $C_1H_{1.8}O_{0.5}N_{0.2}$ = 0.

15. Define degree of reduction.

Degree of reduction ($\delta_i$) is a stoichiometric quantity which can be calculated for each chemical compound for which the elemental composition is known. $\delta_i$ reflects the amount of electrons available in a compound.

16. How degree of reduction is calculated?

Degree of reduction $\delta_i$ is calculated by writing the redox half reaction in which compound i is converted in a set of reference compounds which are $CO_2$, $H_2O$, $H^+$, $Fe^{3+}$, $N_2$ and electrons. The amount of produced electrons equals $\delta_i$. Using this redox half reaction approach we can calculate the degree of reduction of elements and of electric charge.

17. How the complete stoichiometry of the anabolic reaction is obtained?

The complete stoichiometry of the anabolic reaction can be obtained from the elemental and charge balances and that it can be calculated from the balance of degree of reduction that the amount of electron donor needed in the anabolic reaction equals ($\delta_X / \delta_D$) mol electron donor / C mol X.

18. Write down the equations used to calculate the Gibbs energy of formation under nonstandard condition?

The effect of nonstandard concentration at 25°C on Gibbs energy of formation (KJ/mol) of a compound I follow from:

Dissolved compound: $\Delta G_{f_i} = \Delta G^0_{f_i} + RT \ln(C_i / 1)$

Gaseous compound    : $\Delta G_{f_i} = \Delta G^0_{f_i} + RT \ln(P_i / 1)$

Proton           : $\Delta G_{f_i} = -39.87 + RT \ln(H^+ / 10^{-7})$

$\Delta G_{f_i}$ is the Gibbs energy of formation.

$C_1/1$ is the dissolved concentration of compound i ($C_i$, mol/l) divided by the standard con. (1 mol/l)

$P_i/1$ is the partial pressure of compound I ($P_i$ atm), divided by the standard pressure (1 atm).

For $H^+$ the biochemical standard is at $H^+ = 10^{-7}$ M

19. How the effect of temperature on the Gibbs energy of formation is obtained?

The effect of temperature (at standard concentration, pressure) on the Gibbs energy of formation is obtained from the Van't Hoff relation

$$\Delta G^0_f(T) = \Delta H_i - T\Delta S^0_f$$

The value of the enthalpy of formation $\Delta H^0_f$ is obtained from the standard thermodynamic tables.

20. Define ETC.

ETC – Electron Transport Chain. The ETC consists of electron processing proteins embedded in membranes. Because cells are limited in the amount of membrane area and the amount of ETC protein which can be placed in membranes is also physically (space) limited it is to be expected that there is a limit in the electron transport rate per C mol X.

21. Define pmf.

Proton motive force (pmf). The pmf equals about 15 KJ of Gibbs energy for 1 mol $H^+$, and therefore one might expect that a catabolic reaction needs to generate at least 15 KJ of Gibbs energy in order to create pmf.

22. Define yield factor.

Yield factor is used to quantify the nutrient requirements and production characteristics of an organism.

23. Define Theoretical yield.

Theoretical yield is defined as the ratio of total mass or moles of product formed to mass or moles of reactant used to form that particular product.

24. Define apparent yield.

Apparent yield is defined as the ratio of mass or moles of product present to total mass or moles of reactant consumed.

41

25. Define observed yield.

Observed yield is particularly important for cell metabolism because there are always many reactions occurring at the same time. The observed biomass yield based on total substrate consumption is:

$$Y'_{XS} = \frac{-\Delta X}{\Delta S_T}$$

26. Define RQ.

RQ – Respiratory Quotient.

RQ = e / a

RQ is defined as the moles of $CO_2$ produced per mole of oxygen consumed. RQ values provide an indication of metabolic state and can be used in process control.

27. Define overall and instantaneous yields.

$\Delta F$ and $\Delta G$ can be calculated as the difference between initial and final values, this gives an overall yield. If $r_F$ and $r_G$ are volumetric rates of production and consumption of F and G. instantaneous yield may be calculated as follows:

$$Y_{FG} = \lim_{\Delta G \to 0} \frac{-\Delta F}{\Delta G} = \frac{-dF}{dG} = \frac{-dF/dt}{dG/dt} = \frac{r_F}{r_G}$$

28. Define $Y_{kcal}$.

$Y_{kcal}$ is defined as the ratio of mass or moles of biomass formed per kilocalorie of heat evolved during fermentation.

29. Define yield.

Yield is defined as the ratio of amount of product formed or accumulated per amount of reactant provided or consumed.

30. Define yield coefficient.

Yield coefficients can be written as,

$$Y_{FG} = \frac{-\Delta F}{\Delta G}$$

$Y_{FG}$ – yield factor. F and G are substances involved in metabolism

$\Delta F$ – mass or moles of F produced

$\Delta G$ – mass or moles of G consumed.

-ve sign is required because $\Delta G$ for a consumed substance is negative in value, yield is calculated as a positive quantity.

31. Define Catabolism.

Catabolism is the pathway that breaks down molecules into smaller units and produces energy.

32. Define Anabolism

Anabolism is the building up of molecules from smaller units. Anabolism uses up the energy produced by the catabolic break down of your food to create molecules more useful to your body.

33. Give some examples of anabolic products.

(i)     Amino acid

(ii)    Nucleotide

(iii)   Protein

(iv)    Antibiotic
(v)    lipid

34. Define doubling time.
Doubling time ($t_d$) is the time required for the concentration of biomass of a population of suspension cells to double. One of the greatest contrasts between the growths of cultured plant cells refers to their respective growth rates. The doubling time ($t_d$) can be calculated according to the following equation

$$td = \frac{\ln 2}{\mu}$$

35. Critical dilution rate
The maximal value for D ($=\mu$) attainable in the chemostat, is achieved when the maximal $C_S$ in achieved. At critical dilution rate, $C_S \rightarrow C_{S,in}$.

$$D_{crit} = \mu^{max} \frac{C_{S,in} - C_{S,min}}{K_S + C_{S,in}} \approx \mu^{max}$$

## PART B

1. Derive Herbert –Pirt Relation for electron donor consumption and explain the terms. (Apr/May 2017) (or) How to calculate the heat in operational stoichiometry using the Herbert –Pirt Relation for Electron Donor. (Christiana D. Smolke, Page no. 11.4 – 11.17)

2. Explain the thermodynamic relation to calculate the biomass yield on electron donar. (Apr/May 2017) (or) Discuss about the thermodynamics of microbial growth stoichiometry. (May/Jun 2016) (Christiana D. Smolke, Page no. 11.2-11.3)

3. Explain about the formation thermodynamics. (May/Jun 2016) (Explain thermodynamics and stoichiometry of Product Formation. (Christiana D. Smolke, Page no. 11.17-11.19)

4. Giving example find the stoichiometric coefficient for calculation of the anabolic reaction for autotrophic growth. (Christiana D. Smolke, Page no. 11.3-11.4)

5. Giving example find the stoichiometric coefficient for calculation of the anabolic reaction for heterotrophic growth. (Christiana D. Smolke, Page no. 11.3)

6. Calculate the stoichiometric coefficient and Gibbs free energy for catabolic reactions.

$$CH_4O + aNO_3^- + bH^+ + cN_2 + dHCO_3^- + eH_2O = 0$$
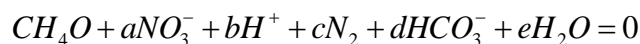
Data:

| Composition | $\Delta G_f^0$ (KJ/mol) |
|---|---|
| $H_2O$ | -237.18 |
| $HCO_3^-$ | -586.85 |
| $CO_2$ | -394.359 |
| $H^+$ | -39.87 |
| $CH_4O$ | -175.39 |
| $N_2$ | 0 |
| $NO_3^-$ | -111.34 |

(Christiana D. Smolke, Page no. 11.7-11.9)

## PART C

1. Explain in detail about calculation of the electron donor needed for anabolism using the balance of degree of reduction. (Christiana D. Smolke, Page no. 11.4-11.5)
2. Write short notes on the elemental balance used in stoichiometric calculations. (Apr/May 2015)(Class notes)
3. Write in detail about the correlations to find the amount of Gibbs energy generated in the anabolic reaction for the synthesis of 1 Cmol of synthesis.
   (Christiana D. Smolke, Page no. 11.10-11.12)

Reg. No. : ☐☐☐☐☐☐☐☐☐☐☐☐

## Question Paper Code : 71491

B.E./B.Tech. DEGREE EXAMINATION, APRIL/MAY 2017.

Fourth Semester

Biotechnology

BT 6402 – APPLIED THERMODYNAMICS FOR BIOTECHNOLOGISTS

(Regulations 2013)

Time : Three hours                                                Maximum : 100 marks

Answer ALL questions.

PART A — (10 × 2 = 20 marks)

1.   What are the limitations of first law of thermodynamics?

2.   What is 'equation of state'?

3.   What is mass and molar concentration?

4.   What are the significance of chemical potential?

5.   Define the term Phase equilibria.

6.   In liquid-liquid equilibrium curve, define plait point with neat sketch.

7.   When the chemical reaction attains equilibrium?

8.   For the gas phase reaction $C_2H_4 + H_2O \rightarrow C_2H_5OH$ the equilibrium constant at 145°C and 1 bar is $K = 6.8 \times 10^{-2}$, how would you calculate the equilibrium constant at 10 atm pressure?

9.   Mention the expression for gibbs energy for thermodynamics of maintainance.

10.  Define specific growth rate.

PART B — (5 × 13 = 65 marks)

11.  (a)   Deduce from fundamentals, the first law of thermodynamics for flow process.

Or

     (b)   Derive Maxwell equations and also mention the applications.

12. (a) Derive an expression for fugacity and fugacity coefficient of pure species.

Or

(b) Briefly derive the Gibbs Duhem equation.

13. (a) At 750mm Hg pressure, the A-B azeotrope boils at 65°C and contains 35 mole % of A. The vapour pressure of A and B are 1000 mm and 800 mm of Hg respectively at 65°C. Calculate the composition of vapour at this temperature in equilibrium with liquid analyzing 10 mole % of A. What is the total pressure at this condition?

Or

(b) Construct a P-X-Y diagram for the cyclohexane (i) benzene (ii) system at 313.15k, the vapor pressures are $P_1^a = 24.62$ kpa and $P_2^a = 24.41$ kpa. The liquid phase activity coefficients are given by ln $\gamma_1 = 0.458x_2^2$ and ln $\gamma_2 = 0.458x_1^2$.

14. (a) The standard heat of formation and std free energy of formation of $NH_3$ at 328k are −46,100 J/mol and 13,650J/mol respectively. Calculate the equilibrium constant for the reaction. $N_2(g) + 3H_2 \rightarrow 2NH_3$ at 500K assuming that the standard heat of reaction is constant in the temperature range of 328 K to 500 K.

Or

(b) Explain how the equilibrium constants expressed for gas and liquid phase reactions.

15. (a) Derive Herbert —Pirt relation for electron donar consumption and explain the terms.

Or

(b) Explain the thermodynamic relation to calculate the biomass yield on electro donar.

PART C — (1 × 15 = 15 marks)

16. (a) A solution consists of 40% methanol (species 1) and 60% water (species 2). Assume that methanol is completely miscible in water and that the solution behaves according to Raoult's Law. The saturation pressure correlations for the pure components are ln $P_1^S = 20.61 - 4719.2/T$.

ln $P_2^S = 20.60 - 5205.2/T$

(i) If the temperature is maintained at 20°C, at what pressure will a vapour bubble begin to form?

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71491

(ii) At this pressure and at 20°C, determine the ratio of moles of vapour in the vapour-liquid mixture and the vapour phase composition?

(iii) At 20°C, what is pressure at which virtually the entire liquid has vapourized? Determine the liquid composition and the quality at this pressure?

Or

(b) Describe the relationship for Solid- Liquid and Solid —Vapour phase transition.

Reg. No. ☐☐☐☐☐☐☐☐☐☐☐

**Question Paper Code : 57123**

PART – A (10 × 2 = 20 Marks)

1.   Discuss on volume expansivity.

2.   Define the principle of corresponding states.

3.   Differentiate between Clayperon and Clausius - Clayperon equations.

4.   State the fugacity criterion for phase equilibrium.

5.   Differentiate bubble point & dew point temperature.

6.   What is an azotrope ? Under what conditions do azeotropes generally form ?

7.   Define partial molar property.

8.   Define equilibrium constant $K_e$ of a chemical reaction. How is it related to $K_f$ and $K_p$ ?

9.   What do you understand by Basal Metabolic Rate ?

10.  Brief on Herbert-Pirt equation.

## PART – B (5 × 16 = 80 Marks)

11. (a) Air initially at 390 K and 8 bar is expanded reversibly and isothermally to such a pressure that when it is cooled to 340 K at constant volume its pressure is 2 bar. Calculate the work, heat transferred, charge in internal engines and change in enthalpies. Assume air to be ideal gas. (16)

### OR

(b) A 0.017 $m^3$ tank contains 1 kg of refrigerant-134a at 110 °C. Determine the pressure of the refrigerant, using (1) the ideal-gas equation, (2) the generalized compressibility chart, and (3) the refrigerant tables. (16)

12. (a) Find the van Laar constants for the binary system benzene (1)-ethanol (2) using the following data : (16)

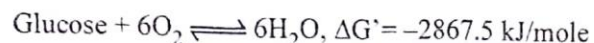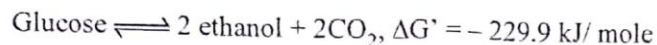| $x_1$ | 0.1 | 0.3 | 0.45 | 0.7 | 0.9 |
|---|---|---|---|---|---|
| $p_1^s$ kPa | 73.31 | 68.64 | 63.98 | 67.98 | 81.31 |
| $p_2^s$ kPa | 75.98 | 69.64 | 67.98 | 69.31 | 79.98 |

### OR

(b) Two substances A and B are known to form ideal liquid solutions. A vapour mixture containing 50% (mol) A and 50% B is at 311 K and 101.3 kPa. This mixture is compressed isothermally until condensation occurs. At what pressure, does condensation occur and what is the composition of the liquid that forms ? The vapour pressures of A and B are 142 kPa and 122 kPa respectively. (16)

13. (a) A vapour mixture containing 18% ethane, 17% propane, 62% isobutene and the rest n-butane is subjected to partial condensation so that 75% of the vapour is condensed. If the condenser temperature is 300 K, determine the pressure. (16)

### OR

(b) At 300 K, the vapour pressure of benzene (A) and toluene (B) are 16 kPa and 5 kPa respectively. Determine the partial pressures and weight composition of the vapour in equilibrium with a liquid mixture consisting of equal weights of the two components. (16)

57123

14. (a) Given the following information:

Glucose $\rightleftharpoons$ 2 ethanol + $2CO_2$, $\Delta G^{\grave{}} = -229.9$ kJ/ mole

Glucose + $6O_2$ $\rightleftharpoons$ $6H_2O$, $\Delta G^{\grave{}} = -2867.5$ kJ/mole

Calculate the number of moles of $\Delta TP$ that could be synthesized from ADP + Pi upon complete oxidation of one mole of ethanol to $2CO_2 + 3H_2O$. Assume an efficiency of energy conservation of 44% under standard conditions. The synthesis of ATP requires 32340 Joules/mole. (16)

**OR**

(b) The gases from the pyrites burner of a contact sulphuric acid plant have the following composition: $SO_2 = 7.8\%$, $O_2 = 10.8\%$ and $N_2 = 81.4\%$. This is then passed into a converter where the $SO_2$ is converted to $SO_3$. The temperature and pressure in the converter are 775 K and 1 bar. The equilibrium constant for the reaction

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$
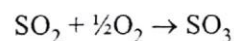
may be taken as $K_e = 85$. Calculate the composition of gases leaving the converter. (16)

15. (a) Discuss about the thermodynamics of microbial growth stoichiometry. (16)

**OR**

(b) Explain about the formation thermodynamics. (16)

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Reg. No. : ☐☐☐☐☐☐☐☐☐☐☐☐☐

Question Paper Code : 77046

B.E./B.Tech. DEGREE EXAMINATION, APRIL/MAY 2015.

Fourth Semester

Biotechnology

BT 6402 — APPLIED THERMODYNAMICS FOR BIOTECHNOLOGISTS

(Regulation 2013)

Time : Three hours                                    Maximum : 100 marks

Answer ALL questions.

PART A — (10 × 2 = 20 marks)

1. Distinguish between internal energy, kinetic energy and potential energy of a system.

2. What are the Maxwell's equations and what is their importance in establishing relationships between thermodynamic properties?

3. Distinguish between molar volume and partial molar volume. Does the partial molar volume of a substance vary with concentration of the substance in the solution.

4. Define chemical potential. What is its physical significance?

5. What is critical solution temperature?

6. Write down the equation for solving general VLE problem.

7. What is reaction coordinate? What is its significance in chemical reaction?

8. What is the effect of pressure on equilibrium conversion of a gas-phase chemical reaction?

9. Define ATP yield coefficient.

10. List the functions of NADH.

PART B — (5 × 16 = 80 marks)

11. (a) (i) Define Joule-Thomson coefficient and explain how it could be used for determining the heat capacity of gases.                    (8)

    (ii) Derive an expression for fugacity coefficient of a gas obeying the equation of state $z = a + bP + cP^2$, where P is in bar. Determine fugacity of oxygen at 293 K and 100 bar, given that $a = 1.0$; $b = -0.753 \times 10^{-3}$, and $c = 0.15 \times 10^{-5}$.                    (8)

Or

(b) (i) Express the volume expansivity and the isothermal compressibility as functions of density p and its partial derivatives. For water at 50°C and 1 bar, $K_T = 44.18 \times 10^{-6}$ bar$^{-1}$. To what pressure must water be compressed at 50°C to change its density by 1%. Assume $K_T$ to be independent of pressure. (8)

(ii) With the help of Maxwell equations prove that the specific heats of ideal gases are functions of temperature only. (8)

12. (a) (i) Describe schematically an experimental technique for the determination of volume change and enthalpy change on mixing. (8)

(ii) A vessel is divided into two parts. One part contains 2 mol nitrogen gas at 353 K and 40 bar and other contains 3 mol argon gas at 423 K and 15 bar. If the gases are allowed to mix adiabatically by removing the partition determine the change in entropy. Assume that the gases are ideal and Cv is equal to 5/2 R for nitrogen and 3/2 R for argon. (8)

Or

(b) (i) Discuss the variable pressure and variable temperature modifications of Gibbs- Duhem equations. (8)

(ii) The enthalpy of a binary liquid mixture containing components 1 and 2 at 298 K and 1.0 bar is given by

$$H = 400x_1 + 600x_2 + x_2 + x_1x_2(40x_1 + 4x_2)$$

where H is in J/mol, Determine

(1) Pure component enthalpies and

(2) Partial molar enthalpies. (8)

13. (a) (i) Water (1) - hydrazine (2) system forms an azeotrope containing 58.5 % (mol) hydrazine at 393 K and 101. 3 kPa. Calculate the equilibrium vapour composition for a solution containing 20 % (mol) hydrazine. The relative volatility of water with reference to hydrazine is 1.6 and may be assumed to remain constant in the temperature range involved. The vapour pressure of hydrazine at 393 K is 124.76 kPa. (8)

(ii) Construct the P-x-y diagram for the cyclohexance (1) - benzene (2) system at 313 K the vapour pressures are $P_1^5 = 24.62\,kPa$ and $P_2^5 = 24.41\,kPa$. The liquid-phase activity coefficients are given by

$$ln\ \gamma_1 = 0.458x_2^2,\ ln\ \gamma_2 = 0.458x_1^2.$$ (8)

Or

(b) (i) Liquids A and B form an azeotrope containing 46.1 mole per cent A at 101.3 kPa and 345 K. At 345 K, the vapour pressure of A is 84.8 kPa and that of B is 78.2 kPa, Calculate the Van Laar constants. (8)

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(ii) A vapor mixture of 20 mole percent methane, 30 mole percent ethane and 50 mole percent propane is available at 30°C. Making use of the K factors determine the pressure at which condensation begins if the mixture is isothermally compressed. Also estimate the composition of the first drop of liquid that forms. (8)

14. (a) (i) In a chemical laboratory, it is proposed to carry out the reaction

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$
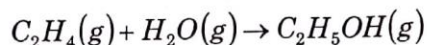
at 1 bar and 298 K. Calculate the standard Gibbs free energy change at 298 K and predict whether it is feasible to carry out the given reaction or not. Also calculate the equilibrium constant. (8)

(ii) Describe the factors affecting equilibrium conversion. (8)

Or

(b) (i) The equilibrium constant for the reaction $A \rightarrow B$ is doubled when temperature is changed from 25°C to 35°C. Calculate the enthaply of reaction. (8)

(ii) Methanol is produced by the following reaction :
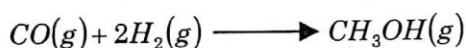
$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(g)$$

Standard heat of formation of CO (g) and CH₃OH (g) at 298 K are −110,500 J/mol and 200,700 J/mol respectively. The standard free energies of formation are −137,200 J/mol and 162,000 J/mol respectively.

(1) Calculate the free energy change and determine whether the reaction is feasible at 298 K.

(2) Determine the equilibrium constant at 400 K assuming that the heat of reaction is constant.

15. (a) (i) Describe briefly about the functions of ATP and NADH in the metabolic pathway. (8)

(ii) Write short notes on the elemental balance used in Stoichiometric calculations. (8)

Or

(b) (i) Discuss about the oxygen consumption and heat evolution in aerobic cultures. (8)

(ii) Estimate the theoretical growth and product yield coefficients for ethanol fermentation by S.cerevisiae as described by the following overall reaction.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2.$$ (8)