## GATEway to Chemical Engineering



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# GATEway to Chemical Engineering 

Volume 1<br>Process Calculations<br>Thermodynamics

(Useful for GATE and other Aptitude Tests)

m subbu<br>d k sandilya

# GATEway to Chemical Engineering (Vol-1) 

## m subbu <br> d k sandilya

2018

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## About the Book Volumes

This book GATEway to Chemical Engineering is a set of 5 volumes:

| Volume | Subjects Covered | Authors |
| :---: | :--- | :--- |
| 1 | Process Calculations, Thermodynamics | m subbu \& d k sandilya |
| 2 | Fluid Mechanics, Mechanical Operations, <br> Mathematics | mubbu \& r pavan |
| 3 | Heat Transfer, Mass Transfer | m subbu \& k nagarajan |
| 4 | Chemical Reaction Engineering, Process <br> Control | m subbu \& d k sandilya |
| 5 | Process Economics, Equipment Design, <br> Chemical Technology | m subbu \& s siddarth |

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R. Pavan Kumar (r pavan) is a chemical engineering graduate from SSN CE. He is currently working for BPCL. He had secured AIR 87 in GATE-2017. He is also a budding engineer who is enthusiastic to investigate diverse aspects of chemical engineering and is fascinated to acquire a realistic exposure to supplement his understanding of subjects. He is a co-author of the book GATEway to General Aptitude.

## FOREWORD

I have known the authors, $m$ subbu, $\mathrm{d} k$ sandilya, and k nagarajan, almost for the past 15 years and am well familiar with their interests and abilities since they used to interact with me both professionally and personally during their doctoral study times at IIT Madras. Dr. M. Subramanian (m subbu) used to discuss with me his research topic on photocatalysis, attend my classes on Chemical Reactor Theory at the masters' level, and take necessary inputs from me as and when required. Dr. D. Krishna Sandilya (d k sandilya) was helping me as a teaching assistant (TA) for the course of Chemical Reactor Theory. He used to solve every problem of Levenspiel and was closely following the developments in the field of Chemical Engineering. Dr. K. Nagarajan was doing Ph.D under my supervision in the area of Fluidization. He was doing his experiments enthusiastically and systematically. Each of these authors used to share their understanding of the Chemical Engineering subjects with me and was found to be having good knowledge with a keen interest towards teaching career. Based on my observation during the constant interaction sessions with the above authors, I believe that they are teaching at their respective institutes with good enthusiasm by citing contemporary examples which can give clear understanding of the concepts.

I came to know about the other two authors, Mr. S. Siddarth \& Mr. R. Pavan Kumar, through Dr. M. Subramanian. They, along with Dr. M. Subramanian, have done an excellent job of solving, compiling and presenting with nice illustrations, the general aptitude aspects of GATE in their book titled "GATE way to General Aptitude". I could learn that these two authors during their time as students at SSN, Chennai had undergone meticulous preparation for GATE, thereby getting a position in IOCL and BPCL respectively, the dream jobs of every aspiring chemical engineer.

I could go through the salient aspects of the book "GATEway to Chemical Engineering" which is logically spread over five volumes. I also observed that the book is presented in a systematic manner, in the form of methodical approach to solutions of GATE-Chemical Engineering questions and questions from other relevant streams of GATE. The solutions to problems are explained with suitable illustrations and well-drawn diagrams, wherever necessary. The title GATEway to (understand) Chemical Engineering is really suitable for this book because of rationally explained solutions to the wise and tricky questions of GATE, covering the important features of each subject of Chemical Engineering by the authors. The added beauty of this assiduous project is brought out in terms of legible text and figures because of the typesetting tool $\mathrm{EA}_{\mathrm{E}} \mathrm{X}$. I am sure this book will be of immense use for every chemical engineer, for sharpening his/her knowledge.

I wish the authors and readers of the book, to have a wonderful future! Happy reading!

Prof. Dr. K. Krishnaiah

Professor and Dean (Academic Affairs), IIT Tirupati
Former Professor \& Dean (Academic Research), IIT Madras
Former Emeritus Professor of Chemical Engineering, IIT Madras

## PREFACE

Having a good grasp of the core subjects of engineering and the ability to use this knowledge wisely in order to understand, and solve new engineering and societal problems are desirable characteristics of a smart engineer. Recognizing the connection between the core subjects by means of learning several concepts in a holistic manner paves the way for a professional to be evolved out of an engineer. Chemical Engineering is a fascinating branch of engineering that deals with the profession of utilizing different forms of materials and energy to economically produce a variety of useful products on a commercial scale by means of conducting several physical and chemical operations in a safe and reliable manner. The primary goal of Chemical Engineering discipline, which is in almost 131 years of existence by now, is to benefit the mankind.

Graduate Aptitude Test in Engineering (GATE) is an annual examination conducted jointly by the premier institutes of India, viz. the Indian Institute of Science (IISc), Bangalore and the Indian Institutes of Technology (IITs) at Bombay, Delhi, Guwahati, Kanpur, Kharagpur, Madras, and Roorkee, on behalf of the National Coordination Board (NCB) GATE, MHRD, Government of India. GATE tests a candidate's complete understanding of a variety of undergraduate subjects in Engineering. The sharpness of an engineering graduate in the application of his/her knowledge to new situations is also aptly tested in GATE. The syllabus of the examination covers the relevant core subjects of that particular stream. Preparing for this examination is a good experience for any engineering graduate, in recollecting the fundamentals and understanding the connections between subjects. The questions asked in GATE are uniquely designed to test the conceptual understanding of the candidate rather than testing his/her memory.

Qualifying GATE examination is a prerequisite for getting admission into higher studies at reputed institutes of India. Marks/Score of GATE examination is also considered as the screening criterion for getting placements in top-notch public sector undertakings (PSU) of India. In other words, GATE is considered as a gateway for entering into elite institutes offering higher studies and/or getting placed in dream companies.

The book titled "An Insight into Chemical Engineering", written by the first author of this book (m subbu) which was published in the year 2003, covered the solutions for GATE questions of 1988-1999 along with brief notes. It was well acknowledged by the chemical engineering community of India for the clarity and concise presentation of the subject. Motivated by this appreciation received, the impetus for writing the present book titled GATEway to Chemical Engineering was conceived.

This book covers all the core subjects of chemical engineering. Theory in a concise manner for the essential topics with suitable illustrations is provided for 11 subjects of Chemical Engineering and Mathematics in the form of "Instant Notes" for ready reference. It is assumed that the reader has already gone through the core subjects in detail. With that in mind, only the key points are touched up on in the notes. Otherwise also, an intelligent reader can understand the concepts presented even on the first reading of this book. However, wherever required, elaborate notes on certain concepts is provided.

The theory of each subject is followed by "Objective Types Questions" and "Problems with Solutions" sections. The present book covers solutions to questions of GATE 20002018 of chemical engineering ( CH ) stream, augmented by selected questions of other related
streams such as engineering sciences (XE), mechanical engineering (ME), metallurgy (MT), civil engineering (CE), biotechnology (BT), petroleum engineering (PE), production and industrial engineering (PI), electrical engineering (EE), instrumentation engineering (IN) etc. This demonstrates the prowess and universality of chemical engineering principles. "Objective Type Questions" section includes theoretical questions and short numerical questions. The "Problems with Solutions" section contains slightly lengthy problems, provided with suitable explanations, which can be solved in a few minutes. As a supplement, typical questions from other sources are also included with solutions. For a detailed study, reference books for each core subject are suggested in "References". All these factors mentioned make the contents of the book GATEway to Chemical Engineering spread across a set of 5 volumes, with logical split of volumes that ensures sequential grouping of subjects in each volume.

Multiple choice questions of theoretical type will be much useful in the preparation for viva voce examinations or any interview/selection process of core jobs. The numerical questions will help the reader to understand, formulate and solve problems encountered in core jobs. The book will be useful for practicing chemical engineers/chemists as well as engineers from other related disciplines working in chemical process industries. The book may also be useful for those who are preparing for The Principles and Practice of Engineering (PE) exam conducted by the National Council of Examiners for Engineering and Surveying (NCEES).

## This book is best useful for:

- GATE aspirants, to understand the nature of questions.
- Teachers, to formulate good questions.
- Undergraduate $2^{\text {nd }}, 3^{\text {rd }}$ and final year students, for enhancing their understanding of the core concepts.
- Industry professionals and graduates, in refreshing their basics.

In a nutshell, the objective of this book to sharpen the chemical engineering community by creating intelligent and prudent chemical engineers, by way of exposing them to nice and wise questions of GATE.

All errors are, of course, our own responsibility. The authors would be thankful to hear from the reader, if any mistake is found by him/her.

## ACKNOWLEDGEMENTS

We would like to acknowledge many people who directly or indirectly helped us in the writing of this book. First and the foremost, we thank the authorities of GATE for forming excellent, unique and interesting questions, which form the base of this book. MS (m subbu), DKS (d k sandilya), and KN (k nagarajan) gratefully acknowledge their professors and mentors, Prof. A. Kannan, IIT Madras and Prof. K. Krishnaiah, IIT Tirupati for providing intellectual guidance in teaching and research and extending moral support.

MS extends his warm appreciation to his wife, Mrs. S. Panchi Subramanian, for her incessant motivation and frequent monitoring of the progress of work. MS also recognizes the understanding nature of his sons, Master S. P. Rishal and Master S. P. Rithish, who were extremely patient about his many evenings and holidays providing him more time to contribute for this book writing project.

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MS feels happy to acknowledge the careful reading of the drafts of solutions and suitable suggestions, provided by Mr. S. Siddarth (SS) and Mr. R. Pavan Kumar (RPK), who are the co-authors of this book, during their time at SSN as students, which improved the arrangement of problems presented. MS thanks the students of SSN, viz. Mr. R. Suriya Narayanan, Mr. G. Sudarshan, Mr. B. Sai Ganesh, Mr. Srinivas Sivaraman, Ms. V. Priyadarshini, Ms. G. Shanmugapriya, and many others of 2015-2019 batch, and other batches for going through the book contents in detail and pointing out the mistakes. MS would like to thank the encouragement provided by the chemical engineering community across the world, through his website: www.msubbu.in.

DKS feels fortunate to have MS as his close companion since 2005, from whom, he received vital care and affection whenever required. During a crucial stage of this mega bookwriting project, when DKS went through some unfortunate suffering, MS extended his earnest warmth and stood by him, in the form of relaxing the deadlines to finish major portions of the manuscript. DKS also appreciates the tolerance evinced by MS during that tough time.

DKS expresses gratitude to his colleagues, Dr. P. Srinivas, Dr. Suman Dutta, Mr. Suresh Kumar Yatirajula, Mr. L. D.N.V.V. Konda, and Mr. Paidinaidu Paluri, at IIT(ISM), Dhanbad, for the encouragement and support received from them.

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All the authors would like to sincerely thank the respective management, faculty, staff and students of: (i) Sri Sivasubramaniya Nadar (SSN) College of Engineering, Chennai, (ii) Indian Institute of Technology (ISM) Dhanbad, and (iii) Rajalakshmi Engineering College, Chennai, for the facilities furnished and support extended.

Finally, we would like to thank the community of $\mathrm{EA}_{\mathrm{E}} \mathrm{X}$ users for providing the necessary help accessible through the internet.

We are indebted to the teachers who first introduced us to this wonderful subject of Chemical Engineering and to the pioneers and luminaries of the Chemical Engineering discipline, whose research papers have contributed enormously to our understanding of the subject. Finally, we thank The ALMIGHTY for providing us with the vigour required to execute this vital project.

We dedicate this book to our family members for their unvarying love and constant support.

Date: 24-August-2018
Chennai
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d k sandilya
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s siddarth
r pavan

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- Tie Substances: Tie material is defined as the material, of necessarily inert or unreactive, which passes through a system from a single input stream to a single output stream, and of course remains completely unchanged during this process.
- The term 'composition on a wet basis' is commonly used to denote the component mole fraction of a gas that contains water, and the composition on a dry basis signifies the component mole fractions of the same gas without water.
- Limiting and Excess Reactants: The reactant that is completely consumed when a reaction is run to completion is known as the limiting reactant. The other reactants are termed as excess reactants.
- To find the limiting reactant: First, balance the stoichiometric equation. Then, take the ratio of the reactant feed rate to their stoichiometric coefficients. The limiting reactant is the reactant that has the lowest ratio.
- Fractional excess: The fractional excess of a reactant is the ratio of excess to the stoichiometric requirement.

$$
\begin{equation*}
\text { Fractional excess of } A=\frac{n_{A} \text { in feed }-n_{A} \text { stoichiometric }}{n_{A} \text { stoichiometric }} \tag{3}
\end{equation*}
$$

' $n_{A}$ ' is the number of moles of $A$-the reactant. ' $n_{A}$ stoichiometric' is the amount of $A$ needed, to react completely with the limiting reactant.

Example: Two moles of nitrogen $\left(\mathrm{N}_{2}\right)$ react with four moles of hydrogen $\left(\mathrm{H}_{2}\right)$ to form ammonia $\left(\mathrm{NH}_{3}\right)$. The reaction is:

$$
\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightarrow 2 \mathrm{NH}_{3}
$$

The ratio of reactant amount to their stoichiometric coefficients:

$$
\mathrm{N}_{2}=\frac{2}{1}=2 \quad \mathrm{H}_{2}=\frac{4}{3}=1.33
$$

The ratio for $\mathrm{H}_{2}$ is the least; therefore, $\mathrm{H}_{2}$ is the limiting reactant.
Stoichiometric $\mathrm{N}_{2}$ requirement: 3 mole of $\mathrm{H}_{2}$ demands 1 mole of $\mathrm{N}_{2}$. Therefore, for 4 mole of $\mathrm{H}_{2}$, the requirement of $\mathrm{N}_{2}=4 / 3$ mole.

$$
\% \text { excess of } \mathrm{N}_{2}=\frac{2-\frac{4}{3}}{\frac{4}{3}} \times 100=50 \%
$$

- Incomplete Reactions: Chemical reactions are generally not complete; that is, even the limiting reactant is not completely used up. This idea is expressed as percent completion, and it is important to note that this completion must be based on the limiting reactant.
- Percent Excess: Percent excess of excess reactant is based on the $100 \%$ completion of the limiting reactant.
- The distinction of constant volume and constant pressure processes is not so important in the case of liquids and solids, as they expand very little with increase in temperature. Hence, for all sensible heating processes (i.e., constant pressure or constant volume heating), simply $C_{P}$ (specific heat at constant pressure) is used.
- The specific heats of solids are lower than those of liquids.
- Specific heat $\left(C_{P}\right)$ is a function of temperature, normally given as

$$
C_{P}=a+b T+c T^{2}
$$

Enthalpy change for sensible heating process is calculated from

$$
\Delta H=\int_{T_{1}}^{T_{2}} C_{P} d T
$$

$T$ values should be used in the unit as specified in the expression of $C_{P}$. For example, in the integrated expression with $T^{2}$, the value in Kelvin scale and Celsius scale give very different values for $T_{2}^{2}-T_{1}^{2}$.
Whereas, if $C_{P}$ is a constant with $T$, then we get $\Delta H=C_{P} \Delta T=C_{P}\left(T_{2}-T_{1}\right)$. Here, $\Delta T$ in ${ }^{\circ} \mathrm{C}$ and K scale are the same.

- Kopp's Rule: It is a simple empirical method for estimating the heat capacity of a solid or liquid at or near $20^{\circ} \mathrm{C}$. According to this rule, $C_{P}$ for a molecular compound is the sum of contributions for each elements in the compound.

$$
C_{P}=\sum_{i} \nu_{i} C_{P, i}
$$

where $\nu_{i}$ is the number of gram atoms of element $i$ in the compound. The specific heat of the elements ( $C_{P, i}$ ) in $\mathrm{J} /$ gram atom. ${ }^{\circ} \mathrm{C}$ are given as below:

|  | C | H | B | Si | O | F | P | S | All others |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Solid | 7.5 | 9.6 | 11 | 16 | 17 | 21 | 23 | 26 | 26 |
| Liquid | 12 | 18 | 20 | 24 | 25 | 29 | 31 | 31 | 33 |

For example, for liquid water $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ :

$$
C_{P}=2 \times 18+1 \times 25=61 \mathrm{~J} / \mathrm{mol} . \mathrm{K}=3.39 \mathrm{~J} / \mathrm{g} \cdot{ }^{\circ} \mathrm{C}
$$

whereas, the experimental value is $4.184 \mathrm{~J} / \mathrm{g} .{ }^{\circ} \mathrm{C}$.

- Heat of Formation: The standard heat of formation $\left(\Delta H_{f}^{\circ}\right)$ is the enthalpy for the formation of 1 mole of a compound from its constituent elements as they normally occur in nature $\left(\mathrm{C}(\mathrm{s}), \mathrm{O}_{2}(\mathrm{~g}), \mathrm{N}_{2}(\mathrm{~g}), \mathrm{H}_{2}(\mathrm{~g})\right.$ are the most important elemental constituents). For example

$$
\mathrm{C}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})
$$

The reactants and products must be at $25^{\circ} \mathrm{C}$ and 1 atm . The reaction may not represent a real reaction. The standard heat of formation of elemental species, in their naturally occurring state, is zero.


Molecular weight of anhydrous salt $=135$
Molecular weight of penta hydrate crystal $=135+5 \times($ MW of water $)$

$$
=135+5 \times 18=225
$$

Mass balance: Basis 100 kg of $F$
Overall balance:

$$
\begin{equation*}
F=P+M \quad \Longrightarrow \quad 100=P+M \tag{1}
\end{equation*}
$$

Balance on anhydrous salt:

$$
\begin{align*}
100 \times 0.4 & =P \times \frac{135}{225}+M \times 0.2 \\
& \Longrightarrow \quad 40=0.6 P+0.2 M  \tag{2}\\
(1) \times 0.6-(2) & \Longrightarrow \quad 20=0.4 M \quad \Longrightarrow \quad M=50 \mathrm{~kg} \\
& \Longrightarrow \quad P=F-M=100-50=50 \mathrm{~kg}
\end{align*}
$$

Hence, for a $P$ of $100 \mathrm{~kg} / \mathrm{s}, F=2 \times 100=200 \mathrm{~kg} / \mathrm{s}$.

## 3 Energy Balance

12. For estimation of heat capacity of a solid compound, one can use
(a) Clapeyron's equation
(b) Gibb's equation
(c) Kopp's rule
(d) Trouton's rule
(c) $\checkmark$ Explanation: Kopp's rule is an empirical formula for estimating heat capacity of solid and liquid compounds based on the data of specific heat of constituent elements. Clapeyron equation is fundamental form of vapor pressure vs. temperature relation. Trouton's rule is an empirical equation for finding the latent heat from normal boiling point data.
13. For the case of fuel gas undergoing combustion with air, if the air/fuel ratio is increased, the adiabatic flame temperature will (G-2001-1.05)

Rearranging, we get

$$
1.36 f=0.36 F
$$

Solving, we get $f / F=\mathbf{0 . 2 7}$.

## Example 3: Metal Recovery Unit

A metal recovery unit (MRU) of intake capacity $5000 \mathrm{~kg} / \mathrm{h}$ treats a liquid product from a plant and recovers $90 \%$ of the metal in pure form. The unrecovered metal and its associated liquid are sent to a disposal unit along with the untreated product from the plant (See figure below). Find the flow rate ( $m_{6}$ ) and the weight fraction of the metal ( $w_{6}$ ). The liquid product flow rate is $7500 \mathrm{~kg} / \mathrm{h}$ of composition 0.1 (wt fraction). Assume steady state. (G-2005-41)

(a) $m_{6}=7500 \mathrm{~kg} / \mathrm{h}, w_{6}=0.0$
(b) $m_{6}=7050 \mathrm{~kg} / \mathrm{h}, w_{6}=0.04255$
(c) $m_{6}=4500 \mathrm{~kg} / \mathrm{h}, w_{6}=0.1712$
(d) $m_{6}=5600 \mathrm{~kg} / \mathrm{h}, w_{6}=0.0314$

## Solution:

Given: Intake capacity of MRU $=m_{2}=5000 \mathrm{~kg} / \mathrm{h} ; 90 \%$ of solid in $m_{2}$ is recovered; and solid in $m_{2}=5000 \times 0.1=500 \mathrm{~kg} / \mathrm{h}$.

Pure metal:

$$
m_{4}=500 \times 0.9=450 \mathrm{~kg} / \mathrm{h}
$$

From overall mass balance:

$$
\begin{aligned}
m_{1} & =m_{4}+m_{6} \\
\text { i.e., } \quad 7500 & =450+m_{6} \\
\Longrightarrow \quad m_{6} & =7050 \mathrm{~kg} / \mathrm{h}
\end{aligned}
$$

From metal balance:

$$
\begin{aligned}
m_{1} w_{1} & =m_{4} w_{4}+m_{6} w_{6} \\
7500 \times 0.1 & =450 \times 1+7050 \times w_{6} \\
w_{6} & =0.04255
\end{aligned}
$$


$\Delta U=Q-W$
(i) Positive heat in, positive work out (Sign convention-1)


$$
\Delta U=Q+W
$$

(ii) Positive heat in, positive work in (Sign convention-2)

Figure 7: First law - Sign Conventions
where $\Delta U$ is the change in internal energy of the system; $\Delta E_{k}$ is the change in kinetic energy of the system; $\Delta E_{p}$ is the change in potential energy of the system; and, $Q$ and $W$ are heat and work interactions between the system and surrounding.

- In many applications of the first law, the system undergoes no change in external potential or kinetic energy, but only changes in internal energy. Under these conditions, the first law becomes:

$$
\begin{equation*}
\Delta U=Q+W \tag{11}
\end{equation*}
$$

## - Sign Conventions for Heat and Work

There are two sign conventions in common use, as represented in Fig.(7). According to the first convention,

$$
\Delta U=Q-W
$$

Here, $W=\int P d V$. i.e., work done by the system is positive.
According to the second convention (In this book this second convention is used),

$$
\Delta U=Q+W
$$

Here, $W=-\int P d V$. i.e., work done on the system is positive.

- Enthalpy

Enthalpy, denoted as $H$, is defined as below:

$$
\begin{equation*}
H=U+P V \tag{12}
\end{equation*}
$$

The quantity $P V$ is called as flow energy; the significance of which will be introduced shortly.

## Relation between Specific Heat and Energy Quantities

- Relation between $d U$ and $C_{V}$

For a constant volume process, the work of expansion is zero. Hence the first law reduces to

$$
d U=d Q \quad(\text { at constant } V)
$$

(iii) $\lambda=\Delta H^{\alpha \beta}=$ constant. Latent heat of vaporization $(\lambda)$ is assumed to remain constant for small changes in $T$.

$$
\ln \frac{P_{2}^{\text {sat }}}{P_{1}^{\text {sat }}}=\frac{\Delta H^{\alpha \beta}}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right) \quad \text { (Clausius-Clapeyron equation) }
$$

The fact that all known substances in the two-phase region fulfill the Clausius-Clapeyron equation, provides the general validity of the first and second laws of thermodynamics (as derivation of this equation is from the combination of first and second laws).

- According to the Clausius-Clapeyron equation $\Delta H^{\mathrm{lv}}$ is almost constant, virtually independent of $T$. This is not true; $\Delta H^{\mathrm{lv}}$ decreases monotonically with increasing temperature from the triple point temperature to the critical point, where it becomes zero. The assumptions on which the Clausius-Clapeyron equation are based, have approximate validity only at low pressures.


## - Antoine Equation

Clausius-Clapeyron equation can be written in empirical form as

$$
\ln P^{\mathrm{sat}}=A-\frac{B}{T}
$$

A satisfactory relation given by Antoine is of the form

$$
\ln P^{\mathrm{sat}}=A-\frac{B}{T+C} \quad \quad \text { (Antoine equation) }
$$

The values of the constants $A, B$ and $C$ are readily available for many species.

- Trouton's Rule: Trouton's rule states that the entropy change of vaporization is almost the same value, about $85-88 \mathrm{~J} /(\mathrm{mol} . \mathrm{K})$, for most of the liquids at their normal boiling points. Since $\Delta S=\Delta H / T=\lambda / T$, we can also say, that, according to this rule, molar latent heat of vaporization $(\lambda)$ at normal boiling point is related to the boiling temperature as

$$
\lambda \approx 10 R T_{b}
$$

(Trouton's rule)
where $T_{b}$ is normal boiling point in Kelvin. This empirical relationship holds good for many systems. Because of its convenience, the rule is used to estimate the enthalpy of vaporization of liquids whose boiling points are known.

- Engineering Rule for Vapor Pressure of Water: The following simple formula, which is easy to remember, gives surprisingly good estimates of the vapor pressure for water for temperatures from $100^{\circ} \mathrm{C}$ (the normal boiling point) and up to $374^{\circ} \mathrm{C}$ (the critical point):

$$
P_{\mathrm{H}_{2} \mathrm{O}}^{\mathrm{sat}}[\mathrm{bar}]=\left(\frac{T\left[{ }^{\circ} \mathrm{C}\right]}{100}\right)^{4}
$$

This formula is very convenient for engineers dealing with steam at various pressure levels. For example, from the formula we estimate $P^{\text {sat }}=2.074$ bar at $120^{\circ} \mathrm{C}$ (the correct value is $=1.987 \mathrm{bar}$ ) and $P^{\text {sat }}=81$ bar at $300^{\circ} \mathrm{C}$ (the correct value is $=85.88$ bar).

| Residual property model | Excess property model |
| :--- | :--- |
| This is based on deviation from ideal gas <br> behavior. | This is based on deviation from ideal so- <br> lution behavior. |
| Applicable for a single component and <br> mixture of components. | Applicable only for mixture of compo- <br> nents; and not for a single component. |
| $\bar{G}_{i}=\bar{G}_{i}{ }^{\text {ig }}+\bar{G}_{i}{ }^{\mathrm{R}}$ | $\bar{G}_{i}=\bar{G}_{i}{ }^{\text {id }}+\bar{G}_{i}{ }^{\mathrm{E}}$ |
| $\bar{G}_{i}^{\mathrm{ig}}=R T \ln \left(y_{i} P\right)+\Gamma_{i}(T)$ | $\bar{G}_{i}{ }^{\text {id }}=R T \ln \left(x_{i} f_{i}\right)+\Gamma_{i}(T)$ |
| $\bar{G}_{i}{ }^{\mathrm{R}}=R T \ln \hat{\phi}_{i}$ | $\bar{G}_{i}^{\mathrm{E}}=R T \ln \gamma_{i}$ |
| $\hat{f}_{i}=\hat{\phi}_{i} y_{i} P$ | $\hat{f}_{i}=\gamma_{i} x_{i} f_{i}$ |

## - Estimation of Fugacity of Pure Component:

By definition,

$$
d G=V d P \quad(\text { at constant } T)
$$

and in terms of fugacity $(f)$,

$$
d G=R T d \ln f \quad(\text { at constant } T)
$$

Equating these two equations, we can write

$$
d \ln f=\frac{V}{R T} d P
$$

Intergrating, we get

$$
\begin{equation*}
\ln \frac{f}{f_{o}}=\frac{1}{R T} \int_{P_{o}}^{P} V d P \tag{58}
\end{equation*}
$$

Given the equation of state, we can estimate $f$ at any value of $P$ by integrating the above expression (note: when $P_{o} \rightarrow 0, f_{o}=P$ ).

From the definition of residual property, we have

$$
d G^{\mathrm{R}}=d G-d G^{\mathrm{ig}}=V d P-V^{\mathrm{ig}} d P=\left(\frac{Z R T}{P}-\frac{R T}{P}\right) d P=(Z-1) R T \frac{d P}{P}
$$

We know that, $d G^{\mathrm{R}}=R T d \ln \phi$. Therefore,

$$
R T d \ln \phi=(Z-1) R T \frac{d P}{P}
$$

22. In a closed system, the isentropic expansion of an ideal gas with constant specific heats is represented by
(G-2014-6)
(a)

(b)



(d) $\checkmark$ Explanation: For isentropic expansion of ideal gas, $P V^{\gamma}=$ constant. This gives, $\ln P \propto-\gamma \ln V$. Therefore, $\ln P$ vs. $\ln V$ gives a straight line with a slope of $-\gamma$.
23. Air enters an adiabatic compressor at 300 K . The exit temperature for a compression ratio of 3 , assuming air to be an ideal gas $\left(\gamma=C_{P} / C_{V}=7 / 5\right)$ and the process to be reversible, is
(G-2001-2.07)
(a) $300\left(3^{2 / 7}\right)$
(b) $300\left(3^{3 / 5}\right)$
(c) $300\left(3^{3 / 7}\right)$
(d) $300\left(3^{5 / 7}\right)$
(a) $\checkmark$ Explanation: For reversible adiabatic process with ideal gas $P V^{\gamma}=\mathrm{constant}$. Equation of state for ideal gas is given as $P V=R T$. Using these two equations, we get $P^{1-\gamma} T^{\gamma}=$ constant. i.e., $T^{\gamma} \propto P^{\gamma-1}$. Hence,

$$
\frac{T_{2}}{T_{1}}=\left(\frac{P_{2}}{P_{1}}\right)^{\frac{\gamma-1}{\gamma}}
$$

Given: $P_{2} / P_{1}=3, T_{1}=300 \mathrm{~K}$, and $\gamma=7 / 5$. Therefore,

$$
T_{2}=300\left(3^{2 / 7}\right)
$$

24. A car tyre of volume $0.057 \mathrm{~m}^{3}$ is inflated to 300 kPa at 300 K . After the car is driven for ten hours, the pressure in the tyre increases to 330 kPa . Assume that air is an ideal gas and $C_{V}$ for air is $21 \mathrm{~J} /(\mathrm{mol} . \mathrm{K})$. The change in internal energy of air in the tyre in $\mathrm{J} / \mathrm{mol}$ is
(G-2004-44)
(a) 380
(b) 630
(c) 760
(d) 880
(a) $\checkmark$ Explanation: The $T-S$ diagram and the process of temperature increase of saturated liquid water at constant entropy is shown below.


State 1 is the start of the process; and 2 is the end. From the process represented it can be seen that state 2 is a liquid phase. If the temperature were reduced at constant entropy, state 2 would be having liquid and vapor in coexistence.

## 6 Flow Processes

57. Which of the following processes, shown in the figure below, represents the throttling of an ideal gas?
(G-XE-2013-E-9)

(a) 1 to 2
(b) 1 to 3
(c) 1 to 4
(d) 1 to 5
(a) $\checkmark$ Explanation: Throttling refers to the irreversible expansion at constant enthalpy. For an ideal gas, at constant enthalpy, $\Delta T=0$. During this irreversible expansion entropy increases. The process 1 to 2 represents this case.

The process 1 to 3 (which is decrease of temperature) occurs with most of the gases and liquids in general.

For isentropic expansion of an ideal gas, the process follows the path 1 to 4 .
58. In a throttling process, the pressure of an ideal gas reduces by $50 \%$. If $C_{p}$ and $C_{v}$ are the heat capacities at constant pressure and constant volume, respectively ( $\gamma=C_{p} / C_{v}$ ), the specific volume will change by a factor of

## Example 12: Work Done in Closed System

An insulated vertical cylinder encloses 0.1 kg of argon (Ar) with the help of a frictionless non-conducting piston as shown in the figure. The mass of the piston is 5 kg and it initially rests on the bottom of the cylinder. The cylinder is connected to a nitrogen ( $N_{2}$ ) tank at 100 bar through a pipeline fitted with a valve. The valve is opened and nitrogen is slowly admitted into the cylinder. During this operation, the piston is lifted through a height of 10 cm by the nitrogen gas. The initial pressure and temperature of argon gas are 100 kPa and 300 K respectively. The final temperature of argon is 320 K . For argon, $C_{P}=520 \mathrm{~J} / \mathrm{kg} . \mathrm{K}$ and $C_{V}=312 \mathrm{~J} / \mathrm{kg} . K$.
(G-XE-2009-E-23,24)

(i) The work done by argon in $k J$ during the process is
(a) 10
(b) 1.041
(c) -0.624
(d) -1.041
(ii) The work done by nitrogen in $k J$ during the process is
(a) 1.046
(b) 0.629
(c) -1.046
(d) -10

## Solution:

Argon can be considered as an ideal gas, at the given $P$ and $T$.

$$
\therefore \quad \Delta U_{\text {argon }}^{\mathrm{t}}=m C_{V} \Delta T=0.1 \times 312 \times(320-300)=624 \mathrm{~J}
$$

From first law of thermodynamics,

$$
\Delta U^{\mathrm{t}}=Q+W
$$

$Q=0$, as the cylinder is insulated and piston is non-conducting.

$$
\begin{aligned}
\therefore & \Delta U^{\mathrm{t}} & =W \\
\Longrightarrow & W & =624 \mathrm{~J}=0.624 \mathrm{~kJ}
\end{aligned}
$$

This much of work is done on argon by nitrogen. i.e., Work done by argon=-0.624 kJ. (i-c) $\checkmark$
Work done by nitrogen $=$ Work done on argon + Work done in rising the piston by 10 cm

$$
\begin{equation*}
=0.624+m g h=0.624+\frac{5 \times 9.812 \times 0.1}{1000}=0.629 \mathrm{~kJ} \tag{ii-b}
\end{equation*}
$$

The above is the expression, for work done on the system.
Work done by the system is given as,

$$
W_{s}=-\int_{\text {inlet }}^{\text {outlet }} V d P
$$

This is derived with the only assumption of reversible process, The process can be isothermal, adiabatic or can have any other relation.
Option(d) is applicable for non flow process in a closed system.

## Example 33: Throttling Process

A saturated liquid at 1500 kPa and 500 K , with an enthalpy of $750 \mathrm{~kJ} / \mathrm{kg}$, is throttled to a liquid-vapor mixture at 150 kPa and 300 K . At the exit conditions, the enthalpy of the saturated liquid is $500 \mathrm{~kJ} / \mathrm{kg}$ and the enthalpy of the saturated vapor is $2500 \mathrm{~kJ} / \mathrm{kg}$. The percentage of the original liquid, which vaporizes, is
(G-2010-18)
(a) $87.5 \%$
(b) $67 \%$
(c) $12.5 \%$
(d) $10 \%$

## Solution:

$P-H$ diagram of the process (with constant $T$ lines) is given as below.
Throttling is an isenthalpic process. i.e., $H_{1}=H_{2}$.


$$
\begin{aligned}
H_{1} & =H_{L_{1}} \quad \text { (saturated liquid) } \\
& =750 \mathrm{~kJ} / \mathrm{kg} \\
H_{2} & =(1-x) H_{L_{2}}+x H_{V_{2}} \\
\text { i.e., } H_{2} & =H_{L_{2}}+x\left(H_{V_{2}}-H_{L_{2}}\right)
\end{aligned}
$$

where $x$ is the fraction of vapor in the vapor liquid mixture, and $(1-x)$ is the fraction of liquid.

$$
H_{2}=500+x(2500-500)
$$

Given: $H_{2}=H_{1}=750 \mathrm{~kJ} / \mathrm{kg}$. Therefore, $750=500+x(2500-500)$
$\Longrightarrow \quad x=0.125$
This is the fraction of vapor in the mixture. i.e., the percentage of original liquid vaporized is $12.5 \%$
(c) $\checkmark$

Example 34: Quality of Steam at Turbine Exit
Steam undergoes isentropic expansion in a turbine from 5000 kPa and $400^{\circ} \mathrm{C}$ (entropy $=6.65$ $\mathrm{kJ} / \mathrm{kg} . \mathrm{K}$ ) to 150 kPa (entropy of saturated liquid $=1.4336 \mathrm{~kJ} / \mathrm{kg} . K$, entropy of saturated vapor $=7.2234 \mathrm{~kJ} / \mathrm{kg} . K)$. The exit condition of steam is
(G-2002-2.07)
(a) superheated vapor
(b) partially condensed vapor with quality of 0.9

Substituting this in Eqn.(1),

$$
\begin{aligned}
\int d \ln \gamma_{2} & =-\int \frac{x_{1}}{x_{2}}\left(2 x_{2}\right) d x_{1} \\
\therefore \quad \ln \gamma_{2} & =-\int_{0}^{x_{1}} 2 x_{1} d x_{1} \quad\left(\text { when } x_{1}=0, x_{2}=1 \quad \Longrightarrow \gamma_{2}=1, \text { and } \ln \gamma_{2}=0\right) \\
& =-2 \frac{x_{1}^{2}}{2}=-x_{1}^{2} \quad \\
& \text { (d) } \checkmark
\end{aligned}
$$

## Example 51: Excess Gibbs Free Energy from VLE Data

A methanol-water vapor liquid equilibrium system is at equilibrium at $60^{\circ} \mathrm{C}$ and 60 kPa . The mole fraction of methanol in liquid is 0.5 and in the vapor is 0.8 . Vapor pressure of methanol and water at $60^{\circ} \mathrm{C}$ are 85 kPa and 20 kPa respectively.
(G-2007-76,77)
(i) Assuming vapor phase to be an ideal gas mixture, what is the activity coefficient of water in the liquid phase?
(a) 0.3
(b) 1.2
(c) 1.6
(d) 7.5
(ii) What is the excess Gibbs free energy ( $G^{E}$, in $J / \mathrm{mol}$ ) of the liquid mixture ?
(a) 9.7
(b) 388
(c) 422
(d) 3227

## Solution:

VLE between ideal vapor mixture and non-ideal liquid solution is given by,

$$
y_{i} P=\gamma_{i} x_{i} P_{i}^{\mathrm{sat}}
$$

For water,

$$
\begin{equation*}
y_{w} P=\gamma_{w} x_{w} P_{w}^{\mathrm{sat}} \tag{1}
\end{equation*}
$$

Given: $y_{m}=0.8 \& x_{m}=0.5$. Therefore, $y_{w}=0.2\left(\right.$ as $\left.y_{m}+y_{w}=1\right)$ and $x_{w}=0.5$. Substituting these in Eqn.(1),

$$
\begin{align*}
0.2 \times 60 & =\gamma_{m} \times 0.5 \times 20 \\
\gamma_{w} & =1.2 \tag{i-b}
\end{align*}
$$

Excess Gibbs free energy $\left(G^{E}\right)$ is related to mole fraction and activity co-efficient as,

$$
\begin{gather*}
\frac{G^{E}}{R T}=\sum x_{i} \ln \gamma_{i}=x_{m} \ln \gamma_{m}+x_{w} \ln \gamma_{w}  \tag{2}\\
\gamma_{m}=\frac{y_{m} P}{x_{m} P_{m}^{s a t}}=\frac{0.8 \times 60}{0.5 \times 85}=1.13
\end{gather*}
$$

Substituting this in Eqn.(2)

$$
\begin{align*}
\frac{G^{E}}{R T} & =0.5 \ln (1.13)+0.5 \ln (1.2)=0.1523 \\
G^{E} & =0.1523 \times 8.314 \times(273+60)=421.6 \mathrm{~J} / \mathrm{mol} \tag{ii-c}
\end{align*}
$$

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Figure 7: Flow curves for time-independent fluids

- Gauge Pressure: Many pressure-measuring devices give the gauge pressure of a fluid, or the pressure relative to atmospheric pressure. A gauge pressure of zero indicates that the absolute pressure of the fluid is equal to atmospheric pressure. The relationship for conversion between absolute and gauge pressure is

$$
P_{\text {absolute }}=P_{\text {gauge }}+P_{\text {atmospheric }}
$$

The abbreviations psia and psig are commonly used to denote absolute and gauge pressure in psi $\left(\mathrm{lb}_{f} / \mathrm{in}^{2}\right)$.
Also, it is common to refer to negative gauge pressures (absolute pressures less than atmospheric) as positive amounts of vacuum. For example, a gauge pressure of -700 $\mathrm{mm} \mathrm{Hg}(60 \mathrm{~mm} \mathrm{Hg}$ absolute if the atmospheric pressure is 760 mm Hg ) may also be called 700 mm Hg vacuum.

## Newtonian and Non-Newtonian Fluids

Refer to Fig.(7).

- Newtonian fluids: the slope of shear stress $(\tau) /$ strain rate $(d u / d y)=\mu$ is a constant regardless of the strain rate.
e.g.: gases, water, liquid hydrocarbons, and most organic liquids of relatively low molecular weight.
- Pseudoplastic (or shear-thinning) fluids: exhibit a viscosity that decreases with increasing strain rate.
e.g.: most polymer solutions and polymer melts.
- Dilatant (or shear-thickening) fluids exhibit a viscosity that increases with increasing strain rate. They are less common than pseudo plastic fluids.


Figure 11: Fanning friction factor for flow through pipes (for various relative roughness values)
where $D=$ diameter of pipe
$v=$ fluid velocity
$L=$ length of pipe over which pressure drop is measured
$\rho=$ density of fluid
$f=$ friction factor
The above equation is also known as Darcy-Weisbach equation. It should be noted that the ' $f$ ' used here is Fanning friction factor.

## - Friction Factor

- Fanning friction factor:

$$
f=\frac{\tau_{w}}{\rho v^{2} / 2}
$$

- Blasius or Moody or Darcy friction factor $\left(f_{D}\right)$ is also commonly encountered in fluid mechanics literature. It is 4 times the Fanning friction factor.

$$
f_{D}=4 f
$$

Care should be taken in reading friction factor charts, that whether the friction factor is Darcy or Fanning.
In general, chemical engineers employ the Fanning friction factor; other engineers prefer the Darcy (or Blasius or Moody) factor. This book employs the Fanning friction factor. Friction factor vs. Reynolds number chart is given in Fig.(11).
9. What is the force required (in Newtons) to hold a spherical balloon stationary in water at a depth of $H$ from the air-water interface? The balloon is of radius 0.1 m and is filled with air.
(G-2004-12)
(a) $\frac{4 \pi g}{3}$
(b) $\frac{0.1 \pi g H}{4}$
(c) $\frac{0.1 \pi g H}{8}$
(d) $\frac{0.04 \pi g H}{3}$
(a) $\checkmark$ Explanation: Net upward force $=$ buoyant force - gravitational force.

$$
\text { Buoyant force }=V \rho_{\text {water }} g=\left(\frac{4}{3} \pi r^{3}\right) \rho_{\text {water }} g=\left(\frac{4}{3} \pi \times 0.1^{3}\right) \times 1000 \times g=\frac{4}{3} \pi g
$$

and

$$
\text { Gravitational force }=V \rho_{\mathrm{air}} g \approx 0
$$

Here, the gravitational force is negligible, as $\rho_{\text {air }} \ll \rho_{\text {water }}$
10. A hydrometer, with stem cross-sectional area of $2.82 \times 10^{-5} \mathrm{~m}^{2}$, is immersed in a very large vessel containing water as shown in the figure. The immersed volume is $15 \times 10^{-6}$ $\mathrm{m}^{3}$ and the length of the stem above water surface is $L_{w}$. If the entire volume of water is replaced by a liquid with specific gravity 1.5 and if the length of the stem above the liquid surface is $L_{l}$, then the difference, $L_{l}-L_{w}$, is
(G-2010-34)

(a) -177 mm
(b) 177 mm
(c) -266 mm
(d) 266 mm
(b) $\checkmark$ Explanation: At buoyant conditions, for the hydrometer,
weight of water displaced $=$ weight of liquid displaced
With $\rho_{l}>\rho_{w}$, the volume of liquid displaced will be less than the volume of water displaced. Hence, the height $L_{l}$ will be higher than $L_{w}$. Let $L_{l}-L_{w}=x$. Then,

$$
\begin{aligned}
\rho_{w} \times 15 g & =\rho_{l} \times[15-x \times 0.282] g \quad \text { (with dimensions in } \mathrm{cm}^{n} \text { units) } \\
1 \times 15 & =1.5 \times[15-0.282 x] \\
15-0.282 x & =10 \quad \Longrightarrow \quad x=17.73 \mathrm{~cm}=177.3 \mathrm{~mm}
\end{aligned}
$$

71. A centrifugal pump is used to pump water through a horizontal distance of 150 m and then raised to an overhead tank 10 m above. The pipe is smooth with an I.D. of 50 mm . What head ( m of water) must the pump generate as its exit ( E ) to deliver water at a flow rate of $0.001 \mathrm{~m}^{3} / \mathrm{s}$ ? The Fanning friction factor, $f$ is 0.0062 .
(G-2003-51)

(a) 10 m
(b) 11 m
(c) 12 m
(d) 20 m
(b) $\checkmark$ Explanation: Pump-head at exit point, E $\left(h_{w}\right)$ :

$$
\begin{aligned}
h_{w}= & \frac{\Delta P \text { due to friction }}{\rho g}+\text { Potential head } \\
= & \left(\frac{2 f L \rho v^{2}}{D}\right) /(\rho g)+10 \mathrm{~m} \\
h_{w}= & \frac{2 \times 0.0062 \times(150+10) \times 1000 \times v^{2}}{0.05 \times 1000 \times 9.81}+10 \\
= & 4.045 v^{2}+10 \\
& \left(v=\frac{Q}{A}=\frac{0.001}{(\pi / 4) \times 0.05^{2}}=0.51 \mathrm{~m} / \mathrm{s}\right)
\end{aligned}
$$

Therefore,

$$
h_{w}=4.045 \times 0.51^{2}+10=11.05 \mathrm{~m} \approx 11 \mathrm{~m}
$$

72. Match the following for a centrifugal pump with impeller speed $n$
(G-2006-8)
(P) Capacity
(1) proportional to $n$
(Q) Head
(2) proportional to $n^{2}$
(3) proportional to $n^{3}$
(a) P-2, Q-1
(b) P-1, Q-3
(c) P-2, Q-3
(d) P-1, Q-2
(d) $\checkmark$ Explanation: The affinity relation is: $Q \propto n D^{3}$. Capacity $(Q)$ has units of $\mathrm{m}^{3} / \mathrm{s}$. The unit of $n$ is $1 / \mathrm{s}$.

Since $\operatorname{Re}_{p}$ is very small compared to one, laminar part of Ergun equation can be used to relate pressure drop $(\Delta P)$ and fluidization velocity $\left(v_{o}\right)$.

$$
\begin{equation*}
\frac{\Delta P}{L}=\frac{150 \mu(1-\epsilon)^{2} v_{o}}{\epsilon^{3} d_{p}^{2}} \tag{2}
\end{equation*}
$$

Equating Eqns.(1) \& (2),

$$
\begin{equation*}
\left(\rho_{p}-\rho\right)(1-\epsilon) g=\frac{150 \mu(1-\epsilon)^{2} v_{o}}{\epsilon^{3} d_{p}^{2}} \tag{3}
\end{equation*}
$$

Substituting for the known quantities in Eqn.(3)

$$
\begin{aligned}
(3000-1000) \times(1-0.5) \times 10 & =\frac{150 \times 0.1 \times(1-0.5)^{2}}{0.5^{3} \times\left(1 \times 10^{-3}\right)^{2}} v_{o} \\
\Longrightarrow \quad v_{o} & =3.33 \times 10^{-4} \mathrm{~m} / \mathrm{s} \quad \text { (a) } \checkmark
\end{aligned}
$$

## Example 27: Minimum Fluidization Velocity

A fluidized bed ( 0.5 m dia, 0.5 m high) of spherical particles (diameter $=2000 \mu \mathrm{~m}$, specific gravity $=2.5$ ) uses water as the medium. The porosity of the bed is 0.4. The Ergun equation for the system is

$$
\Delta P / L=4 \times 10^{5} U_{m f}+1 \times 10^{7} U_{m f}^{2}
$$

(SI unit, $U_{m f}$ in $\mathrm{m} / \mathrm{s} ; g=9.8 \mathrm{~m} / \mathrm{s}^{2}$ )
(G-2007-84,85)
(i) $\Delta P / L$ (SI unit) at the minimum fluidization condition is
(a) 900
(b) 8820
(b) 12400
(d) 17640
(ii) The minimum fluidization velocity $(\mathrm{mm} / \mathrm{s})$ is
(a) 12.8
(b) 15.8
(b) 24.8
(d) 28.8

## Solution:

By force balance,

$$
\begin{align*}
\frac{\Delta P}{L} & =\left(\rho_{p}-\rho\right)(1-\epsilon) g \\
& =(2500-1000) \times(1-0.4) \times 9.8=8820 \mathrm{~Pa} / \mathrm{m} \tag{i-b}
\end{align*}
$$

Substituting for $\Delta P / L$ in the given equation,

$$
\begin{align*}
& 8820=4 \times 10^{5} v_{\mathrm{mf}}+1 \times 10^{7} v_{\mathrm{mf}}^{2} \\
& 1 \times 10^{7} v_{\mathrm{mf}}^{2}+4 \times 10^{5} v_{\mathrm{mf}}-8820=0 \\
& v_{\mathrm{mf}}=\frac{-4 \times 10^{5} \pm \sqrt{\left(4 \times 10^{5}\right)^{2}+4 \times 1 \times 10^{7} \times 8820}}{2 \times 1 \times 10^{7}} \\
& =\frac{-4 \times 10^{5} \pm 7.161 \times 10^{5}}{2 \times 10^{7}}=0.0158 \mathrm{~m} / \mathrm{s}=15.8 \mathrm{~mm} / \mathrm{s} \tag{ii-b}
\end{align*}
$$

4. The large vessel shown in the figure contains oil and water. A body is submerged at the interface of oil and water such that 45 percent of its volume is in oil while the rest is in water. The density of the body is $\qquad$ $\mathrm{kg} / \mathrm{m}^{3}$.
The specific gravity of oil is 0.7 and density of water is $1000 \mathrm{~kg} / \mathrm{m}^{3}$. Acceleration due to gravity $g=10 \mathrm{~m} / \mathrm{s}^{2}$.
(G-ME-2016-S2-39)

(Ans: 865)
5. A three-fluid system (immiscible) is connected to a vacuum pump. The specific gravity values of the fluids $\left(S_{1}, S_{2}\right)$ are given in the figure.
(G-CE-2018-2-46)


Unit weight of water, $\gamma_{w}=9.81 \mathrm{kN} / \mathrm{m}^{3}$
Atmospheric pressure, $P_{\mathrm{atm}}=95.43 \mathrm{kPa}$

The gauge pressure value (in $\mathrm{kN} / \mathrm{m}^{2}$, up to two decimal places) of $P_{1}$ is $\qquad$ (Ans: -8.73)
6. Under isothermal condition, a vertical tube of length $L=100 \mathrm{~m}$ contains a gas of molecular weight equal to 60 . The pressure and temperature at the top of the tube are 100 kPa and $25^{\circ} \mathrm{C}$ respectively. Consider the universal gas constant and acceleration due to gravity as $8.314 \mathrm{~J} / \mathrm{mol} . \mathrm{K}$ and $9.81 \mathrm{~m} / \mathrm{s}^{2}$ respectively. If the gas is ideal, the pressure (in kPa ) at the bottom of the tube will be $\qquad$ (G-2018-37)
(Ans: 102.4)


Figure 8: Plate, Frame, and Wash-plate of Filter Press

## Washing of Filter Cakes

In most filters (except filter-press) the wash liquid follows the same path as that of the filtrate. The rate of flow of wash liquid is, in principle, equal to that of the final rate of filtration, provided the pressure drop remains unchanged in passing from filtration to washing.

In filter-press, washing method differs according to the availability of wash-plates.
Refer to Fig.(8). Buttons on the edge help for easy identification of plate (1-button), frame (2-buttons) and wash-plate (3-buttons).

- Simple Washing: Plate and frame arrangements: -1-2-1-2-1-.

1-refers to plate; 2-refers to frame. There is no wash-plate here.
Slurry passes through the frames. Wash liquid is fed in through the same channel as the slurry (i.e., through frames).

- Thorough Washing: Refer to Fig.(9).
- Plate and frame arrangements: -1-2-3-2-1-2-3-2-1-. $\quad 1$-refers to plate (one button); 2 -refers to frame (2 buttons); 3-refers to wash-plate (three buttons).
- Wash liquid flows through wash-plates.

Let us take, in simple-wash arrangement, for a plate and frame combination of -1-2-1-, wash-liquid flow rate as $Q$. In thorough-wash arrangement, the plate and frame combination is -1-2-3-2-1-. Wash-liquid flows through only half of the plates (i.e., through wash-plates) in comparison with simple-washing. For a given volume of fluid to be handled, this leads to doubling the time requirement.
Thickness of the cake through which the wash-liquid to travel is twice that through which the filtrate passes. For a given volume of fluid to be handled, this too leads to doubling the time requirement.
Hence, with thorough-wash arrangement, the rate of washing is one-fourth that in simple-washing.

$$
Q_{\text {thorough-washing }}=\frac{1}{4} Q_{\text {simple-washing }}=\frac{1}{4} Q_{\text {final-rate of filtration }}
$$



Figure 9: Plate-and-Frame Filter Press with Thorough Washing

- Optimum Time Cycle: For new washing type plate-and-frame filter press operating at a constant pressure with negligible medium resistance, optimum time cycle occurs when the time of filtration equals the time lost in opening, dumping, cleaning, and reassembling the press.


## - Rate of Filtration Including Filter Medium Resistance

$$
\frac{d V}{d t}=\frac{A^{2} \Delta p}{\left(V+V_{f}\right) c \mu \alpha}
$$

where $t=$ time
$V=$ volume of filtrate
$V_{f}=$ volume of filtrate held in filter medium
$A=$ filtration area
$\alpha=$ specific cake resistance, $\mathrm{m} / \mathrm{kg}$
In simple form:

$$
\frac{d t}{d V}=\frac{2 V}{C}+\frac{2 V_{f}}{C}
$$

where $C$ is proportional to $\Delta p / \alpha$.
In the above equation, $2 V_{f} / C=0$, if filter medium resistance can be neglected.

- Rotary Drum Filters: For constant pressure filtration, and where filter medium resistance can be neglected, rate of filtration is proportional to $\sqrt{N}$; where $N$ is the rotational speed of drum.

21. The particle size distribution of the feed and collected solids (sampled for same duration) for a gas cyclone are given below:

| Size range $(\mu \mathrm{m})$ | $1-5$ | $5-10$ | $10-15$ | $15-20$ | $20-25$ | $25-30$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Weight of feed in the size range (g) | 2.0 | 3.0 | 5.0 | 6.0 | 3.0 | 1.0 |
| Weight of collected solids in the <br> size range $(\mathrm{g})$ | 0.1 | 0.7 | 3.6 | 5.5 | 2.9 | 1.0 |

What is the collection efficiency (in percentage) of the gas cyclone?
(G-2011-35)
(a) 31
(b) 60
(c) 65
(d) 69
(d) $\checkmark$ Explanation: The collection efficiency $(E)$ of cyclone is given by

$$
E=\frac{M_{c}}{M} \times 100
$$

where $M_{c}=$ mass of coarse particles collected
$M=$ mass of feed
Given:

$$
\begin{aligned}
M & =2+3+5+6+3+1=20 \mathrm{~g} \\
M_{c} & =0.1+0.7+3.6+5.5+2.9+1.0=13.8 \mathrm{~g} \\
\therefore \quad E & =\frac{13.8}{20} \times 100=69 \%
\end{aligned}
$$

22. Separation factor of a cyclone 0.5 m in diameter and having a tangential velocity of 20 $\mathrm{m} / \mathrm{s}$ near the wall is $\qquad$ (Take $g=10 \mathrm{~m} / \mathrm{s}^{2}$ )
(G-2013-15)
(160) $\checkmark$ Explanation: The separation factor $(s)$ of cyclone is given by

$$
s=\frac{\text { centrifugal force }}{\text { gravity force }}=\frac{m r \omega^{2}}{m g}
$$

Angular rate $(\omega)$ is related to the tangential velocity $(v)$ by: $v=r \omega$. Therefore,

$$
s=\frac{m v^{2} / r}{m g}=\frac{v^{2}}{r g}=\frac{20^{2}}{0.25 \times 10}=160
$$

23. In a cyclone separator used for separation of solid particles from a dust laden gas, the separation factor is defined as the ratio of the centrifugal force to the gravitational force acting on the particle. $S_{r}$ denotes the separation factor at a location (near the wall) that is at a radial distance $r$ from the centre of the cyclone. Which one of the following statements is INCORRECT?
(G-2016-7)
(a) $S_{r}$ depends on mass of the particle
where $a_{1} \vec{\imath}, a_{2} \vec{\jmath}$, and $a_{3} \vec{k}$ are vectors which lie along the coordinate axes $x, y$, and $z$ respectively, and have their origin at a common initial point.

The magnitude, length, or norm of a vector $\vec{a}$, as denoted by $|\vec{a}|$ is:

$$
|\vec{a}|=\sqrt{a_{1}^{2}+a_{2}^{2}+a_{3}^{2}}
$$

- Unit vector is denoted with a hat (i.e., $\left.{ }^{\wedge}\right)$ symbol. To find the unit vector $(\hat{a})$ in the direction of $\vec{a}$, simply divide the vector by its magnitude.

$$
\hat{a}=\frac{\vec{a}}{|\vec{a}|}
$$

The unit vectors in $x, y, z$ directions are given as $\hat{\imath}, \hat{\jmath}, \hat{k}$. They are also given simply as $\vec{\imath}, \vec{\jmath}, \vec{k}$.

- Vector addition or subtraction:

$$
\begin{aligned}
& \vec{a}+\vec{b}=\left(a_{1}+b_{1}\right) \vec{\imath}+\left(a_{2}+b_{2}\right) \vec{\jmath}+\left(a_{3}+b_{3}\right) \vec{k} \\
& \vec{a}-\vec{b}=\left(a_{1}-b_{1}\right) \vec{\imath}+\left(a_{2}-b_{2}\right) \vec{\jmath}+\left(a_{3}-b_{3}\right) \vec{k}
\end{aligned}
$$

- Vector multiplication: There are two types of multiplication.
- Dot product:

$$
\vec{a} \cdot \vec{b}=|\vec{a}||\vec{b}| \cos (\theta)=a_{1} b_{1}+a_{2} b_{2}+a_{3} b_{3}
$$

where $\theta$ is the angle between the vectors, such that $0 \leq \theta \leq \pi$. The dot product yields a scalar answer.

* Dot product is also called as scalar product or inner product.
* Dot product is commutative. i.e.,

$$
\vec{a} \cdot \vec{b}=\vec{b} \cdot \vec{a}
$$

* If $\vec{a} \cdot \vec{b}=0$, with $|\vec{a}| \neq 0$, and $|\vec{b}| \neq 0$, then the vectors are orthogonal (perpendicular) to each other.
* If vectors $\vec{a}$ and $\vec{b}$ are parallel, then

$$
\vec{a} \cdot \vec{b}=|\vec{a}| \cdot|\vec{b}|
$$

* For the unit vectors $\vec{\imath}, \vec{\jmath}$ and $\vec{k}$

$$
\vec{\imath} \cdot \vec{\imath}=\vec{\jmath} \cdot \vec{\jmath}=\vec{k} \cdot \vec{k}=1
$$

and,

$$
\vec{\imath} \cdot \vec{\jmath}=\vec{\jmath} \cdot \vec{\imath}=\vec{\imath} \cdot k=\vec{k} \cdot \vec{\imath}=\vec{\jmath} \cdot \vec{k}=\vec{k} \cdot \vec{\jmath}=0
$$

(a) $\checkmark$ Explanation: The complex number $z$ can be represented in rectangular form as $x+i y$ and in polar form as $r e^{i \phi}$.

$$
z=x+i y=r \cos \phi+i r \sin \phi=r e^{i \phi}
$$

where

$$
r=|z|=\sqrt{x^{2}+y^{2}} \quad \text { and } \quad \phi=\tan ^{-1}(y / x)
$$

Here, $z=2+i 2$. Therefore, $r=\sqrt{2^{2}+2^{2}}=2 \sqrt{2}$, and $\phi=\tan ^{-1}(2 / 2)=\pi / 4$. Hence, $z=2 \sqrt{2} e^{i \pi / 4}$.
53. Given that $i=\sqrt{-1}, \imath^{i}$ is equal to
(G-2010-14)
(a) $\pi / 2$
(b) -1
(c) $i \ln i$
(d) $e^{-\pi / 2}$
(d) $\checkmark$ Explanation: From Euler's formula, $e^{i x}=\cos x+i \sin x$. By taking $x=\pi$, we get

$$
e^{i \pi}=\cos \pi+i \sin \pi=-1+i \times 0=-1 \quad \Longrightarrow \quad-1=e^{i \pi}
$$

Taking square root on both sides,

$$
(-1)^{1 / 2}=\left[e^{i \pi}\right]^{1 / 2} \quad \Longrightarrow \quad \sqrt{-1}=e^{i \pi / 2} \quad \Longrightarrow \quad i=e^{i \pi / 2}
$$

Therefore,

$$
i^{i}=\left[e^{i \pi / 2}\right]^{i} \quad \Longrightarrow \quad i^{i}=e^{i^{2} \pi / 2}=e^{-\pi / 2}
$$

Another Method: With $x=\pi / 2$, we get

$$
e^{i \pi / 2}=\cos (\pi / 2)+i \sin (\pi / 2)=0+i \times 1=i
$$

Therefore,

$$
i^{i}=\left[e^{(i \pi / 2)}\right]^{i}=e^{\left(i^{2} \pi / 2\right)}=e^{(-\pi / 2)}
$$

54. If $z=x+i y$ is a complex number, where $i=\sqrt{-1}$, then which of the following is an analytic function of $z$ ?
(G-2005-35)
(a) $x^{2}+y^{2}$
(b) $2 i x y$
(c) $x^{2}+y^{2}-2 i x y$
(d) $x^{2}-y^{2}+2 i x y$
(d) $\checkmark$ Explanation: For a function $f(z)=u+i v$ to be an analytic function of $z$, it should satisfy the Chauchy-Riemann (CR) equations:

$$
\frac{\partial u}{\partial x}=\frac{\partial v}{\partial y} \quad \text { and } \quad \frac{\partial v}{\partial x}=-\frac{\partial u}{\partial y}
$$

Simply by looking the options (a) and (b), it can be said that they will not satisfy the CR equations.
87. For an even function $f(x)$,
(a) $\int_{-a}^{a} f(x) d x=0$
(b) $\int_{-a}^{a} f(-x) d x=0$
(c) $f(x)=-f(-x)$
(d) $f(x)=f(-x)$
(d) $\checkmark$ Explanation: A function defined on $[-a, a]$ is
(i) even if $f(-x)=f(x)$
(ii) odd if $f(-x)=-f(x)$

For eg, $x, x^{3}, \sin x$ are odd on $[-\pi, \pi]$, and $x^{2}, \cos x$ are even functions.
For odd function on $[-a, a]$,

$$
\int_{-a}^{a} f(x) d x=0
$$

For even function on $[-a, a]$,

$$
\int_{-a}^{a} f(x) d x=2 \int_{0}^{a} f(x) d x
$$

88. Value of the integral $\int_{-2}^{2} \frac{d x}{x^{2}}$ is
(G-2004-36)
(a) 0
(b) 0.25
(c) 1
(d) $\infty$
(d) $\checkmark$ Explanation: For an even function, $f(x)=f(-x)$, and

$$
\int_{0}^{a} f(x) d x=\int_{-a}^{0} f(x) d x
$$

Therefore,

$$
\int_{-a}^{a} f(x) d x=2 \int_{0}^{a} f(x) d x
$$

For an odd function, $f(x)=-f(-x)$, and

$$
\int_{0}^{a} f(x) d x=-\int_{-a}^{0} f(x) d x
$$

Therefore,

$$
\int_{-a}^{a} f(x) d x=0
$$

The function $f(x)=1 / x^{2}$ is an even function. Hence,

$$
\int_{-a}^{a} f(x) d x=2 \int_{0}^{a} f(x) d x=2 \int_{0}^{2} \frac{d x}{x^{2}}=2\left[\frac{-1}{x}\right]_{0}^{2}=2\left(\frac{-1}{2}+\frac{1}{0}\right)=\infty
$$

(94.67) $\checkmark$ Explanation: By Simpson's $1 / 3$ rule, with 4 equally spaced intervals, the integral value $(I)$ is given by:

$$
I=\frac{h}{3}\left[f_{0}+4 f_{1}+2 f_{2}+4 f_{3}+f_{4}\right]
$$

Given: $h=1$, and $f_{0}=3, \quad f_{1}=10, \quad f_{2}=21, \quad f_{3}=36, \quad f_{4}=55$. Therefore

$$
I=\int_{0}^{4} f(x) d x=\frac{1}{3}(3+4 \times 10+2 \times 21+4 \times 36+55)=94.67
$$

138. Match the problem type in Group-1 with the numerical method in Group-2. (G-2017-28)

| Group-1 | Group-2 |
| :--- | :--- |
| P) System of linear algebraic equations | I) Newton-Raphson |
| Q) Non-linear algebraic equations | II) Gauss-Seidel |
| R) Ordinary differential equations | III) Simpson's rule |
| S) Numerical integration | IV) Runge-Kutta |

(a) P-II, Q-I, R-III, S-IV
(b) P-I, Q-II, R-IV, S-III
(c) P-IV, Q-III, R-II, S-I
(d) P-II, Q-I, R-IV, S-III
(d) $\checkmark$

## 8 Probability

139. A pair of fair dice is rolled simultaneously. The probability that the sum of the numbers from the dice equals six is
(G-2000-1.1)
(a) $\frac{1}{6}$
(b) $\frac{7}{36}$
(c) $\frac{5}{36}$
(d) $\frac{1}{12}$
(c) $\checkmark$ Explanation: A die contains 6 faces; and upon throwing will show either of

For two dice thrown simultaneously, the possible number combinations (i.e., possible outcomes), and the sum of numbers of two dice equaling six (i.e., favorable outcomes) are as follows:

$$
\left[\begin{array}{cccccc}
(1,1) & (1,2) & (1,3) & (1,4) & \boxed{(1,5)} & (1,6) \\
(2,1) & (2,2) & (2,3) & (2,4) & (2,5) & (2,6) \\
(3,1) & (3,2) & (3,3) & (3,4) & (3,5) & (3,6) \\
(4,1) & (4,2) & (4,3) & (4,4) & (4,5) & (4,6) \\
\hdashline(5,1) & (5,2) & (5,3) & (5,4) & (5,5) & (5,6) \\
\hdashline(6,1) & (6,2) & (6,3) & (6,4) & (6,5) & (6,6)
\end{array}\right]
$$

Probability $=\frac{\text { number of favorable outcomes }}{\text { total number of possible outcomes }}=\frac{5}{36}$

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## GATEway to Chemical Engineering



Rishal Publications

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(Useful for GATE and other Aptitude Tests)

m subbu k nagarajan

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## m subbu

k nagarajan

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(a) Flat Surface

(b) Curved Surface

Figure 1: Heat Transfer through Multiple Resistances in Series

$$
Q=\frac{T_{1 \infty}-T_{1 s}}{R_{1}}=\frac{T_{1 s}-T_{2}}{R_{2}}=\frac{T_{2}-T_{2 s}}{R_{3}}=\frac{T_{s 2}-T_{2 \infty}}{R_{4}}
$$

where

$$
R_{1}=\frac{1}{h_{1} A} \quad R_{2}=\frac{L_{1}}{k_{1} A} \quad R_{3}=\frac{L_{2}}{k_{2} A} \quad R_{4}=\frac{1}{h_{2} A}
$$

Adding the numerators and denominators separately, we get

$$
Q=\frac{T_{1 \infty}-T_{2 \infty}}{R_{1}+R_{2}+R_{3}+R_{4}}
$$

## Composite Curved Surfaces

Refer to Fig.(1-b).

$$
Q=\frac{T_{1 \infty}-T_{2 \infty}}{R_{1}+R_{2}+R_{3}+R_{4}}
$$

Cylindrical Surface:

$$
R_{1}=\frac{1}{h_{1} 2 \pi r_{1 i} H} \quad R_{2}=\frac{\ln \left(r_{1 o} / r_{1 i}\right)}{2 \pi k_{1} H} \quad R_{3}=\frac{\ln \left(r_{2 o} / r_{2 i}\right)}{2 \pi k_{2} H} \quad R_{4}=\frac{1}{h_{2} 2 \pi r_{2 o} H}
$$

Spherical Surface:

$$
R_{1}=\frac{1}{h_{1} 4 \pi r_{1 i}^{2}} \quad R_{2}=\frac{\left(r_{1 o}-r_{1 i}\right)}{4 \pi k_{1} r_{1 i} r_{1 o}} \quad R_{3}=\frac{\left(r_{2 o}-r_{2 i}\right)}{4 \pi k_{2} r_{2 i} r_{2 o}} \quad R_{4}=\frac{1}{h_{2} 4 \pi r_{2 o}^{2}}
$$



Figure 7: Variation of Fin Temperature

From any of the above two equations, we get

$$
Q=A k \theta_{0} m \quad \Longrightarrow \quad Q=\theta_{0} \sqrt{P h k A}
$$

Pin Fin: It is a cylindrical extended surface. Here, $A=(\pi / 4) D^{2}$, and $P=\pi D$.

## Fin Efficiency

Temperature of a fin gradually drops along the length. Typical variation is given in Fig.(7). In the limiting case of zero thermal resistance $(k \rightarrow \infty)$, the temperature of the fin will be uniform at the base value of $T_{0}$. The heat transfer from the fin will be maximized in this case:

$$
Q_{\mathrm{fin}, \max }=h A_{\mathrm{fin}}\left(T_{0}-T_{\infty}\right)
$$

Fin efficiency $\left(\eta_{\text {fin }}\right)$ can be defined as:

$$
\eta_{\mathrm{fin}}=\frac{Q_{\mathrm{fin}}}{Q_{\mathrm{fin}, \max }}=\frac{\text { actual heat transfer rate from the fin }}{\begin{array}{c}
\text { ideal heat transfer rate from the fin } \\
\text { (if the entire fin were at base temperature) }
\end{array}}
$$

Fin efficiency decreases with increasing fin length because of decrease in fin temperature with length. For the 'long-fin'

$$
\eta_{\mathrm{fin}}=\frac{Q_{\mathrm{fin}}}{Q_{\mathrm{fin}, \max }}=\frac{\sqrt{P h k A}\left(T_{0}-T_{\infty}\right)}{h A_{\mathrm{fin}}\left(T_{0}-T_{\infty}\right)}=\frac{\sqrt{P h k A}}{h P L}=\frac{1}{L} \sqrt{\frac{k A}{h P}}=\frac{1}{m L}
$$

## Fin Effectiveness

The performance of fins is judged on the basis of the enhancement in heat transfer relative to the no-fin case, and expressed in terms of the fin effectiveness:

$$
\varepsilon_{\text {fin }}=\frac{Q_{\text {fin }}}{Q_{\text {no fin }}}=\frac{\text { heat transfer rate from the fin }}{\text { heat transfer rate without fin }}
$$



Figure 16: LMTD Calculations

- When one of the fluid proceeds through the apparatus isothermally (e.g. condensing steam), parallel flow and counterflow yield identical temperature differences.
- Correction factor for LMTD, $\left(F_{t}\right)$ for multipass and cross-flow exchangers:

$$
\Delta T_{\text {corrected }}=F_{t} \times \text { LMTD for counterflow }
$$

- Generally $F_{t}$ is less than unity for cross flow and multipass arrangements; it is unity for true counterflow heat exchanger. $F_{t}$ represents the degree of departure of the true mean temperature difference from LMTD for counterflow.
- Less heat transfer area is required for counterflow arrangement.


### 6.3 Effectiveness Method or $\varepsilon$-NTU Method of Heat Exchanger Calculations

If the terminal temperatures of cold and hot fluids are not given, then LMTD cannot be calculated. For such cases, to rate or size a heat exchanger, $\varepsilon$-NTU method can be used, at ease.

## - Effectiveness of an exchanger

$$
\varepsilon=\frac{Q}{Q_{\max }}=\frac{\text { actual heat transfer rate }}{\text { maximum possible heat transfer rate from one stream to the other }}
$$

where

$$
Q=m_{h} C_{P h}\left(T_{h, i}-T_{h, o}\right)=m_{c} C_{P c}\left(T_{c, o}-T_{c, i}\right)
$$

and

$$
Q_{\max }=\left(m C_{P}\right)_{\min }\left(T_{h, i}-T_{c, i}\right)
$$

Here $\left(m C_{P}\right)_{\text {min }}$ is the the smaller of $m_{h} C_{P h}$ and $m_{c} C_{P c}$ for the hot and cold fluids.
(a) 35
(b) 1.53
(c) 0.66
(d) 0.03
(b) $\checkmark$ Explanation:

$$
q=h\left(T_{\infty}-T_{S, I}\right)=\frac{T_{S, I}-T_{S, O}}{\frac{L_{A}}{k_{A}}+\frac{L_{B}}{k_{B}}+\frac{L_{C}}{k_{C}}}
$$

Substituting the known quantities, we get

$$
25 \times(800-600)=\frac{600-20}{\frac{0.3}{20}+\frac{0.15}{k_{B}}+\frac{0.15}{50}}
$$

Solving, we get $k_{B}=1.53 \mathrm{~W} / \mathrm{m} . \mathrm{K}$
16. A composite wall is made of four different materials of construction in the fashion shown below. The resistance (in $\mathrm{K} / \mathrm{W}$ ) of each of the sections of the wall is indicated in the diagram.


The overall resistance (in $\mathrm{K} / \mathrm{W}$, rounded off to the first decimal place) of the composite wall, in the direction of heat flow, is $\qquad$ (G-2016-9)
(3.9) $\checkmark$ Explanation: Total resistance of the composite wall is given by

$$
R_{\text {overall }}=R_{1}+R_{23}+R_{4}
$$

Here, materials 2 and 3 are in parallel. Combined resistance of them is given by

$$
\frac{1}{R_{23}}=\frac{1}{R_{2}}+\frac{1}{R_{3}}=\frac{R_{2}+R_{3}}{R_{2} R_{3}} \quad \Longrightarrow \quad R_{23}=\frac{R_{2} R_{3}}{R_{2}+R_{3}}
$$

Hence,

$$
\begin{aligned}
R_{\text {overall }}=R_{1}+R_{23}+R_{4} & =R_{1}+\frac{R_{2} R_{3}}{R_{2}+R_{3}}+R_{4} \\
& =3+\frac{0.25 \times 1}{0.25+1}+0.7=3.9 \mathrm{~K} / \mathrm{W}
\end{aligned}
$$

83. The space between two hollow concentric spheres of radii 0.1 m and 0.2 m is under vacuum. Exchange of radiation (uniform in all directions) occurs only between the outer surface $\left(S_{1}\right)$ of the smaller sphere and the inner surface $\left(S_{2}\right)$ of the larger sphere. The fraction (rounded off to the second decimal place) of the radiation energy leaving $S_{2}$, which reaches $S_{1}$ is $\qquad$ (G-2016-42)
(0.25) $\checkmark$ Explanation: For flat or convex surface, $F_{i i}=0$. Hence, $F_{11}=0$.

From summation rule,

$$
F_{11}+F_{12}=1 \quad \Longrightarrow \quad F_{12}=1
$$

From reciprocity relation,

$$
A_{2} F_{21}=A_{1} F_{12} \quad \Longrightarrow \quad F_{21}=\frac{A_{1}}{A_{2}} F_{12}=\frac{4 \pi r_{1}^{2}}{4 \pi r_{2}^{2}} \times 1=\frac{0.1^{2}}{0.2^{2}}=0.25
$$

84. A well-insulted hemispherical furnace (radius $=1 \mathrm{~m}$ ) is shown below:


The self-view factor of radiation for the curved surface 2 is
(G-2009-33)
(a) $1 / 4$
(b) $1 / 2$
(c) $2 / 3$
(d) $3 / 4$
(b) $\checkmark$ Explanation: By reciprocity rule, we have

$$
A_{1} F_{12}=A_{2} F_{21}
$$

$F_{12}=1$, as surface 1 is a flat one. Therefore, from the above relation we get, $F_{21}=$ $A_{1} / A_{2}$. From summation rule, we have

$$
F_{21}+F_{22}=1
$$

Therefore, we get

$$
F_{22}=1-F_{21}=1-\left(A_{1} / A_{2}\right)=\frac{A_{2}-A_{1}}{A_{2}}=\frac{2 \pi r^{2}-\pi r^{2}}{2 \pi r^{2}}=\frac{1}{2}
$$

85. The view factor matrix for two infinitely long co-axial cylinders, shown in the figure below, is

## Solution:

$$
Q=\left(\dot{m} C_{P} \Delta T\right)_{\mathrm{cold}}=\left(\dot{m} C_{P} \Delta T\right)_{\mathrm{hot}}=U A \Delta T_{\mathrm{lm}}
$$

Given:

$$
\Delta T_{\text {cold }}=80-40=40^{\circ} \mathrm{C} \quad \text { and } \Delta T_{\text {cold }}=100-60=40^{\circ} \mathrm{C}=\Delta T
$$

And,

$$
\Delta T_{\operatorname{lm}}=100-80=60-40=20^{\circ} \mathrm{C}
$$

Since, $\Delta T_{\text {cold }}=\Delta T_{\text {hot }}$, we get $\left(\dot{m} C_{P}\right)_{\text {cold }}=\left(\dot{m} C_{P}\right)_{\text {hot }}=\dot{m} C_{P}$. Since, $Q$ reduces by half, for no change in $\dot{m} C_{P}$ i.e., $Q_{\text {new }}=0.5 Q_{\text {old }}$, we get

$$
\Delta T_{\text {new }}=0.5 \Delta T_{\text {old }}=0.5 \times 40=20^{\circ} \mathrm{C}
$$

For no change in inlet temperatures, we get the new values of exit temperatures of cold and hot fluids as: $60^{\circ} \mathrm{Cand} 80^{\circ} \mathrm{C}$, respectively.
With these new exit temperatures,

$$
\begin{equation*}
\Delta T_{\mathrm{lm}, \text { new }}=(100-60)=40=(80-40)=40^{\circ} \mathrm{C} \tag{c}
\end{equation*}
$$

Additionally, we can get to know the new value of $U$ with reference to its old, as below:

$$
Q_{\text {new }}=0.5 Q_{\text {old }} \quad \Longrightarrow \quad U_{\text {new }} A \Delta T_{\text {lm,new }}=0.5 U_{\text {old }} A \Delta T_{\text {lm }, \text { old }}
$$

i.e.,

$$
U_{\text {new }} A \times 40=0.5 U_{\text {old }} A \times 20 \quad \Longrightarrow \quad U_{\text {new }}=0.25 U_{\text {old }}
$$

## Example 18: Stirred Vessel with Jacket Cooling

A hot fluid entering a well-stirred vessel is cooled by feeding cold water through a jacket around the vessel. Assume the jacket is well-mixed. For the following data,
mass flowrates of the hot fluid $=0.25 \mathrm{~kg} / \mathrm{s}$
mass flow rate of cold water $=0.4 \mathrm{~kg} / \mathrm{s}$
specific heats of oil $=6000 \mathrm{~J} /(\mathrm{kg} . \mathrm{K})$
specific heat of cold water $=4184 \mathrm{~J} /(\mathrm{kg} . \mathrm{K})$
the inlet and exit temperature of the hot fluid is $150^{\circ} \mathrm{C}$ and $100^{\circ} \mathrm{C}$ respectively.
inlet temperature of cold water $=20^{\circ} \mathrm{C}$
the overall hat transfer coefficient is $500 \mathrm{~W} /\left(\mathrm{m}^{2} . K\right)$.
the heat transfer area in $\mathrm{m}^{2}$, is
(G-2007-44)
(a) 1.82
(b) 2.1
(c) 3
(d) 4.26

## Solution:

By energy balance,

$$
\begin{aligned}
\left(m C_{P} \Delta T\right)_{\text {hot fluid }} & =\left(m C_{P} \Delta T\right)_{\text {cold water }} \\
0.25 \times 6000 \times(150-100) & =0.4 \times 4184 \times(T-20)
\end{aligned}
$$

Exit temperature of water $(T)=64.8^{\circ} \mathrm{C}$
For well-stirred vessel, and well-mixed jacket, the temperature profile is shown below:


The fluid inside the stirred vessel is at a temperature of the exit temperature of its fluid. Similarly, the fluid inside the well-mixed jacket is at the exit temperature of its fluid (Note: This approach is used in concentration data of CSTR, i.e., $C_{\text {reactor }}=C_{\text {exit }}$ ).
From the above temperature profiles, we see that, $T_{\text {stirred vell }}=100^{\circ} \mathrm{C}$, and that of $T_{\text {jacket }}=$ $64.8^{\circ} \mathrm{C}$. Therefore,

$$
\Delta T_{\mathrm{lm}}=100-64.8=35.2^{\circ} \mathrm{C}
$$

Heat transfer rate $(Q)$ is given by

$$
Q=m C_{P} \Delta T=0.25 \times 6000 \times(150-100)=75000 \mathrm{~J} / \mathrm{s}
$$

We know that, $Q=U A \Delta T_{\mathrm{lm}}$. Therefore,

$$
A=\frac{Q}{U \Delta T_{\mathrm{lm}}}=\frac{75000}{500 \times 35.2}=4.26 \mathrm{~m}^{2}
$$

(d) $\checkmark$

If one has not considered the well-mixed condition of agitated vessel and jacket fluid, then

$$
\Delta T_{\mathrm{lm}}=\frac{(150-64.81)-(100-20)}{\ln \left(\frac{150-64.81}{100-20}\right)}=82.56^{\circ} \mathrm{C}
$$

and,

$$
A=\frac{Q}{U \Delta T_{\mathrm{lm}}}=\frac{75000}{500 \times 82.56}=1.82 \mathrm{~m}^{2} \quad \text { (the wrong answer!) }
$$

## Example 19: LMTD from Effectiveness Method

Water ( $C_{p}=4.18 \mathrm{~kJ} / \mathrm{kg} . \mathrm{K}$ ) at $80^{\circ} \mathrm{C}$ enters a counterflow heat exchanger with a mass flow rate of $0.5 \mathrm{~kg} / \mathrm{s}$. Air ( $\left.C_{p}=1 \mathrm{~kJ} / \mathrm{kg} . \mathrm{K}\right)$ enters at $30^{\circ} \mathrm{C}$ with a mass flow rate of $2.09 \mathrm{~kg} / \mathrm{s}$. If the effectiveness of the heat exchanger is 0.8 , the LMTD (in ${ }^{\circ} \mathrm{C}$ ) is
(G-ME-2012-41)
(a) 40
(b) 20
(c) 10
(d) 5

## Solution:

By definition, effectiveness of heat exchanger $\varepsilon$ is given by

$$
\varepsilon=\frac{Q}{Q_{\max }}=\frac{m_{h} C_{P h}\left(T_{h, \text { in }}-T_{h, \text { out }}\right)}{\left(m C_{P}\right)_{\min }\left(T_{h, \text { in }}-T_{c, \text { in }}\right)}
$$


(a) Dry bulb (normal)
(b) Wet bulb

Figure 14: Dry-bulb and Wet-bulb Thermometers

The vapor pressure is a function of temperature. It increases with increase in temperature. Hence, when the temperature increases the $\%$ relative humidity and $\%$ humidity decreases.
At constant temperature, as the humidity increases the \% humidity and the \% relative humidity increases. Refer to Fig.(13).

- The distinction between percentage humidity and relative humidity should be noted. The difference in values of the two quantities does not usually exceed 7 to 8 percent.
- Dry Bulb Temperature (DBT):

The temperature of a vapor-gas mixture as recorded by immersing the bulb of a thermometer in the mixture is called dry-bulb temperature.

- Wet Bulb Temperature (WBT):

Wet bulb temperature is the steady-state temperature of the vapor-gas mixture measured by a thermometer whose bulb is covered with a wet wick or saturated completely by the same fluid. Refer to Fig.(14).
The bulb of the thermometer is covered by a liquid. This when contacted with the vaporgas mixture the liquid is evaporated by losing its latent heat of vaporization. This latent heat of vaporization is transferred from the vapor-gas mixture and loses its sensible heat. Hence, the temperature is less when the wet bulb temperature is measured.

$$
\text { WBT }<\text { DBT(except at } 100 \% \text { saturation) }
$$

The difference between DBT and WBT is called wet bulb depression.

## - Dew Point (DP):

It is the temperature at which a vapor-gas mixture becomes saturated when cooled at constant pressure in the absence of the liquid.


Slope of operating line is $R /(R+1)$. At minimum reflux, $q$-line and operating line intersects, and this point is at the equilibrium curve, i.e., at $\left(x^{\prime}, y^{\prime}\right)$.
Given: $x_{D}=0.9 ; x^{\prime}=0.5$; and $y^{\prime}=0.7$. Therefore,

$$
\text { Slope }=\frac{x_{D}-y^{\prime}}{x_{D}-x^{\prime}}=\frac{0.9-0.7}{0.9-0.5}=0.5=\frac{R_{m}}{R_{m}+1} \quad \Longrightarrow \quad R_{m}=1
$$

66. An aqueous solution of methanol is to be distilled in a tray column. High-pressure steam is available as a source of heat. For a given reflux ratio and overhead composition, two options are being explored: (i) a reboiler is used, and (ii) no reboiler is used but steam is fed directly to the bottom of the column. As compared to option (i), in option (ii):
(a) less number of trays are required
(b) composition of the residue remains unchanged
(c) more number of trays are required but the residue composition remains unchanged
(d) more number of trays are required and the residue composition is more dilute in methanol
(G-2004-70)
(a) $\checkmark$ Explanation: Fig.(15) shows the comparison of case with reboiler, and that with open-steam for a typical system. Usage of open-steam in comparison with reboiler leads to the following: (i) for a given number of stages in the stripping section, opensteam usage produce a residue with less amount of more-volatile component, (ii) for a given change in composition, open-steam usage requires less number of trays.
67. A distillation column at a pilot plant is scaled up by 3 times for industrial use at steady state. After scaling up
(G-2005-4)
(a) the number of theoretical trays increases by 3 times
(b) the minimum reflux ratio is increased by three times
(c) the feed flow rate and product flow rates are increased by three times
(d) the feed composition and product compositions are increased by three times
(c) $\checkmark$ Explanation: Scaling-up refers to increasing the flow rate. Pilot plant and industrial plant will have same compositions of the key variables. Hence the number of trays required will be the same.


Figure 15: Open Steam Usage in Distillation

## 6 Extraction

68. For a system containing species $P, Q$ and $R$, composition at point $k$ on the ternary plot is
(G-2008-8)

(a) $62.5 \% P, 12.5 \% Q, 25 \% R$
(b) $25 \% P, 62.5 \% Q, 12.5 \% R$
(c) $12.5 \% P, 62.5 \% Q, 25 \% R$
(d) $12.5 \% P, 25 \% Q, 62.5 \% R$
(a) $\checkmark$ Explanation: At the corner points, the variables take their maximum values (100\%). At the top corner, $\boldsymbol{P}$ is $100 \%$; likewise the other variables. The point $k$ is closer to the maximum value of $\boldsymbol{P}$.

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(Useful for GATE and other Aptitude Tests)

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Figure 17: Change in Gas-phase Volumetric Flow Rate down the Length of the Reactor

## Variation of Volumetric Flow Rate of Material Passing through the Reactor

- For constant density systems $\left(\varepsilon_{A}=0\right)$, i.e., all liquid-phase reactions, the material travels through the reactor at a constant volumetric flow rate $\left(v=v_{0}\right)$ and hence, $\bar{t}=\tau=V / v_{0}$.
- For variable density systems $\left(\varepsilon_{A} \neq 0\right)$, i.e., gas-phase reactions with changing number of moles, $\bar{t} \neq \tau$.
- For variable density systems $\left(\varepsilon_{A} \neq 0\right), \bar{t}<\tau$, when the total number of moles increase as the reaction proceeds.
- For variable density systems $\left(\varepsilon_{A} \neq 0\right), \bar{t}>\tau$, when the total number of moles decrease as the reaction proceeds.

Fig.(17) depicts the profiles of the volumetric flow rates along the length of the ideal tubular reactor.

## Damköhler Number

- Damköhler number (Da) is defined based on the inlet conditions of a flow reactor.
- Damköhler number (Da) gives an approximate idea about the degree of conversion $\left(X_{A}\right)$ that can be accomplished in a flow reactor.
- Physical significance of Damköhler number (Da):

$$
\mathrm{Da}=\frac{\left(-r_{A 0}\right) V}{F_{A 0}}=\frac{\left(-r_{A 0}\right)}{\left(F_{A 0} / V\right)}=\frac{\text { Rate of reaction at the reactor inlet }}{\text { Rate of flow of } A \text { entering the reactor }}
$$

In an MFR, the concentration can drop in a single step from the initial concentration $\left(C_{A 0}\right)$ to the concentration corresponding to the maximum rate ( $C_{\mathrm{A}, \mathrm{opt}}$ ). Hence, the MFR in this series must operate at an outlet concentration of ( $C_{\mathrm{A}, \mathrm{opt}}$ ) so as to minimize the reactor volume / space time requirement.

Conversely, if the unconverted reactant could be separated and recycled back, a single MFR operated at $\left(C_{\mathrm{A}, \mathrm{opt}}\right)$ is the best of all alternatives since it requires the smallest volume (maximum possible rate of reaction).

Nevertheless, one needs to consider the overall economics along with the cost of recycle and of separation, which will decide which system is the most favorable.


## 6 Multiple Reactions

A multiple reaction refers to that reaction system whose kinetic behavior can be understood completely only when two or more rate laws are used, i.e., multiple reactions are represented by more than one stoichiometric equation.

A single reaction requires only one stoichiometric equation and a rate equation to describe the reaction system.

In single reactions, the type of flow (mixed or plug) influences only the reactor size (volume) required to achieve a given duty.

In multiple reactions, the type of flow not only influences the reactor size (volume) but also the product distribution.

We know that, CSTR is a reactor with $R \rightarrow \infty$. Any further increase in $R$ will not influence the exit conversion. So, the conversion remains as $50 \%$ itself.
45. The following reaction rate curve is shown for a reaction $A \rightarrow P$. Here, $\left(-r_{A}\right)$ and $X_{A}$ represent reaction rate and conversion, respectively. The feed is pure $A$ and $90 \%$ conversion is desired.


Which amongst the following reactor configurations gives the lowest total volume of reactor( s )?
(G-2017-17)
(a) CSTR followed by PFR
(b) Two CSTRs in series
(c) PFR followed by CSTR
(d) A single PFR
(a) $\checkmark$ Explanation: The shaded area represents total volume in each case:


Note: The given reaction rate curve is a characteristic of the autocatalytic reaction. Hence, a CSTR followed by a PFR is the best scheme (minimum total volume).

Now, we need to calculate $N$ for $t=10 \mathrm{~min}$ :

$$
\begin{aligned}
N & =N_{0} e^{-k_{d} t}=\left(10^{8}\right) \times\left(e^{-0.10 \times 10}\right) \\
& =\left(10^{8}\right) \times\left(e^{-1}\right) \\
\Longrightarrow \quad N & =3.7 \times 10^{7}
\end{aligned}
$$

## Example 9: Kinetics of Cell Growth

Mammalian cells in active growth phase were seeded at a density of $1 \times 10^{5}$ cells $/ \mathrm{mL}$. After 72 hours, $1 \times 10^{6}$ cells $/ \mathrm{mL}$ were obtained. The population double time of the cells in hours is (up to two decimal places) $\qquad$ (G-BT-2018-48)

## Solution:

The growth kinetics of cells is represented by

$$
\frac{d C}{d t}=+k C
$$

where $C$ is the number of cells $/ \mathrm{mL}$ at time $t$ and $k$ is the rate constant of growth of cells. Let $C_{0}$ be the number of cells $/ \mathrm{mL}$ at time $t=0$. Integrating the above equation, we have,

$$
\begin{aligned}
\int_{C_{0}}^{C} \frac{d C}{C} & =k \int_{0}^{t} d t \\
\Longrightarrow \quad \ln \left(\frac{C}{C_{0}}\right) & =k t
\end{aligned}
$$

Given: $C_{0}=1 \times 10^{5}$ cells $/ \mathrm{mL} ; C=1 \times 10^{6}$ cells $/ \mathrm{mL}$ for $t=72 \mathrm{~h}$.

$$
\begin{aligned}
\Longrightarrow \quad \ln \left(\frac{1 \times 10^{6}}{1 \times 10^{5}}\right) & =(k) \times(72 \mathrm{~h}) \\
\Longrightarrow \quad k & =\frac{\ln (10)}{72 \mathrm{~h}}=0.0320 \mathrm{~h}^{-1}
\end{aligned}
$$

Now, the population doubling time $\left(t_{d}\right)$ is to be estimated. Population doubling time $\left(t_{d}\right)$ is the time required for the initial population of cells to get doubled: i.e., $C=2 C_{0}$ for $t=t_{d}$.

$$
\begin{aligned}
\Longrightarrow \quad \ln \left(\frac{2 C_{0}}{C_{0}}\right) & =k t_{d} \\
\Longrightarrow \quad t_{d} & =\frac{\ln (2)}{k}=\frac{0.6931}{0.0320 \mathrm{~h}^{-1}}=21.66 \mathrm{~h}
\end{aligned}
$$

## 3 Ideal Reactors

## Example 10: Pollutant Degradation in MFR

A pollutant $P$ degrades according to first order kinetics. An aqueous stream containing $P$ at $2 \mathrm{kmol} / \mathrm{m}^{3}$ and volumetric flow rate $1 \mathrm{~m}^{3} / \mathrm{h}$ requires a mixed flow reactor of volume $V$ to bring down the pollutant level to $0.5 \mathrm{kmol} / \mathrm{m}^{3}$. The inlet concentration of the pollutant is now

Combining Eqn.(3) and Eqn.(4), we get, for 9 mm particles,

$$
\begin{align*}
\frac{\tau^{\prime}}{C_{A 0}} & =\int_{0}^{X_{A}} \frac{d X_{A}}{k_{1} C_{A 0}\left(1-X_{A}\right)} \\
k_{1} \tau^{\prime} & =-\left.\ln \left(1-X_{A}\right)\right|_{0} ^{0.632}=0.9997 \\
\tau^{\prime} & \approx \frac{1}{k_{1}} \tag{5}
\end{align*}
$$

For 18 mm pellets (assuming that $W$ is fixed and hence $\tau^{\prime}$ is the same in both cases):

$$
\begin{aligned}
\frac{\tau^{\prime}}{C_{A 0}} & =\int_{0}^{X_{A}} \frac{d X_{A}}{k_{2} C_{A 0}\left(1-X_{A}\right)} \\
k_{2} \tau^{\prime} & =-\left.\ln \left(1-X_{A}\right)\right|_{0} ^{X_{A}}
\end{aligned}
$$

Using Eqn.(5) in above

$$
k_{2}\left(\frac{1}{k_{1}}\right)=-\ln \left(1-X_{A}\right)
$$

Using Eqn.(2) in above

$$
\begin{aligned}
\left(\frac{1}{2} k_{1}\right)\left(\frac{1}{k_{1}}\right) & =-\ln \left(1-X_{A}\right) \\
\ln \left(1-X_{A}\right) & =-1 / 2 \\
X_{A} & =1-e^{-1 / 2}=0.3935
\end{aligned}
$$

## Example 37: Catalytic Reaction with Diffusion and Reaction Resistances

Consider an irreversible, solid catalyzed, liquid phase first order reaction. The diffusion and reaction resistances are comparable. The overall rate constant ( $k_{o}$ ) is related to the overall mass transfer coefficient ( $k_{m}$ ) and the reaction rate constant ( $k$ ) as (G-2011-21)
(a) $k_{o}=\frac{k k_{m}}{k+k_{m}}$
(b) $k_{o}=\frac{k+k_{m}}{k k_{m}}$
(c) $k_{o}=\frac{k+k_{m}}{2}$
(d) $k_{o}=k+k_{m}$

## Solution:

The catalytic reaction $A(l)+B(s) \rightarrow R(l)$ is represented schematically in the diagram below:
Main body
of liquid

The flux of $A$ by diffusion to the surface is given by

$$
\begin{align*}
r_{A 1}^{\prime \prime} & =\frac{1}{S} \frac{d N_{A}}{d t}=-\frac{\mathcal{D}}{\Delta x}\left(C_{A l}-C_{A s}\right) \\
\Longrightarrow \quad r_{A 1}^{\prime \prime} & =k_{m}\left(C_{A l}-C_{A s}\right) \tag{1}
\end{align*}
$$

The rate of the first order reaction, based on unit surface is given by

$$
\begin{equation*}
r_{A 2}^{\prime \prime}=\frac{1}{S} \frac{d N_{A}}{d t}=k C_{A s} \tag{2}
\end{equation*}
$$

Given: Diffusion resistance $=$ reaction resistance. Therefore,

$$
r_{A 1}^{\prime \prime}=r_{A 2}^{\prime \prime}
$$

So, from Eqns.(1) and (2), we get

$$
\begin{align*}
k_{m}\left(C_{A l}-C_{A s}\right) & =k C_{A s} \\
k_{m} C_{A l} & =k_{m} C_{A s}+k C_{A s} \\
\Longrightarrow \quad C_{A s} & =\frac{k_{m}}{k_{m}+k} C_{A l} \tag{3}
\end{align*}
$$

Since $C_{A s}$ cannot be measured, we will substitute for $C_{A s}$ of Eqn.(1) with Eqn.(3).

$$
\begin{aligned}
r_{A 1}^{\prime \prime}=r_{A 2}^{\prime \prime}=r_{A}^{\prime \prime} & =k_{m}\left(C_{A l}-\frac{k_{m}}{k_{m}+k} C_{A l}\right) \\
& =k_{m}\left(\frac{k_{m}+k-k_{m}}{k_{m}+k}\right) C_{A l} \\
\Longrightarrow \quad r_{A}^{\prime \prime} & =\frac{k k_{m}}{k_{m}+k} C_{A l} \\
\text { (or) } \quad r_{A}^{\prime \prime} & =k_{o} C_{A l} \quad\left(\text { where } k_{o}=\frac{k k_{m}}{k_{m}+k}\right)
\end{aligned}
$$

## Example 38: Effectiveness Factor of a Catalyst Slab

A catalyst slab of half-thickness $L$ (the width and length of the slab $\gg L$ ) is used to conduct the first order reaction $A \rightarrow B$. At 450 K , the Thiele modulus for this system is 0.5 . The activation energy for the first order rate constant is $100 \mathrm{~kJ} / \mathrm{mol}$. The effective diffusivity of the reactant in the slab can be assumed to be independent of temperature, and external mass transfer resistance can be neglected. If the temperature of the reaction is increased to 470 K , then the effectiveness factor at 470 K (up to two decimal places) will be $\qquad$ -.
Value of universal gas constant $=8.314 \mathrm{~J} / \mathrm{mol} . \mathrm{K}$

## Solution:

Effectiveness factor $(\xi)$, for a catalytic slab is given by

$$
\xi=\frac{\tanh \phi}{\phi}
$$



Figure 1: Relationship between Pole Location and the Resulting Transient


Figure 16: Fail-safe Design of Control Valves

- Equal Percentage Valve: A control valve is said to be EQUAL \% if equal increment of valve travel or opening produces equal PERCENT (\%) increment in flow $q$.
It is the most commonly used control-valve.
While the flow characteristic of the valve itself may be equal percentage, most control loops will produce an installed characteristic approaching linear when the overall system pressure drop is large relative to that across the valve.
- As a general rule, systems with a significant amount of pipe and fittings (the most common case) are best suited to equal percentage inherent characteristic valves. Systems with very little pipe (where the pressure drop available to the control valve remains nearly constant and as a result the inherent characteristic of the valve is also the installed characteristic) are better suited to linear inherent characteristic valves.


## Fail-safe Position of Control Valves

- Control valves come in two sorts: air to open; and air to close. Refer to Fig.(16). Air to open valves are normally held closed by the spring and require air pressure (a control signal) to open them - they open progressively as the air pressure increases. Air to close valves are held open by the valve spring and require air pressure to move them towards the closed position.
- The reason for the two types of valves is to allow fail-safe operation. In the event of instrument air failure it is important that all control valves fail in a safe position (e.g. an exothermic reactor's feed valves should be fail closed (air to open) and its coolant system valves fail open (air to close)).


Figure 19: Asymptotic Bode Plot of: $G=\frac{3(s+1)}{(0.05 s+1)(10 s+1)}$ (construction details are given below)

Constructing the Bode Plot: Transfer function of the given system is factored into a product of four transfer functions as below:

$$
3, \quad \frac{1}{10 s+1}, \quad(s+1), \quad \frac{1}{0.05 s+1}
$$

with the following corner frequencies (in the same order):

$$
\omega_{1}=\text { none }, \quad \omega_{2}=1 / 10=0.1, \quad \omega_{3}=1 / 1=1, \quad \omega_{4}=1 / 0.05=20
$$

The following four regions are identified on the frequency (in $\omega$ ) scale:

$$
\begin{array}{llrl}
0 \leq \omega \leq \omega_{2}, & \omega_{2} \leq \omega \leq \omega_{3}, & \omega_{3} & \leq \omega \leq \omega_{4},
\end{array} \quad \omega_{4} \leq \omega<\infty
$$

| Frequency region | Slopes of the asymptotes of the transfer functions |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $K=3$ | $\frac{1}{10 s+1}$ | $(s+1)$ | $\frac{1}{0.05 s+1}$ | Overall |
| $0 \leq \omega \leq 0.1$ | 0 | 0 | 0 | 0 | 0 |
| $0.1 \leq \omega \leq 1$ | 0 | -1 | 0 | 0 | -1 |
| $1 \leq \omega \leq 20$ | 0 | -1 | 1 | 0 | 0 |
| $20 \leq \omega<\infty$ | 0 | -1 | 1 | -1 | -1 |

43. The Bode plot of a transfer function $G(s)$ is shown in the figure below.


The gain $(20 \log |G(s)|)$ is 32 dB and -8 dB at $1 \mathrm{rad} / \mathrm{s}$ and $10 \mathrm{rad} / \mathrm{s}$ respectively. The phase is negative for all $\omega$. Then $G(s)$ is
(G-EE-2013-15)
(a) $\frac{39.8}{s}$
(b) $\frac{39.8}{s^{2}}$
(c) $\frac{32}{s}$
(d) $\frac{32}{s^{2}}$

## (b) $\checkmark$ Explanation:



The given semilog plot is plotted in log-log scales as shown above. From the figure it is seen that the slope of the given curve is $(32-(-8))=40 \mathrm{~dB}$ /decade which is equal to -2 . This is characteristic of the transfer function $K / s^{2}$.
For $1 / s^{2}, \mathrm{AR}=1$ at $\omega=1$. But, it is given that, at $\omega=1,20 \log _{10}(\mathrm{AR})=32 \mathrm{~dB}$.
$20 \log _{10}(\mathrm{AR})=32 \quad \Longrightarrow \quad \log _{10}(\mathrm{AR})=32 / 20 \quad \Longrightarrow \quad \mathrm{AR}=10^{32 / 20}=39.81=K$
Hence, the given Bode plot corresponds to $39.81 / s^{2}$.

From the above table, it can be seen that the option (a) is having the response with negative initial slope. In addition, by analysing the poles of transfer function it can be seen that the options (c) and (d) produce unstable response because of the existence of positive pole(s). $\Longrightarrow \quad$ (a) $\checkmark$

## Example 10: Transfer Functions and their Responses to Unit Step Input

Match the transfer functions with the response to a unit step input shown in the figure.
i. $\frac{-2.5(-4 s+1)}{4 s^{2}+4 s+1}$
ii. $\frac{-2 e^{-10 s}}{10 s+1}$
iii. $\frac{-5}{-20 s+1}$
iv. $\frac{-0.1}{s}$
v. $\frac{4 s+3}{2 s+1}$

$\begin{array}{ll}\text { (a) } i-E, i i-C, i i i-A, i v-D, v-B & \text { (b) } i-A, i i-B, i i i-C, i v-D, v-E \\ \text { (c) } i-B, i i-A, i i i-C, i v-E, v-D & \text { (d) } i-E, i i-A, i i i-C, i v-B, v-D\end{array}$
(G-2007-61)

## Solution:

By simply seeing the curves, we can say that:

- curve-C corresponds to a system with dead-time (i.e., corresponding to ii). $\Longrightarrow \quad$ ii-C
- curve-D corresponds to that of a system with $1 / s$ in its transfer function (corresponding to iv).

$$
\Longrightarrow \quad \text { iv-D }
$$

- curve-E corresponds to inverse response. Inverse response systems have positive zero.
- Transfer function-v has negative zero; i.e., $4 s+3=0 \quad \Longrightarrow \quad s=-3 / 4$.
- Transfer function-i has positive zero; i.e., $-2.5(-4 s+1)=0 \quad \Longrightarrow \quad 10 s-2.5=$ $0 \quad \Longrightarrow \quad s=0.25$. Hence, curve-E corresponds to i. $\quad \Longrightarrow \quad \mathrm{i}-\mathrm{E}$

These corresponds to answer option (a). However, a detailed analysis is needed for getting convinced.

## Detailed Analysis:

Transfer function-iii can be written as $\frac{-5}{-20 s+1}$. This is a first order system with $K_{p}=-5$, and $\tau_{p}=-1 / 20$. Response of this system for unit step change in input is $y=-5\left(1-e^{t / 20}\right)=$ $e^{t / 20}-5$. This will show a ever growing response with $t$.
In addition, this system has a positive pole. Hence this system will show an unstable response. Such a response is shown by curve-A.
iii-A $\sqrt{ }$
From the figure, it can be seen the curve-C has a dead time of about 10 units. Systems with dead time have a transfer function of $e^{-\tau_{d} s}$. This shows that, curve-C corresponds to that of transfer function-ii

Transfer function-iv indicates that it is a integrating system. For this, for unit step change in input, we get, $Y(s)=-0.1 / s^{2}$. By taking inverse Laplace transform, we get $y(t)=-0.1 t$. When $t=40$, we get $y=-4$. From looking at the figure, this corresponds to curve-D. Hence, curve-D corresponds to transfer function-iv.

The curve-B has a initial value of about 2 . We can get the initial value of responses the remaining unmatched functions-i, and vand check for matching this value.
By initial value theorem,

$$
y(0)=\lim _{s \rightarrow \infty} s Y(s)
$$

Therefore, for transfer function (i), with input transfer function of $1 / s$ we get

$$
Y(s)=\frac{-2.5(-4 s+1)}{4 s^{2}+4 s+1} \frac{1}{s}
$$

and

$$
y(0)=\lim _{s \rightarrow \infty} s \frac{-2.5(-4 s+1)}{4 s^{2}+4 s+1} \frac{1}{s}=\lim _{s \rightarrow \infty} \frac{10 s-2.5}{4 s^{2}+4 s+1}
$$

By L'Hospital rule,

$$
y(0)=\lim _{s \rightarrow \infty} \frac{10 s-2.5}{4 s^{2}+4 s+1}=\lim _{s \rightarrow \infty} \frac{10}{8 s+4}=\lim _{s \rightarrow \infty} \frac{10 / s}{8+4 / s}=\frac{10 / \infty}{8+4 / \infty}=0
$$

For transfer function-v

$$
y(0)=\lim _{s \rightarrow \infty} \frac{4 s+3}{2 s+1}=\lim _{s \rightarrow \infty} \frac{4+3 / s}{2+1 / s}=\frac{4+0}{2+0}=2
$$

Hence, from the above initial value analysis, it can be concluded that the response-B corresponds to the transfer function-v.

$$
\mathrm{v}-\mathrm{B} \sqrt{ }
$$

From the given figure, it can be seen that the responses $B$ and $E$ reach there steady final ultimate values as $t \rightarrow \infty$. From the final value theorem, we can get the response values of each function $y(t)$ as $t \rightarrow \infty$.

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The asset value (or book value) $V_{a}$ of the equipment at any time

$$
V_{a}=V-a D
$$

where $a$ is the number of years in actual use.
Straight line method is also called as fixed installment method. Depreciation of fixed assets is uniform throughout the year.

## - Declining Balance or Fixed Percentage Method

$$
V_{a}=V(1-f)^{a}
$$

where

$$
\begin{equation*}
f=1-\left(\frac{V_{s}}{V}\right)^{1 / n} \tag{Text-bookmethod}
\end{equation*}
$$

The text-book relationship presented in above equation is seldom used in actual practice, because it places too much emphasis on the salvage value of the property and is certainly not applicable if the salvage value is zero.
In comparison with the straight line method, declining-balance depreciation permits the investment to be paid off more rapidly during the early years of life.
Double Declining Balance Method: Here $f$ is two times the depreciation rate of straight line method. i.e., $f=2 / n$.

## - Sum of Years Digits Method

$$
\text { Depreciation for year } a=\frac{n-a+1}{\sum_{1}^{n} a}\left(V-V_{s}\right)
$$

For example, with $n=5$ years, depreciation for the first year is

$$
D_{1}=\frac{5-1+1}{1+2+3+4+5}=\frac{5}{15}\left(V-V_{s}\right)
$$

and, depreciation for the second year is

$$
D_{2}=\frac{4}{15}\left(V-V_{s}\right)
$$

- Sinking Fund Method: The use of compound interest is involved in the sinkingfund method. It is assumed that the basic purpose of depreciation allowances is to accumulate a sufficient fund to provide for the recovery of the original capital invested in the property.
Annual depreciation amount $(D)$ is calculated from:

$$
D=\left(V-V_{s}\right)\left[\frac{i}{(1+i)^{n}-1}\right]
$$

This amount $D$ is nothing but the annuity to generate a future worth of $\left(V-V_{s}\right)$.
Book value at the end of year $a$ is calculated from:

$$
V_{a}=V-D\left[\frac{(1+i)^{a}-1}{i}\right]
$$



Figure 2: Break-even Plot

## 4 Profitability Estimates

- Operating Cash Flow: 'Operating Cash Flow' is the cash flow generated from the project's operations. Fig.(3) gives the calculation procedure for the same.
- The most commonly used methods for profitability evaluation are:
- Payback period
- Rate of return on investment
- Net present value (NPV)
- Discounted cash flow based on full-life performance or Internal rate of return (IRR) method
- Capitalized cost


## - Payback Period

$$
\text { Payback Period }=\frac{\text { depreciable fixed capital investment }}{\text { after-tax cash flow }}
$$

- This measure is often used as a "quick and dirty" measure of profitability.
- Also called as Payout Time. Defined in units of time (months or years).
- This methodology does not consider the time value of money; and does not consider any of the costs or benefits of the investment following the payback period.
$(60,395) \checkmark$ Explanation: The relation between present worth $(P)$ and annuity $(A)$ is given by

$$
P=A \frac{(1+i)^{n}-1}{i(1+i)^{n}}
$$

where $i$ is the nominal annual interest rate and $n$ is the number of years.
Given: $A=$ Rs. 12,$000 ; \quad i=9 \%=0.09 ; \quad n=7$ year. Therefore,

$$
P=12,000 \times \frac{(1+0.09)^{7}-1}{0.09 \times(1+0.09)^{7}}=\text { Rs. } 60,395
$$

11. Which of the following statements is TRUE? (Assume that the yearly cash flows are identical for both annuities and that the common interest rate is greater than zero.)
(a) The present value of an annuity due is greater than the present value of an ordinary annuity
(b) The present value of an ordinary annuity is greater than the present value of an annuity due
(c) The future value of an ordinary annuity is greater than the future value of an annuity due
(d) Both (b) and (c) are correct
(a) $\checkmark$ Explanation: Payments made under an ordinary-annuity occur at the end of the period, while payments made under an annuity-due occur at the beginning of the period, as shown in the following figure.


The relation for the future worth of annuities for annuity-due and ordinary-annuity are given as:

$$
F_{\text {ordinary }}=A\left[\frac{(1+i)^{n}-1}{i}\right] \quad F_{\text {due }}=A\left[\frac{(1+i)^{n}-1}{i}\right](1+i)
$$

i.e.,

$$
F_{\text {due }}=(1+i) F_{\text {ordinary }}
$$

Similarly, for the present value $(P)$,

$$
P_{\text {due }}=(1+i) P_{\text {ordinary }}
$$

For the same number of equal payments, both present value and future value (called as maturity amount) will be higher with annuity due. Annuity-due method is followed by the banking industry in India, for recurring deposits (RD). Whereas ordinary-annuity method is used with loan repayments, as equated monthly installments (EMI).

Therefore,

$$
\begin{aligned}
\text { Interest rate per month }\left(i_{m}\right) & =0.01332=1.332 \% \\
\text { Nominal annual interest rate }(i) & =12 \times i_{m}=12 \times 1.332=15.984 \% \\
\text { Effective annual interest rate }\left(i_{\mathrm{eff}}\right) & =\left(1+i_{m}\right)^{12}-1 \\
& =(1+0.01332)^{12}-1=0.1721=17.21 \%
\end{aligned}
$$

## Example 6: EMI for Car Loan

You plan to buy a car that has a total "drive-out" cost of $\$ 25,700$. You will make a down payment of $\$ 3,598$. The remainder of the car's cost will be financed over a period of 5 years. You will repay the loan by making equal monthly payments. Your quoted annual interest rate if $8 \%$ with monthly compounding of interest. (The first payment will be due one month after the purchase date). What will your monthly payment be?

## Solution:

From the given nominal annual interest rate find the effective annual interest rate:

$$
\begin{aligned}
\left(1+i_{\mathrm{eff}}\right) & =\left(1+\frac{i}{n_{c}}\right)^{n_{c}} \\
& =\left(1+\frac{0.08}{12}\right)^{12} \\
\Longrightarrow \quad i_{\mathrm{eff}} & =0.083=8.3 \%
\end{aligned}
$$

Using the effective annual interest rate, find the monthly interest rate:

$$
\begin{aligned}
\left(1+i_{m}\right)^{12} & =\left(1+i_{\mathrm{eff}}\right) \\
& =(1+0.083) \\
\Longrightarrow \quad i_{m} & =0.00667=0.667 \%
\end{aligned}
$$

Note: Here we can calculate $i_{m}$ simply as: $i_{m}=i / 12=0.08 / 12=0.00667$. This is applicable here, because of payment frequency per year and interest addition frequency per year are the same. If they are different, we need to do the calculation in a step-by-step manner as above. The relation between present-worth and annuity is given as:

$$
P=A\left[\frac{\left(1+i_{m}\right)^{n_{m}}-1}{i_{m}\left(1+i_{m}\right)^{n_{m}}}\right]
$$

Here, $P=25700-3598=\$ 22102 ; n_{m}=5 \times 12=60$. Therefore,

$$
A=P\left[\frac{i_{m}\left(1+i_{m}\right)^{n_{m}}}{\left(1+i_{m}\right)^{n_{m}}-1}\right]=22102 \times\left[\frac{0.00667(1+0.00667)^{60}}{(1+0.00667)^{60}-1}\right]=\$ 448.15
$$

## - Joint Efficiency

No radiography : 70\%
Spot radiography : 85\%
$100 \%$ radiography : $100 \%$
Joint efficiency is $100 \%$ for seamless heads.

- Thickness calculation using code formulas:

Circumferential, longitudinal and radial stresses are acting due to internal pressure of the vessel. Thickness calculation is as per the controlling stress acting on the part of the vessel. Simple formulas as given earlier (Eqns.6, 7, 8) ignores the radial stress. Whereas, Codes recognizes that the radial stress may not be negligible, and adjustments have been made in the appropriate formulas. The following are as per ASME Sec VIII Div 1.

- Cylindrical Vessels:
* Circumferential stress (Longitudinal joints)

$$
t=\frac{P R}{f J-0.6 P}=\frac{P D}{2 f J-1.2 P}
$$

* Longitudinal stress (Circumferential joints)

$$
t=\frac{P R}{2 f J+0.4 P}=\frac{P D}{4 f J+0.8 P}
$$

- Spherical Vessels:

$$
t=\frac{P R}{2 f J-0.2 P}=\frac{P D}{4 f J-0.4 P}
$$

where $R$ is the inside radius; $D$ is the inside diameter.

- A cylindrical vessel under internal pressure tends to retain its shape in that any out of roundness or dents resulting from shop fabrication or erection tend to be removed when the vessel is placed under internal pressure. Thus any deformation resulting from internal pressure tends to make an imperfect cylinder more cylindrical. However, the opposite is true for imperfect cylindrical vessels under external pressure, and any imperfection will tend to be aggravated with the result of possible collapse of the vessel. For this reason, a given vessel under external pressure in general has a pressure rating only $60 \%$ as high as it would have under internal pressure.


### 1.4 Closures for Vessels

- The ends of a cylindrical vessel are closed by heads of various shapes. Heads are typically curved rather than flat. The reason is that curved configurations are stronger and allow the heads to be thinner, lighter and less expensive than flat heads. The principal types used are:
- Flat plates and formed flat heads
- Hemispherical heads


Figure 9: Lap-joint and Slip on Flanges Welded with Pipe
or concentric grooves approximately $1 / 64$ inch deep with $1 / 32$ inch spacing. The edges of this grooves serve to deform and hold the gasket. The other types of flange facing are: flat face, tongue and groove facing, ring type joint etc.

The gasket, which is really the focal point of the bolted flange connection, is subjected to compressive force by the bolts. Gaskets are made of nonmetallic materials with composite construction. The serrated surfaces of the flange faces help to maintain the leak-proof joint as the material expands to fill up the irregularities on the face of the flanges.

In flat face flanges, the gasket covers the entire outer diameter of flange. Flat face flanges are used used on pump facings or on fiberglass flanges where the torque of compressing the gasket will damage the flange body and on cast iron flanges sometimes found on mechanical equipment that can cause complications due to the brittle nature of cast iron.

Dimensions of flanges and flanged fittings confirm to the ANSI / ASME B 16.5 standard.

## The Most Commonly Used Raised Face Flanges:

- Slip-on Raised Face (SORF) Flange: This is the most common flange. It has greater ease in welding assembly.
- Welding Neck Raised Face (WNRF) Flange: This has a long tapered hub between the flange ring and the weld joint. This hub provides a more gradual transition from the flange ring thickness to the pipe wall thickness, thereby decreasing the discontinuity stresses and consequently increasing the strength of the flange. They are normally used for extreme service conditions such as high pressure, cold or hot temperature.
- Lab-Joint Flange: Lap-Joint Flanges are similar to slip-on flanges, the difference is it has a curved radius at the bore and face to accommodate a lap joint stub end. The lap joint flange and stub end assembly are normally used in systems requiring frequent dismantling for inspection.
- The other types such as: socket weld raised face (SWRF) and threaded type are used rarely.


Figure 15: Horizontal-cut Segmental Baffles

* Typically lowest cost TEMA design per square foot of heat transfer surface.
* Provides maximum amount of surface for a given shell and tube diameter and length.
* Shell side can only be chemically cleaned.
* No natural provision to allow for differential thermal expansion, an expansion joint must be used.


## - U-tube Heat Exchanger

* U-tube design allows for differential thermal expansion between the shell and the tube bundle as well as for individual tubes.
* Less costly than floating head.
* Because of U-bend, tubes can be cleaned only by chemical means.
* No single tube pass or true countercurrent flow is possible.
* Draining of tube circuit is difficult when mounted with the vertical position with the head side up.


## - Floating Head Exchanger

* Refer to Fig.(13). Floating tubesheet allows for differential thermal expansion between the shell and tube bundle.
* All tubes are attached to two tubesheets. Tubes cannot expand independently so that large thermal shock applications should be avoided.
- Design Codes for Shell-and-tube Heat Exchangers:
- Standards developed by Tubular Exchanger Manufacturers Association, USA, popularly known as TEMA are universally used for design of shell and tube heat exchangers. Equivalent Indian code is IS: 4503.
- These codes specify the standard sizes of shell, tubes, etc., and also maximum allowable baffle spacing, minimum tube sheet thickness, baffle thickness, number of tie-rods required, etc.
- TEMA is comprised of three different classes to categorize designs: TEMA R, TEMA B \& TEMA C.
* TEMA R: for the generally severe requirements of petroleum and related processing applications.
- Resistance to pitting and crevice corrosion are very important if the steel is to be used in chloride environments. Resistance to pitting and crevice corrosion typically increases with increasing contents of chromium, molybdenum, and nitrogen.

| SS 304 | $18-20 \% \mathrm{Cr}, 8-12 \%$ <br> $\mathrm{Ni}, 0.08 \%(\max ) \mathrm{C}$ | $18-8$ stainless steel, most com- <br> monly used material for process <br> equipments. |
| :--- | :--- | :--- |
| SS 304L | $18-20 \% \mathrm{Cr}, 8-12 \%$ <br> $\mathrm{Ni}, 0.03 \%(\max ) \mathrm{C}$ | Low carbon version of SS 304. |
| SS 316 | $16-18 \% \mathrm{Cr}, 10-14 \%$ <br> $\mathrm{Ni}, 2-3 \% \mathrm{Mo}, 0.1 \%$ <br> $(\max ) \mathrm{C}$ | Addition of molybdenum im- <br> proves resistance to chloride en- <br> vironments. |
| SS 316L | $16-18 \% \mathrm{Cr}, 10-14 \%$ <br> $\mathrm{Ni}, 2-3 \% \mathrm{Mo}, 0.03 \%$ <br> $(\max ) \mathrm{C}$ | Low carbon version of SS 316. |
| SS 430 | $14-18 \% \mathrm{Cr}, 0.5 \% \mathrm{Ni}$ | Tableware. The first chemical <br> plant application of stainless steel <br> was SS 430 tank-car for shipping <br> nitric acid. |

## - Intergranular Corrosion with Stainless Steels

- When an austenitic stainless steel is held in the temperature range of $430^{\circ} \mathrm{C}$ to $900^{\circ} \mathrm{C}$ (for example, during welding) the carbon in the metal has a tendency to migrate to grain boundaries and react with the chromium to form its carbide, which precipitates there. As a consequence, the areas around the grain boundaries are depleted of chromium. The reduction of chromium introduces heterogenity and concentration gradient which are fertile grounds for corrosive attack. The local depletion of chromium can also take place to the extent of a non-protective or nonpassive level. During welding operation, a zone just outside the actual weld about 3 mm from it, is in such corrosion susceptible condition. This intergranular corrosion can be eliminated by taking such measures as:
(i) reduction in the amount of carbon to a level as low as $0.03 \%$ (max) as in SS 304 L and 316 L .
(ii) making stainless steel alloys that contain titanium or columbium which have greater affinity for carbon than chromium and will therefore preferentially combine with it during welding.


## Aluminum

- It has a specific gravity of 2.7 , which is about $1 / 3^{\text {rd }}$ of steel.
- It has excellent low temperature properties and is widely used in noncorrosive cryogenic services such as gas treating and air separation.

22. A separation column for vapor-liquid processes $200 \mathrm{kmol} / \mathrm{h}$ of vapor. The flooding velocity is $3 \mathrm{~m} / \mathrm{s}$. If the column operates at $85 \%$ of flooding velocity and the downcomer area is $10 \%$ of the total cross sectional area, what is the diameter of the column? Average density of vapor $=2 \mathrm{~kg} / \mathrm{m}^{3}$ and its molecular weight $=44$.
(G-2005-76)
(a) 0.82 m
(b) 0.72 m
(c) 0.78 m
(d) 1 m
(a) $\checkmark$ Explanation:

Mass flow rate of vapor $=$ molar flow rate $\times$ molecular weight $=200 \times 44=8800 \mathrm{~kg} / \mathrm{h}$
Volumetric flow rate $=\frac{\text { mass flow rate }}{\text { density }}=\frac{8800}{2}=4400 \mathrm{~m}^{3} / \mathrm{h}$
Operating velocity $=0.85 \times$ flooding velocity

$$
=0.85 \times 3=2.55 \mathrm{~m} / \mathrm{s}=2.55 \times 3600=9180 \mathrm{~m} / \mathrm{h}
$$

Net flow area of vapor $=\frac{\text { volumetric flow rate }}{\text { operating velocity }}=\frac{4400}{9180}=0.479 \mathrm{~m}^{2}$
Since, $10 \%$ of area is occupied by downcomer,
Total area of column $=\frac{0.479}{0.9}=0.533 \mathrm{~m}^{2}$

$$
\text { i.e., } \quad \frac{\pi}{4} D^{2}=0.533 \quad \Longrightarrow \quad D=0.82 \mathrm{~m}
$$

23. The flooding velocity in a plate column, operating at 1 atm pressure, is $3 \mathrm{~m} / \mathrm{s}$. If the column is operated at 2 atm pressure, under otherwise identical conditions, the flooding velocity will be
(G-2010-25)
(a) $3 / \sqrt{2}$
(b) $3 / 2$
(c) 1
(d) $3 / 4$
(a) $\checkmark$ Explanation: Flooding velocity $\left(v_{f}\right)$ of plate column is given by

$$
v_{f} \propto \sqrt{\frac{\rho_{L}-\rho_{V}}{\rho_{V}}}
$$

where $\rho_{L}$ is density of liquid; and, $\rho_{V}$ is density of vapor (or gas).
For a gas $\rho \propto P$. For a liquid $\rho$ is almost a constant for low changes in pressure. The quantity $\left(\rho_{L}-\rho_{V}\right) \approx \rho_{L}$, as $\rho_{L} \gg \rho_{V}$. Hence,

$$
v_{f} \propto \frac{1}{\sqrt{\rho_{V}}} \quad \Longrightarrow \quad v_{f} \propto \frac{1}{\sqrt{P}}
$$

Therefore, for doubling the pressure,

$$
\frac{v_{f 2}}{v_{f 1}}=\sqrt{\frac{P_{1}}{P_{2}}} \quad \Longrightarrow \quad v_{f 2}=3 \times \sqrt{\frac{1}{2}}=\frac{3}{\sqrt{2}}
$$

If oleum is to be produced at the plant, it is made in a separate oleum tower upstream of the absorber.
Direct reaction of $\mathrm{SO}_{3}$ with water tends to produce mists of $\mathrm{H}_{2} \mathrm{SO}_{4}$ which are difficult to absorb.

- Recovery of sulfur as sulfuric acid:
- Single Conversion Single Absorption (SCSA) process: 97-98\% recovery; the remainder is lost to the atmosphere as $\mathrm{SO}_{2}$.
- Double Conversion Double Absorption Process (DCDA): 99.8\% recovery.


### 4.3 Sulfur Trioxide $\left(\mathrm{SO}_{3}\right)$

- $\mathrm{SO}_{3}$ is also called as sulfuric anhydride.
- Liquid sulfur trioxide is used for sulfonation, especially in the manufacture of detergents.
- In the past, the difficulty with sulfur trioxide was its instability. However, now stabilized forms of sulfur trioxide are available (for example, Sulfan ${ }^{\circledR}$ ). Inhibitors such as boron compounds, methane sulfonyl chloride, sulfur, tellurium, and phosphorus oxychloride inhibit crystallization or conversion of $\mathrm{SO}_{3}$ to a polymer.


## 5 Chlor-Alkali Industries

### 5.1 Caustic Soda (NaOH)

- The term caustic soda is widely used for NaOH because this compound is corrosive to the skin.
- Over $95 \%$ of the capacity to produce chlorine and essentially $100 \%$ of the capacity to produce caustic soda are based on the electrolysis of brine.

$$
\mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \xrightarrow{\text { electrical energy }} \frac{\text { anode }}{\frac{1}{2} \mathrm{Cl}_{2}(\text { gas })}+\frac{\text { cathode }}{\frac{1}{2} \mathrm{H}_{2}(\text { gas })+\mathrm{NaOH}(\mathrm{aq})}
$$

- Brine electrolysis produces chlorine at the anode and hydrogen along with the lye (aqueous NaOH ) at the cathode.
- Reversible potential of cell reaction is about 2.20 V (theoretical voltage). Actual operating voltage is $3.7-4.0 \mathrm{~V}$.
- Chlorine and sodium hydroxide are produced approximately in equal quantities (wt\%) by the chloralkali process and their share in the total income from the process is approximately the same.
- Sea water contains about $3.4 \%$ salt with a pH of 8 .
- Other side products of Kraft process include materials such as dimethyl sulfoxide, turpentine, tall oil (a source of oleic and linoleic acids which are used in making soaps and greases) may also be obtained.
- The Kraft process is an outgrowth of the now obsolete, soda process, that cooked with a strong ( $12 \%$ ) solution of sodium hydroxide and sodium carbonate. The soda process gave low yields and worked well only with short-fibred hardwoods.


## - Sulfite Process:

- The usage of sulfite process in paper making in restricted to areas where soft white confierous woods are abundant (e.g.: in Canada). But in all other countries, the process has been replaced with the less environmentally harmful and acid free paper produced by Kraft process. Sulfite process chemistry involves attack of sulfurous acid $\left(\mathrm{H}_{2} \mathrm{SO}_{3}\right)$ on lignin.
- The acid sulfite process is used to obtain a higher quality paper, tissues, and soft fibres. It is also more water polluting.
- Digestion occurs in a mixture of sulfur dioxide and calcium or magnesium bisulfite. Since calcium sulfite being insoluble in water, which makes preparation of digestion liquor difficult and recovery of chemicals expensive, most modern sulfite mills have switched from calcium-based to magnesium-, sodium-, or ammonium-based systems.
- Sulfite paper has a relatively short life span due to the embrittlement caused by the hydrolysis of cellulose by residual acids.
- Difference between Kraft and Sulfite Processes:

| Kraft process | Sulfite process |
| :--- | :--- |
| Alkaline: carbon-steel vessels can be | Acidic: must use corrosion-resistant |
| used, though stainless steel is better. | (stainless steel) vessel. |
| Gives long fibres, therefore strong | Shorter fibres because of acid hydrolysis; |
| paper (kraft means strength in | paper is weaker, and residual acid may |
| Swedish and German). | cause long-term embrittlement. |
| Any kind of wood may be used. | Spruce or fir chips only can be used. |
| Product is brown unless bleached. | Product is white. |
| Typical uses: packaging, high qual- | Typical use: general purpose white pa- |
| ity white paper (when bleached). | per, tissue paper |

- Neutral Sulfite Semichemical Process (NSSC):
- In the NSSC process sodium sulfite is buffered with sodium carbonate, bicarbonate, and hydroxide to maintain a slightly alkaline pH during the cook.
- NSSC hardwood pulp is the premier pulp for corrugating medium - cardboard type products.


## - Reid Vapor Pressure:

- The Reid vapor pressure (RVP) is frequently used as an indication of volatility of liquid hydrocarbons. The RVP of a product is the vapor pressure determined in a volume of air four times the liquid volume at $37.8^{\circ} \mathrm{C}\left(100^{\circ} \mathrm{F}\right)$.
- This property measures the vapor-lock tendency of gasoline.
- It also indicates the explosion and evaporation hazards of the fuel.
- Flash Point: It is the lowest temperature at which application of test flame causes vapor to ignite. It differs from autoignition temperature because in the latter there is no source of ignition.
- It is measured by Cleveland closed cup and Pensky Martin open cup apparatus.
- It indicates the explosive range of a fuel.
- Fire Point: It is the temperature at which vapors of the flammable liquid continue to burn even after removal of ignition source.
It is typically $5-10^{\circ} \mathrm{C}$ more than flash point.


## - Boiling Point Curves:

- ASTM distillation and TBP distillation characterize the volatility of petroleum fractions and crude oils. Both are batch distillation methods which differ mainly in the degree of fractionation obtained during distillation.
- ASTM Distillation: This is essentially a batch distillation with one equilibrium stage and no reflux and minimum separation of the components of the fractions. The temperature of the rising vapors is recorded at specific interval of the collected distillates.
- True Boiling Point (TBP) Distillation: It is performed in columns with 15 theoretical plates or equilibrium stages and a reflux ratio of 5. Data from TBP distillation provides more detailed characterization of the volatility of crude oil or petroleum fraction.
- Since the degree of separation for a TBP distillation test is much higher than that of the ASTM distillation test, its initial boiling point is lower and its end point is higher than those of the ASTM test.


## - PONA Number:

- Properties of petroleum feedstock is measured by the Paraffin, Olefin, Naphthene, and Aromatic content (PONA), in volume percent.
- The PONA number is significant in determining the quality of naphtha. There are various grades of naphtha produced depending on the PONA specifications, such as $60 / 15,65 / 12,70 / 10$, etc. The first number is the minimum allowable total paraffins percentage and the second number specifies the maximum allowable aromatics percentage.
- PIONA or PIANO analysis includes Isoparaffin content in addition to the PONA content.


## - SBR

- The most widely used synthetic rubber is styrene-butadiene rubber (SBR).
- Trade names: Buna, GR-S, Philprene.
- Styrene: Butadiene $=1: 3$.
- The main use of SBR is for tire production. Other uses include belting, hose, molded and extruded goods, flooring, shoe soles, coated fabrics, and electrical insulation.
- As styrene contents is increased above $50 \%$, the product become increasingly plastic.
- Nitrile rubber (NBR) is a copolymer of butadiene and acrylonitrile. It has the special property of being resistant to hydrocarbon liquids.
- Acrylonitrile-butadiene-styrene (ABS) polymers: The most important mechanical properties of ABS are impact resistance and toughness.
- Neoprene (poly chloroprene)
- Neoprene is the oldest synthetic rubber.
- It is made from chloroprene monomers.
- It is flame resistant.
- It is more expensive than natural rubber.
- Butyl rubber is a copolymer of isobutylene (97.5\%) and isoprene (2.5\%). It has low permeability to air. The major use of butyl rubber is for tire inner tubes.
- Polyisoprene: cis-1,4-polyisoprene has structure close to that of natural rubber. Modern radial ply tires require increased amounts of natural rubber because it has greater resilience and lower hysteresis losses (i.e., less heat build-up) than styrene-butadiene rubber. The demand can be satisfied with synthetic cis-1,4-polyisoprene.
- Polybutadiene
- Butadiene $\left(\mathrm{CH}_{2}=\mathrm{CHCH}=\mathrm{CH}_{2}\right)$ is obtained as a coproduct of steam cracking of petroleum for ethylene production.
- Dehydrogenation of butane or butene is an alternate route when supplies are short.
- Ethylene-propylene rubbers (also called EPDM and EPM) continue to be one of the most widely used and fastest growing synthetic rubbers having both specialty and generalpurpose applications. Ethylene-propylene rubbers are valuable for their excellent resistance to heat, oxidation, ozone and weather aging due to their stable, saturated polymer backbone structure. They are used for automobile parts, hose, electrical insulation, and footwear.

64. Commercially, ethylene is produced from naphtha by
(G-2000-1.23)
(a) catalytic cracking
(b) catalytic dehydrogenation
(c) pyrolysis
(d) hydrocracking
(a) $\checkmark$ Explanation: The main route for producing light olefins-ethylene and propylene, is steam cracking of hydrocarbons, such as naphtha.

Fluid catalytic cracking is also used to supplement the demand for these light olefins.
65. The chief raw material for the commercial production of methanol is
(G-2005-24)
(a) Synthesis gas
(b) Formaldehyde
(c) Acetic acid
(d) Ethanol
(a) $\checkmark$ Explanation: Methanol is produced from synthesis gas using copper based catalyst.
66. Styrene is produced from ethylbenzene by the process of
(G-2001-1.24)
(a) Dehydrogenation
(b) Oxidation
(c) Alkylation
(d) Dehydration
(a) $\checkmark$ Explanation: Styrene $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}=\mathrm{CH}_{2}\right)$ is produced from ethylbenzene by dehydrogenation. This process accounts for $85 \%$ of the commercial production. The reaction is carried out in the vapor phase with steam over a catalyst consisting primarily of iron oxide.

$$
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}_{2} \mathrm{H}_{5} \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}=\mathrm{CH}_{2}+\mathrm{H}_{2}
$$

Presence of steam has the following roles:

- It lowers the partial pressure of ethylbenzene, shifting the equilibrium toward styrene and minimizing the loss to thermal cracking of styrene to benzene, ethane, and carbon.
- It supplies the necessary heat of reaction (as styrene production is endothermic reaction).
- It cleans the catalyst by reacting with carbon to produce carbon dioxide and hydrogen.

67. Each of the products mentioned in the left-hand column requires one or more of the reactants mentioned in the right-hand column. Match the products with the appropriate reactant(s).
(G-2000-18.a)
(c) $\checkmark$ Explanation: Nylon-66 polymer contains 12 carbon atoms in each repeating unit; whereas nylon- 6 contains 6 carbon atoms.
Terylene and Dacron are the well known brand names of polyethene terephthalate (PET) textile fibers. They are commonly called as polyester. PET is manufactured by reacting terephthalic acid with ethylene glycol.
68. Pair the following polymers with their chain characteristics
(G-2006-68)
P. HDPE 1. Very few branches
Q. LDPE 2. Short and regular branches
R. LLDPE 3. High branching with both short and long chain branches
(a) $\mathrm{P}-1, \mathrm{Q}-2, \mathrm{R}-3$
(b) $\mathrm{P}-2, \mathrm{Q}-1, \mathrm{R}-3$
(c) $\mathrm{P}-1, \mathrm{Q}-3, \mathrm{R}-2$
(d) $\mathrm{P}-2, \mathrm{Q}-3, \mathrm{R}-1$
(c) $\checkmark$ Explanation: High-density polyethylene (HDPE) is characterized by a higher crystallinity and higher melting temperature than LDPE due to the absence of branching. Low-density polyethylene (LDPE) (also called as high-pressure polyethylene) is more highly branched (both short and long branches) than high-density polyethylene (also called as low-pressure polyethylene) and is therefore lower in crystallinity ( $40-60 \% \mathrm{vs}$. $70-90 \%$ ) and density ( $0.91-0.93 \mathrm{~g} / \mathrm{cm}^{3}$ vs. $0.94-0.96 \mathrm{~g} / \mathrm{cm}^{3}$ ).
Linear low density polyethylene (LLDPE) has properties between HDPE and LDPE. It has fewer branches, higher density, and higher crystallinity than LDPE.
Because LDPE is flexible and transparent, it is mainly used to produce film and sheets. HDPE is important for producing bottles and hollow objects.
69. Match the synthetic fibres in Group 1 with their classification in Group 2. (G-2007-69)

| Group 1 | Group 2 |
| :--- | :--- |
| P. Rayon | (1) polyamide |
| Q. Orlon | (2) polyester |
| R. Dacron | (3) cellulose |
|  | (4) acrylic |

(a) $\mathrm{P}-2, \mathrm{Q}-3, \mathrm{R}-1$
(b) $\mathrm{P}-3, \mathrm{Q}-4, \mathrm{R}-2$
(c) $\mathrm{P}-3, \mathrm{Q}-1, \mathrm{R}-3$
(d) $\mathrm{P}-3, \mathrm{Q}-3, \mathrm{R}-4$
(b) $\checkmark$ Explanation: Rayon is a manufactured fiber made of cellulose. Orlon, Acrilan, and Courtelle are popular trade names of acrylic fibers. Dacron and Terylene are popular trade names of PET polyester fiber.
92. Match the polymer in Group I to the polymer characteristic in Group II
(G-2012-47)
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