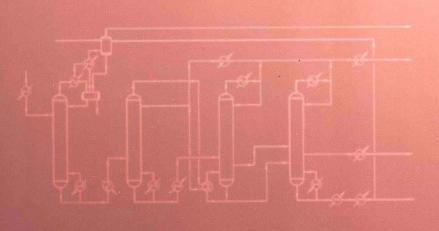
高等教育双语教学推荐教材

分离工程

(英文版)

SEPARATION ENGINEERING

徐东彦 叶庆国 陶旭梅 编



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●化学工业出版社

图书在版编目(CIP)数据

分离工程(英文版)Separation Engineering/徐东彦, 叶庆国, 陶旭梅编. 一北京: 化学工业出版社, 2012.1 ISBN 978-7-122-12910-9

Ⅰ. 分… Ⅱ. ①徐… ②叶… ③陶… Ⅲ. 分离-化工 过程-双语教学-高等学校-教材 IV. TQ028

中国版本图书馆 CIP 数据核字(2011) 第 245158 号

责任编辑: 徐雅妮

装帧设计: 关 飞

责任校对: 顾淑云

出版发行: 化学工业出版社(北京市东城区青年湖南街 13 号 邮政编码 100011)

装: 北京白帆印务有限公司

787mm×1092mm 1/16 印张 16½ 字数 440 千字 2012 年 3 月北京第 1 版第 1 次印刷

购书咨询: 010-64518888 (传真: 010-64519686) 售后服务: 010-64518899

址: http://www.cip.com.cn

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Section Sectio

教育部关于《加强高等学校本科教学工作提高教学质量的若干意见》以及《进一步加强高等学校本科教学工作若干意见(征求意见稿)》均提出本科教育要创造条件使用英语等外语进行公共课和专业课教学。此外,《普通高等学校本科教学工作水平评估指标体系》中也对双语教学有明确要求。由此可见,双语教学是我国高等教育与国际接轨和教育改革发展的必然趋势,也是当前教学改革的重点和热点。

分离工程是化学工程学科的重要分支,是研究各种化学物质的分级、分离、浓缩和纯化的方法、工艺、材料、设备等方面的过程工程科学。化工分离过程在现代化学工业和相关工业领域中应用广泛,地位十分重要。在大力倡导节能减排、资源高效利用和绿色化工的 21 世纪,化工分离技术将在石油化工、资源环境、能源、材料等诸多领域发挥更为重要的作用。随着化学工业的飞速发展,新型化工分离技术已经成为化工领域研究的热点。

众所周知,当今世界已经进入知识大爆炸时代,科学技术与知识日新月异,其中绝大部分新成果都需要通过英文报道。目前,国际上有关分离工程与科学的专业期刊有 Journal of Separation Science, Journal of Membrane Science, Journal of Membrane Biology, Separation and Purification Technology, Separation & Purification Reviews, Adsorption Science & Technology, Filtration & Separation, Solvent Extraction & Ion Exchange, Molecular Membrane Biology 等。为追踪国际上有关分离理论与技术的研究热点,需要阅读大量相关专业期刊和专利,这就要求相关研究人员能熟练掌握和运用有关分离科学与工程专业英语。因此,作为化工类专业及其相关专业的一门骨干专业课程,开展《分离工程》的双语教学具有重要意义。一本适合双语教学的好教材是正常开展双语教学及保证教学效果的基础。

国外原版教材在语言上原汁原味,但在内容上却未必完全符合我国的教学要求。原版教材存在的主要问题是内容较多、篇幅巨大且知识点跨度较大,很难在有限学时内学习使用。如果能与现有中文教材相对照编写双语教材则更便于学生掌握相关英文专业术语与内容,还可以在有限学时内掌握相关专业知识,更适宜于双语教学需要。为此,我们在编写、出版《分

离工程》中文教材的基础上,编写了《分离工程》(英文版)教材。

本书内容共分七章,分别介绍多级平衡分离基础、精馏、多组分吸收、多级分离的严格计算、分离过程设备的效率和过程优化、其他新型分离方法等内容。每章后有词汇、注释、习题与参考文献,便于学生学习参考。

本书由青岛科技大学的徐东彦副教授、叶庆国教授和陶旭梅博士编写。其中第1章、第5章、第6章和第7章由徐东彦编写,第2章和第3章由叶庆国编写,第4章由陶旭梅编写。最后,感谢博士研究生刘永卓、硕士研究生王海振、卢鹏、胡鸿宾、宋红荣、席玉蕾、孙晋良和程世超等在资料收集过程中提供的帮助。

由于编写人员水平有限,书中不妥之处在所难免,衷心希望广大读者和有关专家学者批评指正。

编者 2011 年 10 月

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Chapter 1 Separation Processes

The basic components of a typical chemical process are shown in Figure 1.1, in which each block represents a stage in the overall process for producing a product from the raw materials. Figure 1.1 represents a *generalized* process, not all the stages will be needed for any particular process and the complexity of each stage will depend on the nature of the process. In the first stage after the reactor in stage 4, the products and by-products are separated from any unreacted materials. If in sufficient quantity or high price, the unreacted materials will be recycled to the reactor. They could be returned directly to the reactor, or to the feed *purification* and preparation stage. The *by-products* may also be separated from the products at this stage.

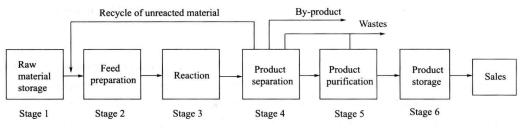


Figure 1.1 Typical chemical process

In chemistry and chemical engineering, a separation process is used to transform a mixture of substances into two or more distinct products. The separated products could differ in chemical properties or some physical properties, such as size, or *crystal* modification. With a few exceptions, almost every *element* or *compound* is found naturally in an impure state such as a mixture of two or more substances. Many times the need to separate it into its individual components arises.

Separation processes are used for three primary functions: purification, concentration, and fractionation. Purification is the removal of undesired components in a feed mixture from the desired species. For example, acid gases, such as sulfur dioxide and nitrogen oxides, must be removed from power-plant combustion gas effluents before they are discharged into the atmosphere.

Concentration is performed to obtain a higher concentration of desired components that are initially dilute in a feed stream. An example is the concentration of metals present in an electroplating process by removal of water. This separation allows metals to be recycled back to the electroplating process rather than discharged to the environment. Lastly, in fractionation, a feed stream of two or more components is segregated into product streams of different components, typically relatively pure streams of each component. The separation of radioactive wastes with short half-lives from those having much longer half-lives facilitates proper handling and storage.

Separation applications in the field of chemical engineering are very important. A good example is that of *crude oil*. Crude oil is a mixture of various *hydrocarbons* and is valuable in this natural form. In an oil refinery or petroleum refinery, the crude oil is processed and refined into more useful petroleum products, such as natural gases, gasoline, *diesel, jet fuel, lubricating oils, asphalt*, etc.

1.1 Characteristics of separation process and separation factor

1.1.1 Characteristics of separation process

The mixing of chemicals to form a mixture is a spontaneous, natural process that is accompanied by an increase in entropy or randomness. The inverse process, the separation of the mixture into its constituent chemical species, is not a spontaneous process that is accompanied by a decrease in entropy; it requires an expenditure of energy. A mixture to be separated usually originates as a single, homogenous phase. If it exists as two or more immiscible phases, it is often best to first use some mechanical means based on gravity, centrifugal force, pressure reduction, or an electric and/or magnetic field to separate the phases. Then, appropriate separation techniques are applied to each phase. Usually the energy input required for the separation is supplied with the separating agent, and generally the separating agent will cause the formation of a second phase of matter.

A schematic diagram of a general separation process is shown in Figure 1.2. The feed mixture can be vapor, liquid, or solid, while the two or more products may differ in composition from each other and in phase state from each other and/or from the feed. Many separation processes are based on the formation of an additional phase that has a different composition from the feed stream(s). One possible way of forming another phase is the addition of energy (energy separating agent) to convert a liquid stream to a vapor stream. Distillation exploits this idea to separate mixtures of liquids that boil at different temperatures. Crystallization processes use energy to separate liquid mixtures with components that solidify at different temperatures. The temperature is lowered until the species with the higher solidification temperature crystallizes out of solution. Evaporation and

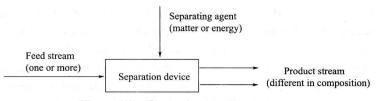


Figure 1.2 General separation process

drying are other processes in which energy addition promotes the separation by formation of a new phase. Another large class of separations makes use of a change in solute distribution between two phases in the presence of mass not originally present in the feed stream. This mass separating agent, MSA, is added as another process input to cause a change in solute distribution. The MSA can alter the original phase equilibrium or facilitate the formation of a second phase with a concentration of components different from that in the original phase. One of the components of the original feed solution must have higher affinity for the MSA than for the original solution. This solute will then preferentially transfer from the original feed solution to the MSA phase. Once the MSA has been used to facilitate a separation, it must normally be removed from the products and recovered for recycle in the process. Hence, use of an MSA requires two separation steps; one to remove a solute from a feed stream and a second to recover the solute from the MSA.

Some general statements regarding the use of separating agents can be made.

1. Separation processes use mass and/or energy separating agents to perform the separation.

A mass separating agent can be a solid, a liquid, or a gas. Heat is the most common energy separating agent, used in distillation. External fields, such as magnetic and electric, are sometimes used as energy separating agents.

2. A different component distribution between two phases is obtained.

This distribution change can be accomplished in two ways.

(1) The original phase equilibrium is altered. Two phases are originally present and the role of the separating agent is to change the composition in each phase relative to the initial values. For examples,

Mass separating agent: one approach is the addition of a selective *complexing agent* to a liquid phase to increase the solubility of a solute. For example, a selective *chelating agent* can be added to an organic phase to form a complex with a metal ion in an aqueous phase when the two phases are in contact.

Energy separating agent: heat input to change the temperature of a gas/liquid system. The most common example is distillation.

(2) A second phase is generated, with a different component distribution. For examples,

Mass separating agent: addition of a solid sorbent that is selective for a solute in a feed stream. An example is the removal of VOCs from an air stream using activated carbon.

Energy separating agent: heat input to a liquid phase to change the solute solubility in that phase. An example is evaporation to remove water from a waste stream and concentrate the stream prior to disposal.

3. Separating agents employ four methods to generate selectivity.

(1) Modification of phase equilibrium. For examples,

Mass separating agent: an ion-exchange resin used to selectively partition ions into the resin. Energy separating agent: heat removal to precipitate salts from an aqueous stream.

(2) Geometry differences. For examples,

Mass separating agent: a membrane to filter suspended solids based on size.

Energy separating agent: gravity settling to separate particles by size.

(3) Kinetics (rate of exchange) between phases. For examples,

Mass separating agent: the use of amines in gas sorption to change the rate of acid gas uptake into the liquid phase.

Energy separating agent: heat input into the amine solution to accelerate the rate of gas desorption, which regenerates the solution.

(4) Rate of mass transfer within a phase. For examples,

Mass separating agent: intra-particle diffusion in a porous sorbent.

Energy separating agent: application of an electric field across a liquid phase to accelerate charged particles relative to uncharged ones.

The separation is accomplished by forcing the components in the feed into different spatial locations by any of five general separation techniques, or combinations thereof, as shown in Figure 1.3. The most common industrial technique, Figure 1.3(a), involves the creation of a second phase that is immiscible with the feed phase. The creation is accomplished by energy transfer to or from the process or by pressure reduction. A second technique, Figure 1.3(b), is to introduce the second phase into the system in the form of a solvent that selectively dissolves some of the species in the feed mixture. Less common, but of growing importance, is the use of a barrier, Figure 1.3(c), which restricts and/or enhances the movement of certain chemical species with respect to other species. This method will be described in detail in Chapter 7. Also of growing importance are techniques that involve the addition of solid particles, Figure 1.3(d), which act directly or as *inert* carriers for other substances so as to cause separation. Finally, external fields, Figure 1.3(e), of various types are sometimes applied for specialized separations.

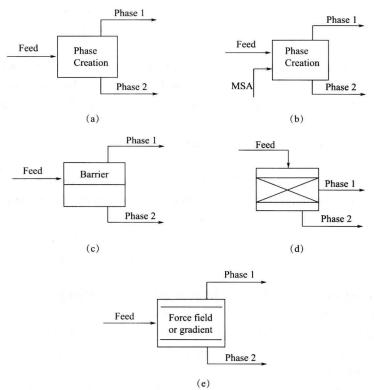


Figure 1.3 General separation techniques: (a) separation by phase creation; (b) separation by phase addition; (c) separation by barrier; (d) separation by solid agent; (e) separation by force field or gradient

For all of the general techniques of Figure 1.3, the separations are achieved by enhancing the rate of mass transfer by diffusion of certain species relative to mass transfer of all species by bulk movement within a particular phase. The driving force and direction of mass transfer by diffusion is governed by thermodynamics, with the usual limitations of equilibrium. Thus, both transport and thermodynamic considerations are crucial in separation operations. The rate of separation is governed by mass transfer, while the extent of separation is limited by thermodynamic equilibrium.

1.1.2 Separation factor

The degree of separation which can be obtained with any particular separation process is indicated by the *separation factor*. Because the aim of a separation device is to produce products of differing compositions, it is logical to define the separation factor in terms of product compositions.

$$\alpha_{i,j}^{s} = \frac{x_{i,1}/x_{j,1}}{x_{i,2}/x_{j,2}} \tag{1-1}$$

The separation factor $\alpha_{i,j}^s$ between components i and j is the ratio of the mole fractions of those two components in product 1 divided by the ratio in product 2. The separation factor will remain unchanged if all the mole fractions are replaced by weight fractions, by mole flow rates of the individual components, or by mass flow rates of the individual components.

An effective separation is accomplished to the extent that the separation factor is significantly different from unity. If $\alpha_{i,j}^s = 1$, no separation of components i and j has been accomplished. If $\alpha_{i,j}^s > 1$, component i tends to concentrate in product 1 more than component j does, and component j tends to concentrate in product 2 more than component i does. On the other hand, if $\alpha_{i,j}^s < 1$, component j tends to concentrate preferentially in product 1 and component i tends to concentrate preferentially in product 2. Generally, components i and j are selected so that $\alpha_{i,j}^s$ defined by Equation (1-1) is greater than unity.

It is obvious that the separation factor reflects the differences in equilibrium compositions and transport rates due to the fundamental physical phenomena underlying the separation. It can also reflect the construction and flow configuration of the separation device. For this reason, it is convenient to define an *inherent separation factor*, which is denoted by $\alpha_{i,j}$ with no superscript. This inherent separation factor is the separation factor which would be obtained under idealized conditions. For equilibrium separation processes the inherent separation factor corresponds to those product compositions which will be obtained when simple equilibrium is attained between the product phases (Equation 1-2). For rate-governed separation processes the inherent separation factor corresponds to those product compositions which will occur in the presence of the underlying physical transport mechanism alone, with no complications from competing transport phenomena, flow configurations, or other extraneous effects.

$$\alpha_{i,j} = \frac{y_i / y_j}{x_i / x_j} \tag{1-2}$$

It must be noted that both the inherent separation factor $\alpha_{i,j}$ and the actual separation factor $\alpha_{i,j}^s$, can be used for the analysis of separation processes. If $\alpha_{i,j}$ can be derived relatively easily,

the most common approach is to analyze a separation process on the basis of the inherent separation factor $\alpha_{i,j}$ and allow for deviation from ideality through efficiencies. On the other hand, there are situations where the physical phenomena underlying the separation process are so complex or poorly understood that an inherent separation factor cannot readily be defined. In these instances one must necessarily work with $\alpha_{i,j}^s$ derived empirically from experimental data. The quantity $\alpha_{i,j}^s$ may be closer to, further from, unity than $\alpha_{i,j}$, but if $\alpha_{i,j}$ is unity, it is imperative that $\alpha_{i,j}^s$ be unity, no matter what the flow configuration or other added effects.

1.2 Classifications of separation process

Separation processes rely on various mechanisms, *implemented* via a unit operation, to perform the separation. The mechanism is chosen to exploit some property difference between the components. They fall into two basic categories: the partitioning of the feed stream between phases and the *relative motion* of various chemical species within a single phase. These two categories are often referred to as equilibrium and mass transfer rate processes, respectively. Separation processes can often be analyzed with either equilibrium or mass transfer models. **However, one of these two mechanisms will be the limiting, or controlling, factor in the separation and is, therefore, the design mechanism.** For a separation to occur there must be difference in either chemical or physical property between the various components of the feed stream. This difference is the driving force basis for the separation. Separation processes generally use one of these differences as their primary mechanism.

Separation processes can essentially be termed as mass transfer processes. The classification can be based on the means of separation, mechanical or chemical. The choice of separation depends on *the pros and cons* of each. Mechanical separations are usually favored if possible due to the lower cost of the operations as compared to chemical separations. As for systems that can not be separated by purely mechanical means, chemical separation is the remaining solution. The mixture at hand could exist as a combination of any two or more states: solid-solid, solid-liquid, solid-gas, liquid-liquid, liquid-gas, gas-gas, solid-liquid-gas mixture, etc.

These separation categories are designed using thermodynamic equilibrium relationships between phases and the rate of transfer of a species from one phase into another, respectively. The choice of which analysis to apply is governed by which is the limiting step. If mass transfer is rapid, such that equilibrium is quickly approached, then the separation is equilibrium limited. On the other hand, if mass transfer is slow, such that equilibrium is not quickly approached, the separation is mass-transfer limited. In some separations, the choice of analysis depends upon the type of process equipment used.

Equilibrium processes are those in which cascades of individual units, called stages, are operated, with two streams typically flowing *countercurrent* to each other. The degree of separation in each stage is governed by a thermodynamic equilibrium relationship between the phases. One example is distillation, in which a different temperature at each stage alters the vapor-phase equilibrium between the components of mixture. The driving force for separation is the tendency to establish a new equilibrium between the two phases at the temperature of each stage. In an

equilibrium process, two phases are brought into contact with each other, mixed thoroughly, and then separated with a redistribution of the components between phases. Often multiple contacts are made in a series of cascading steps in which the two phases flow countercurrent to each other. At each contact the phases are allowed to approach thermodynamic equilibrium. Once equilibrium is reached, there can be no more separation without a change in the operating parameters of the system that affects the equilibrium relationship. The next stage in the cascade, therefore, has at least one process change that alters the equilibrium relationship to establish a new equilibrium relationship. The cascade should be designed such that conditions are altered at each stage to move closer towards the desired separation. For example, distillation is a fractionating separation in which a binary (or greater) feed stream is separated into two (or more) product streams based upon their differences in boiling point. One type of distillation column has a series of cascading contact trays such that the temperature increases from the top tray, which is just above the boiling point of the lower boiling point component, to the bottom tray, which is just below the boiling point of the higher boiling point component. Thus, the lower boiling point component is enriched in the gas phase, while the higher boiling point component is enriched in the liquid phase. Each tray from the top to the bottom of the column operates at a higher temperature such that a new equilibrium is established down the length of the column. As the temperature increases down the column, the lower boiling point species tends to vaporize more and move up the column as a gas stream, while the higher boiling point component continues down the column as a liquid. The final result is a vapor stream leaving the top of the column which is almost pure in the lower boiling point species and a liquid stream exiting the bottom of the column that is almost pure in the higher boiling point component. The multicomponent distillation will be introduced in Chapter 2 and 3.

Rate processes, on the other hand, are limited by the rate of mass transfer of individual components from one phase into another under the influence of physical stimuli. Concentration gradients are the most common stimuli, but temperature, pressure, or external force fields can also cause mass transfer. One mass-transfer based process is gas absorption, a process by which a vapor is removed from its mixture with an inert gas by means of a liquid in which it is soluble. Desorption, or stripping, on the other hand, is the removal of a volatile gas from a liquid by means of a gas in which it is soluble. Adsorption consists of the removal of a species from a fluid stream by means of a solid adsorbent with which it has a higher affinity. Ion exchange is similar to adsorption, except that the species removed from solution is replaced with a species from the solid resin matrix so that electroneutrality is maintained. Lastly, membrane separations are based upon differences in permeability due to size and chemical selectivity for the membrane material between components of a feed stream.

Many times two or more of these processes have to be used in combination to obtain the desired separation. Separations, including enrichment, concentration, purification, and *refining*, are important to chemists and chemical engineers. The former uses analytical separation methods, such as *chromatography*, to determine compositions of complex mixtures quantitatively. **Chemical engineers are more concerned with the manufacture of chemicals using economical, large-scale separation methods, which may differ considerably from laboratory techniques.** For example, in a laboratory, chemists separate and analyze light-hydrocarbon mixtures by gas-liquid chromatography, while in a large manufacturing plant a chemical engineer uses distillation to separate the same hydrocarbon mixtures.

1.3 Selection of separation processes

The selection of a best separation process must frequently be made from among a number of feasible candidates. When the feed mixture is to be separated into more than two products, a combination of two or more operations may be best. Even when only two products are to be produced, a hybrid process of two or more operations may be most economical. The factors include feed and product conditions, property differences that can be exploited, and certain characteristics of the candidate separation operations. The most important feed conditions are composition and flow rate, because the other conditions (temperature, pressure, and phase condition) can be altered by *pumps, compressors*, and heat exchangers to fit the required conditions of a particular candidate separation operation. In general, however, the *vaporization* of a liquid feed that has a high heat of vaporization, the condensation of a vapor feed with a *refrigerant*, and/or the compression of a vapor feed can add significantly to the cost. The most important product conditions are the required purities because the other conditions listed can be altered by energy transfer after the separation is achieved.

Some separation operations are well understood and can be readily designed from a mathematical model and/or scaled up to a commercial size from laboratory data. The results of a survey by Keller, shown in Figure 1.4, show that the degree to which a separation operation is technologically mature correlates well with its commercial use. Operations based on a barrier are more expensive to stage than those based on the use of a solid agent or the creation or addition of a second phase. Some operations are limited to a maximum size. For capacities requiring a larger size, parallel units must be provided. The choice of single or parallel units must be given careful consideration. Except for size constraints or fabrication problems, the capacity of a single unit can be doubled for an additional investment cost of only about 50%. If two parallel units are installed, the additional investment is 100%. Those operations ranked near the top are frequently designed without the need for any laboratory data or pilot-plant tests. Operations near the middle usually

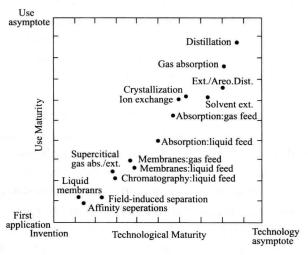


Figure 1.4 Technological and use maturities of separation processes