MASS TRANSFER OPERATIONS: ABSORPTION AND EXTRACTION

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Summary

Gas absorption and liquid-liquid extraction are separation processes used in the chemical industry and for environmental control. In this review chapter, these two processes are discussed emphasizing their similarities regarding the mechanism of mass transfer, because both take place by unidirectional mass transfer. Some industrial applications of both processes are described. Traditional calculations for both separation processes are outlined, with less coverage than in textbooks or handbooks. A short description of the equipment used for absorption and liquid-liquid extraction is included, together with some guidelines for the selection of equipment. A few rules of thumb for preliminary process design and cost estimation are also considered. This concise review cannot cover many variations of both processes. These variations are mainly influenced by reaction or surface phenomena, or by process integration and their synthesis and optimization. Extensive literature on gas absorption and liquid-liquid extraction has been published in textbooks, handbooks, monographs and articles in the chemical engineering literature.

1. Introduction

Separations of solids, liquids and gases are required in nearly all chemical and biochemical processes. These processes often involve mass transfer between two phases, so that some components from a rich stream are selectively transferred into a lean mass separating agent (MSA). Rich streams are typically process or effluent streams that contain valuable materials or undesirable components. The MSAs, are streams employed to carry out the separation (*e.g.*, solvents, stripping agents, adsorbents, ion exchange resins, etc.) The MSAs are used for different purposes, such as: feed preparation, product separation, product finishing, and recovery of valuable materials. Separation processes depend primarily upon differences in *physical* properties, which lead to different interphase mass transfer rates for the components of the mixture. Lately, industry has expressed increasing interest in separation processes involving *chemical* reactions, in which the reaction is used as a separation tool or the chemical reaction and physical separation are coupled in a single unit operation.

Mass transfer operations involving the diffusion of the component to be separated through a stationary phase (*unidirectional mass transfer*) include: gas absorption, liquid extraction, adsorption, and ion exchange. Distillation is a typical process in which the rates of mass transfer of the more and the less volatile components between phases are equal in magnitude, but opposite in direction (*equimolar mass transfer).* The design equations will depend on the mass transfer mechanism, and it may be expected that similar expressions will be obtained for processes such as gas absorption and liquid-liquid extraction, where unidirectional mass transfer takes place.

The two key design and operating parameters in separation processes are *efficiency*, which indicates how well components are separated, and *capacity*, which is related to the hydrodynamics of the contacting device and the overall rate at which the desired material can be processed without loss of efficiency. Column height is determined by the efficiency of the separation process, while the diameter of the column is governed by the required capacity. Phase equilibria, mass balances and design parameters are required for the reliable design of a separation process and these topics will be considered briefly.

Progress in separation processes will contribute to waste minimization by reduction and recycle of waste components, and by decreasing the energy consumption of the chemical process per unit of product. Innovations in separation processes (*e.g.,* mass exchange networks, reactive separation processes, hybrid separations using membranes, etc.) are needed for more efficient utilization of resources. Such utilization will contribute to the ability of the chemical and biochemical industries to sustainable development.

2. Gas absorption

Gas absorption is a process in which one or more soluble components (*solutes*) are removed from a gas phase by contact with a liquid phase (*solvent*) into which the components of interest dissolve. In general the absorbed gas is then removed from the solvent, and the solvent liquid stream is subsequently returned to the system. The solvent-recovery process is called *stripping*. Stripping is also employed when volatile components have to be removed from a liquid mixture. The stripping agent is either a gas (*e.g.,*. air) or a superheated vapor (*e.g.,* superheated steam). Absorption and stripping employ special contactors for bringing gas and liquid phases into intimate contact. In most common units the solvent enters the top of the absorber/stripper and flows downwards, countercurrent to the rising gas stream. The two phases mix and contact one another, either on plates or packing, and the solute is transferred from the gas phase to the solvent. A schematic diagram of an absorption-stripping process is shown in Figure 1.

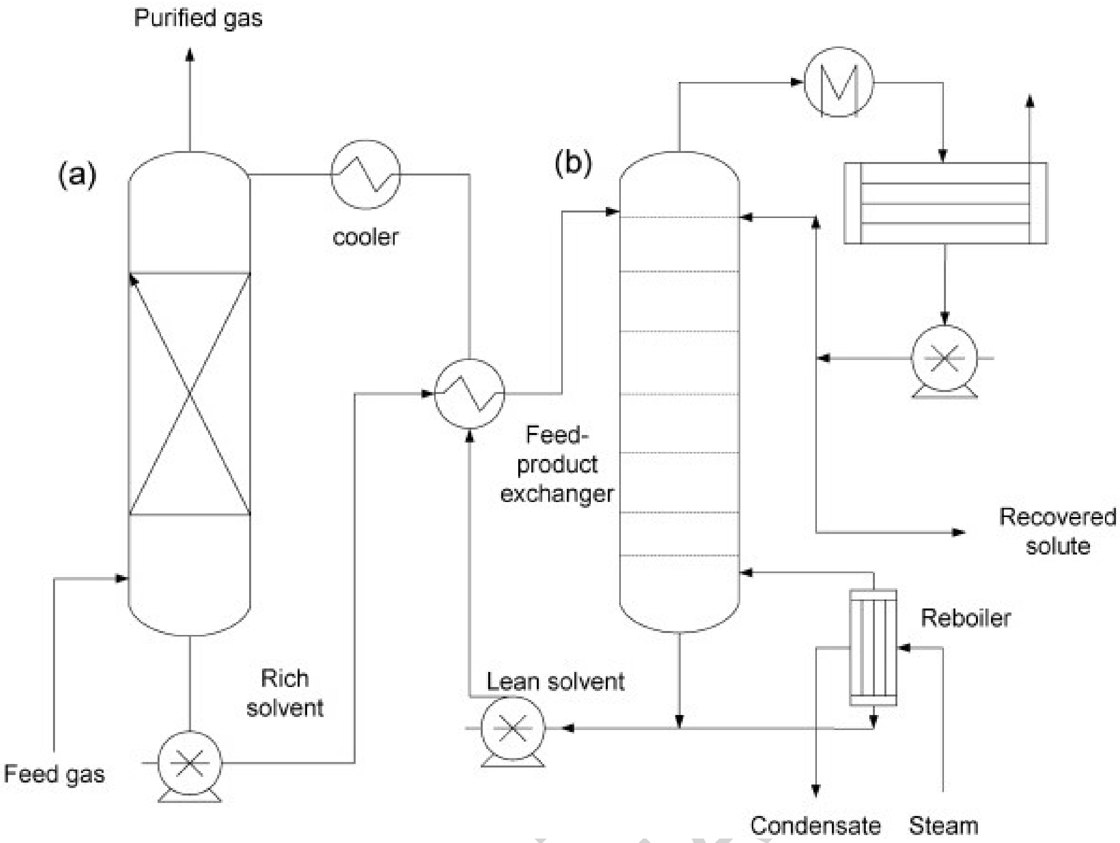

Figure 1: Typical absorption-stripping process with recycle of solvent: (a) absorber, (b) stripper

Some processes involving *physical* or *chemical* absorption are listed in Table 1, while Figure 2 is the flow diagram of an industrial process involving gas-liquid absorption.

Industry	**Compound to be removed**	**Solvent**
Wood industry (Kraft and sulphite methods) Glass production	SO_2	water
Carbon industry	CO_2	water, basic liquids (K_2CO_3) or other solvents (acetone, etc.)
H_2SO_4 production	SO_3	H2SO4 (98 %)
HNO_3 production	NO_x	Water (absorption + chemical reaction)
HCl production	HCl	water
Explosive manufacture	NO_x	water

Obtaining of Cl_2 without NaOH (*American Cianamid Co Method*)	Cl_2	SCl_2, CCl_4
	SO_2	H_2SO_4

Table 1: Examples of industrial gas absorption processes

Figure 2: Industrial process involving gas-liquid absorption (gas depuration)

Water is a cheap solvent conventionally used to remove ammonia from gas streams containing 1-5 % NH_3. The process is highly exothermic (7500-8500 kcal $kg^{-1}mol^{-1}$ of NH_3 absorbed in water) and the energy effect accompanying the absorption process has to be taken into account in the design calculations. Additional examples of absorption industrial processes with physical or chemically reactive solvents are: water removal from natural gas streams using glycols as solvents; absorption of HCl present at low concentrations in the gas stream using a water-wash tower, absorption of CO_2 with ethanolamines, and sweetening of natural gas.

Physical solvents are easier to regenerate, but their use can result in higher impurity levels in the product stream.

2.1. Phase Equilibrium

The state of a system is established when its temperature, T, pressure, P, and phase composition x_i, are fixed. However, when equilibrium is reached, these variables are not all independent one another, and fixing a limited number of these variables, automatically establishes the others. The Gibbs phase rule relates the degrees of freedom $\mathcal{F}$ for a non-reactive system to the number of coexisting phases $\mathcal{P}$ and the number of components C:

$$\mathcal{P}+\mathcal{F}=C+2 \qquad (1)$$

For a gas system containing n components, and taking as intensive properties P, T, and concentration, $\mathcal{F}$ equals $n+1$ and the specification of P, T and $n-1$ concentration variables completely defines the state of the system. If a solvent S is used to absorb gas A from a binary mixture, and P, T and y_A are specified, all the other variables are determined and phase equilibrium diagrams such as those in Figure 3 can be constructed.

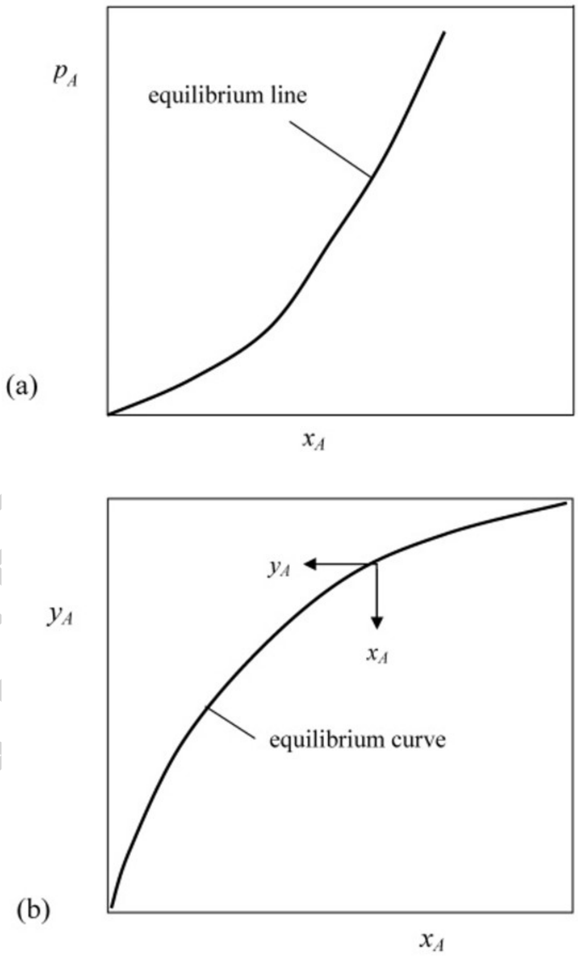

Figure 3: Gas-liquid phase equilibrium diagrams at constant P and T

For dilute concentrations of the gas that dissolves in a liquid, the equilibrium relationship is given by Henry’s law, which relates the gas phase partial pressure of an arbitrary species A in a liquid S:

$$p_A = Hx_A \tag{2}$$

or

$$p_A = H'c_A \tag{3}$$

where H is Henry's constant expressed in kilopascals per mole-fraction of solute in the liquid and H' is the Henry's constant expressed in kilopascals per kilomol per cubic meter.

For many gas-liquid systems Henry's law is valid when the partial pressure of the solute is less than 100 kPa (1 atm), but for higher values of H, this parameter depends on the partial pressure of the solute gas. Under such conditions the linear form of Henry's-law relation is not appropriate for use in engineering calculations.

Pure-component vapor pressures can be used to predict solubilities for systems in the range of partial pressures where Raoult's law is valid:

$$p_A = p_A^0 x_A \tag{4}$$

where p_A^0 is the vapor pressure of the pure solute and p_A is the partial pressure in the gas phase. Extreme care should be exercised when attempting to use pure-component vapor pressures to predict gas-absorption behavior. Both liquid-phase and vapor-phase non-idealities may result in significant deviations from the behavior predicted by Raoult's law and Henry's law.

When data are available for a given system under similar conditions of temperature, pressure and composition, the *equilibrium distribution coefficients* ($K = y/x$) provide a much more reliable basis for representing gas-liquid equilibria in engineering calculations. It should be noted that Henry´s law is a particular case, valid for diluted systems, of these coefficients.

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Biographical Sketches

José Coca-Prados is Professor of Chemical Engineering since 1972 at the Department of Chemical Engineering and Environmental Technology at the University of Oviedo, in Oviedo, Spain. He received his undergraduate and M.S. degree in Chemistry (1964) and his Ph.D. in Sciences (1968) from the University of Salamanca. After finishing his Ph.D. he worked as a postdoctoral fellow at the Department of Chemical Engineering of the University of Wisconsin (1968-70) and has been Visiting professor in that university on many occasions.

Prior to joining the University of Oviedo in 1972, he held the positions of Assistant Professor of Chemical Engineering at the Universities of Salamanca y Valladolid. He served as Dean of the Faculty of Sciences during the period 1976-1980. He has received the Distinguished Service Citation from the University of Wisconsin (1989), the Chemical Engineering-Expoquimia award, Barcelona (1993), and the Solvay award, Madrid (1996). He is member of the American Chemical Society, American Institute of Chemical Engineers and is the Spanish representative in the Working parties of "Absorption, distillation and extraction" and "Membranes" of the European Federation of Chemical Engineering. He has been member of the "Sciences pour l'ingenieur" committee of the French CNRS (2001-2006).

Dr. Coca has delivered lectures at several international meetings and has been a guest lecturer in many universities and congresses and in courses sponsored by the European Union. Dr. Coca is consultant to industry on extraction related processes, membrane technology and hybrid reaction-separation processes. In the course of his research, Prof. Coca has published 280 papers, obtained three patents, and has supervised 42 doctoral dissertations and 75 master theses.

Salvador Ordóñez-García received his PhD at the University of Oviedo in 1999. He is Assistant Professor of Chemical Engineering at the Department of Chemical Engineering and Environmental Technology at the University of Oviedo since 2004.

His research interests are focused on heterogeneous catalysis, chemical reactors and process engineering. He is author of more than 50 scientific publications in refereed journals, 2 patents, and more than 70 presentations in congresses. He has been invited speaker at several national and international meetings, and has participated in several industrial projects and international research programs. He has offered consulting services and courses related to the environment policy in Spain.

Eva Díaz-Fernández received her B.S. (2002) and PhD (2005) in Chemical Engineering from the University of Oviedo. She is Lecturer of Chemical Engineering of the University of Oviedo since 2005. Dr. Díaz research interests are in the areas of adsorption processes, new materials (especially meso and microporous ones) and heterogeneous catalysis. She has 20 scientific publications in refereed journals, and about 10 congress communications.