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fundamentals & applications

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ABSORPTION

Fundamentals & Applications

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PERGAMON PRESS

OXFORD · NEW YORK · SEOUL · TOKYO

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CONTENTS

CALCULATION OF ABSORBERS

NOTATION

a   - specific surface of packing, m^2/m^3

a   - mass transfer area in unit volume of equipment, m^2/m^3
b   - mass fraction, dimensionless
C   - molar concentration, $kmol/m^3$
c_p - heat capacity at constant pressure, J/(kg K)
C_p - molar heat capacity at constant pressure, J/(kmol K)
CF - capacity factor, m/s
d   - diameter, m

D   - multicomponent diffusion coefficient, m^2/s

$\mathscr{D}$ - binary diffusion coefficient, m^2/s

Đ   - generalized Stefan-Maxwell diffusion coefficient, m^2/s

D_D - dispersion coefficient, m^2/s

D^T - binary thermal diffusion coefficient, m^2/s
E   - enhancement factor, dimensionless
E_∞ - enhancement factor for instantaneous reaction, dimensionless

E   - point efficiency, dimensionless
E_o - overall plate efficiency, dimensionless

E_M - Murphree plate efficiency, dimensionless
FP - flow parameter, dimensionless
g   - mass rate of gas, kg/s
g_z - acceleration of gravity, m/s^2

G   - molar rate of gas, kmol/s
h   - enthalpy per unit mass, J/kg
H   - enthalpy per unit kilomole, J/kmol, kJ/lmol
He   - Henry's law constant, Pa
H   - Henry's law constant, $(Pa\ m)^3$/kmol

H'   - Henry's law constant, Pa^{-1}
I   - mass transfer rate, kmol/s
k   - binary mass transfer coefficient, m/s
k_x - binary liquid mass transfer coefficient, $kmol/(m^2 s)$

k_y - binary gas mass transfer coefficient, $kmol/(m^2 s)$

k_X - binary liquid mass transfer coefficient, $kmol/(m^2 s)$

k_Y - binary gas mass transfer coefficient, $kmol/(m^2 s)$

k - chemical reaction rate constant, different dimensions
K   - overall mass transfer coefficient, m/s
l   - liquid mass rate, kg/s
L   - liquid molar rate, kmol/s
m   - molarity, kmol/kg
m   - slope of equilibrium line, dimensionless
M   - molecular weight, kg/kmol
M   - reaction factor, dimensionless
n   - number of components in fluid
n   - mass flux with respect to stationary coordinates, $kg/(m^2 s)$
N   - Avogadro's number, 1/kmol
N   - molar flux with respect to stationary coordinates, $kmol/(m^2 s)$
p   - number of plates in plate column
P   - pressure, Pa
q   - heat flux, W/m^2
q   - mass transfer factor, dimensionless
Q   - heat rate, W
r   - number of chemical reaction
R   - molar rate of chemical reaction, $kmol/(m^2 s)$
R   - universal gas constant, J/(kmol K)
S   - cross-sectional area, m^2
t   - time, s
T   - temperature, K
u   - superficial fluid velocity in equipment, m/s
v   - volumetric flow rate, m^3/s
V   - molar volume, m^3/kmol
w   - superficial mass fluid velocity, $kg/(m^2 s)$

W   - superficial molar fluid velocity, $kmol/(m^2s)$
x   - rectangular coordinate, m
x_i - mole fraction of component i in liquid phase, dimensionless
y   - rectangular coordinate, m
y_i - mole fraction of component i in the gas phase, dimensionless
z   - rectangular coordinate, m
Z   - height of the equipment, m

α - heat transfer coefficient, $W/(m^2K)$
α - gas hold-up, m^3/m^3
β - volumetric fraction, dimensionless
β - liquid hold-up, m^3/m^3
γ - solid volumetric fraction, m^3/m^3
δ - film thickness, m
ε - voidage of bed, dimensionless
ε - energy flux, W/m^2
η - viscosity, $kg/(m\ s)$
λ - conductivity, $W/(mK)$
υ - kinematic viscosity, m^2/s
υ - stoichiometry coefficient, dimensionless
ρ - density, kg/m^3
σ - surface tension, N/m
σ_c - critical surface tension, N/m
$\varXi_H$ - correction factor for the effect of high fluxes on heat
         transfer coefficient, dimensionless
$\varPhi_H$ - dimensionless heat transfer factor, dimensionless

Subscripts

A, B, C - components in multicomponent systems
av   - average
c   - at critical point
d   - dynamic quantity
G   - gas phase
i, j, k, 1 - components in multicomponent system
ij   - pair i-j in multicomponent system
in   - inert

k   - column
l   - laboratory
L   - liquid phase
m   - logarithmic mean value
p   - bubble, element of packing
r   - reduced relative to critical value
s   - static quantity
t   - total mass (molar) flux
0   - reference state
1   - quantity evaluated at lower cross section of equipment
2   - quantity evaluated at upper cross section of equipment

Superscripts

ef   - effective
r   - equilibrium value
*   - gas-liquid interface
**   - liquid-solid interface
-     - mean value
~   - partial value
o   - at infinite dilution
●   - for finite mass-transfer flux
▼   - relative to the molar average velocity of fluid
■   - relative to the volumetric average velocity of fluid
δ - in the bulk of fluid

Vectors and Matrices

$\mathbf{d}_i = [d_{ix}, d_{iy}, d_{iz}]$ - vector of driving forces for diffusion, m^{-1}

$\mathbf{f}_i = [f_{ix}, f_{iy}, f_{iz}]$ - vector of external force on unit mass of component i, N/m

$\mathbf{J}^{\blacktriangledown} = [J_1^{\blacktriangledown},...,J_{n-1}^{\blacktriangledown}]^T$ - vector of molar diffusion flux, $kmol/(m^2 s)$

$\mathbf{J}_i^{\omega} = [J_{ix}^{\omega}, J_{iy}^{\omega}, J_{iz}^{\omega}]$ - vector of molar diffusion flux of component i relative to velocity ω, $kmol/(m^2 s)$

$\mathbf{j}_i^{\omega} = [j_{ix}^{\omega}, j_{iy}^{\omega}, j_{iz}^{\omega}]$ - vector of mass diffusion flux of compoent i relative to velocity ω, $kg/(m^2 s)$

$\mathbf{k} = (k_{ij})_{i,j \leq n-1}$ - matrix of multicomponent mass transfer coefficients for "zero" mass transfer flux, m/s

$\mathbf{k}^{\bullet} = (\overset{\bullet}{k}_{ij})_{i,j \leq n-1}$ — matrix of multicomponent mass transfer coefficients for finite mass transfer flux, m/s

$\mathbf{N} = [N_1,...,N_{n-1}]^T$ — vector of molar flux, $kmol/(m^2 s)$

$\mathbf{N}_i = [N_{ix}, N_{iy}, N_{iz}]$ — vector of molar flux of component i, $kmol/(m^2 s)$

$\mathbf{n}_i = [n_{ix}, n_{iy}, n_{iz}]$ — vector of mass flux of component i, $kg/(m^2 s)$

$\mathbf{q} = [q_x, q_y, q_z]$ — vector of heat flux, W/m

$\mathbf{u} = [u_x, u_y, u_z]$ — vector of mass average velocity, m/s

$\mathbf{u}^{\blacktriangledown} = [u_x^{\blacktriangledown}, u_y^{\blacktriangledown}, u_z^{\blacktriangledown}]$ — vector of molar average velocity, m/s

$\mathbf{u}^{\blacksquare} = [u_x^{\blacksquare}, u_y^{\blacksquare}, u_z^{\blacksquare}]$ — vector of volume average velocity, m/s

$\mathbf{u}_i = [u_{ix}, u_{iy}, u_{iz}]$ — vector of macroscopic velocity of component i, m/s

$\mathbf{w}_i^{(\alpha)} = [w_{ix}^{(\alpha)}, w_{iy}^{(\alpha)}, w_{iz}^{(\alpha)}]$ — vector of mass flow velocity of gas phase in absorber, $kg/(m^2 s)$

$\mathbf{w}_i^{(\beta)} = [w_{ix}^{(\beta)}, w_{iy}^{(\beta)}, w_{iz}^{(\beta)}]$ — vector of mass flow velocity of liquid phase in absorber, $kg/(m^2 s)$

$\mathbf{W}_i^{(\alpha)} = [W_{ix}^{(\alpha)}, W_{iy}^{(\alpha)}, W_{iz}^{(\alpha)}]$ — vector of molar flow velocity of gas phase in absorber, $kmol/(m^2 s)$

$\mathbf{W}_i^{(\beta)} = [W_{ix}^{(\beta)}, W_{iy}^{(\beta)}, W_{iz}^{(\beta)}]$ — vector of molar flow velocity of liquid phase in absorber, $kmol/(m^2 s)$

$\mathbf{x} = [x_1,...,x_{n-1}]^T$ — vector of mole fraction in liquid phase, dimensionless

$\mathbf{y} = [y_1,...,y_{n-1}]^T$ — vector of mole fraction in gas phase, dimensionless

$\mathbf{\Gamma} = (\Gamma_{ij})_{i,j \leq n-1}$ — matrix of thermodynamic factors, dimensionless

$\mathbf{\Phi} = (\Phi_{ij})_{i,j \leq n-1}$ — matrix of mass transfer factor, dimensionless

Dimensionless Groups

$$Bo = \frac{g_z \, d_p \, \rho_L}{\sigma}$$ - Bond number

$$De = \frac{u \, \lambda}{d_p}$$ - Deborah number

$$Ga = \frac{g_z \, d_k^3}{v_L^3}$$ - Galillei number

$$Fr = \frac{u_G}{(g_z d_k)^{1/2}}$$ - Froude number

$$Re = \frac{u \, d \, \rho}{\eta}$$ - Reynolds number

$$Sc = \frac{\eta}{\rho \, \mathcal{D}}$$ - Schmidt number

$$Sh = \frac{k \, d}{\mathcal{D}}$$ - Sherwood number

Chapter 1

INTRODUCTION

Since the foundation of modern industry until the present time, absorption of gases in liquids has been of interest to practitioners and theoreticians of chemical and process engineering. This reflects the fact that it is one of the basic operations in many technological processes. The fertilizer industry provides a good example of the role of absorption processes. Absorption is also very important in gas and crude oil processing. Many intermediate and final products in the manufacture of organic chemicals are obtained as a result of the absorption of gases with their simultaneous reaction in the liquid phase. Recently, environmental protection has emerged as a significant problem. One of the basic operations of use in the solution of these problems is absorption.

The theory of absorption initially concentrated on kinetics and the design of absorbers for the case of physical absorption of one component in a liquid. Theoretical and experimental studies were also carried out on absorption accompanied by a simple chemical reaction. The culmination of these studies was the classical monograph by Sherwood and Pigford, "Absorption and Extraction", the second edition of which was published in 1952.

In the 1960s studies on absorption accompanied by a chemical reaction developed. Of particular importance were the investigations carried out by Astarita and Danckwerts. The results of many of these studies found practical applications. Until now these studies have represented one of the most quickly developing branches of chemical engineering. Another branch is multicomponent absorption, with special reference to multicomponent diffusion, which was initiated by Standard and Krishna in the 1970s. The

results of these studies have applications in the calculation of absorbers and chemical reactors.

The aim of this book is to present the modern theory of calculation of absorbers for binary and multicomponent physical absorption and absorption with simultaneous chemical reaction. The book consists of two parts: the theory of absorption and the calculation of absorbers. Part I covers basic knowledge on diffusion and the theory of mass transfer in binary and multicomponent systems. Significant stress is laid on diffusion theory because this forms the basis for the absorption process. In the next chapters the fundamentals of simultaneous mass transfer and chemical reaction, the theory of the desorption of gases from liquids and the formulation of differential mass balances are discussed. In fact, all of the material in part I concerns mass transfer in the cross section of an absorber.

At the beginning of part II, which is devoted to the calculation of absorbers, the classification of absorbers and the basis for their calculation is discussed. The next chapters present calculation methods for the basic types of absorber with a detailed analysis of the calculation methods for packed, plate and bubble columns.

This book is a revised version of the monograph which we wrote in 1985 and published in Poland in 1987. However, the present version differs significantly from the previous one and more than 70% of the material is revised or new. The description of multicomponent diffusion is limited and diffusion in electrolytes is omitted; no other types of absorber except for those mentioned above are considered. The material on simultaneous absorption with a chemical reaction and calculation methods for three main types of absorber has been extended. There is one further difference. In the Polish version binary systems were treated as special cases of multicomponent systems, while in this book some basic information on binary systems is given, and then multicomponent systems are discussed. This approach makes some repetition unavoidable; this approach was dictated by teaching aims. The reader is provided with knowledge on the nature of phenomena which can be easily explained on the basis (by example) of binary systems, and only in the next stage are mass transfer processes in multicomponent systems discussed. The latter description is more formalized.

We have attempted to illustrate the presented material with a large number of examples, starting with simple ones for binary systems and ending with column calculation for multicomponent systems. This sometimes required applications of quite complex

numerical techniques. In Chapter 14 the main methods of calculation are discussed.

Readers may be interested to know that, to complement the book, a suite of programs is available from the authors for numerical solution of the quoted calculation problems and for simulation of the processes described in the examples for different operating conditions. In addition, the software includes numerical procedures which can be used by readers in writing programs for physical or chemical absorption of binary or multicomponent mixtures. The programs and numerical procedures are written in Turbo Pascal. Calculation problems are described very thoroughly so that using the presented numerical procedures readers can write their own programs to solve problems similar to the examples quoted in the book.

The amount of monographs, review papers and other publications on the process of absorption is enormous. Therefore we decided to quote them very economically.

Acknowledgements

The authors wish to thank Miss Joanna Janczyk for preparing the English version of the book.

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THEORY OF ABSORPTION

Chapter 2

GAS-LIQUID EQUILIBRIA

The thermodynamics of gas (vapour)-liquid equilibria has been discussed in numerous studies and monographs [1-5], which are often more extensive than the present book. This chapter, therefore,should be treated as an introduction to the general description of absorption processes. More details on gas-liquid equilibria thermodynamics can be found in the books by Walas [1], Prausnitz [2, 3] and others [4, 5].

Before discussing the equilibrium problems, various methods for the determination of liquid composition will be presented briefly.

2.1. EXPRESSIONS OF CONCENTRATIONS AND PROPERTIES OF FLUIDS

There are two main ways of expressing the amount of mass which forms a determined volume of fluid.

In the first method the mass of particular components of the fluid is taken into account using the notion of mass concentration ρ_i, which expresses the mass of the i-th component per unit volume of solution. The sum of all mass concentrations is called the mass density of the solution.

$$\rho = \sum_{i=1}^{n} \rho_i \tag{2-1}$$

The second method corresponds to the number (frequency) of molecules of specific components of the solution. It involves the

notion of molar concentration of component C_i, defined as the number of kilomoles of the i-th component contained in the unit volume of fluid. The sum of all molar concentrations of components is called the molar density of the solution.

$$C = \sum_{i=1}^{n} C_i \tag{2-2}$$

The relation between mass concentrations and molar concentrations is given by the equation

$$\rho_i = M_i C_i \qquad (i = 1,\dots,n) \tag{2-3}$$

where M_i is the molecular weight of the i-th component.

The concentration of a particular component in a multicomponent solution is determined by its fraction. The fraction of a component is the ratio of the amount of the component to the total amount of the solution. Depending on the method of determination of this ratio, various fractions are obtained.

The mass fraction b_i is the ratio of the mass of the i-th component to the mass of all components present in a given volume. Thus, it can be defined by means of densities.

$$b_i = \frac{\rho_i}{\rho} \qquad (i = 1,\dots,n) \tag{2-4}$$

Similarly, the mole fraction x_i is the ratio of the number of kilomoles of the i-th component to the number of kilomoles of all components in the solution, that is it can be defined by means of molar densities.

$$x_i = \frac{C_i}{C} \qquad (i = 1,\dots,n) \tag{2-5}$$

In particular, in the case of gaseous mixtures which obey Dalton's law, whose components conform to the ideal gas law, the ratio of molar densities in equation (2-5) can be replaced by the ratio of the corresponding pressures. Hence,

$$x_i = \frac{P_i}{P} \qquad (i = 1,\dots,n) \tag{2-6}$$

where P_i denotes the pressure of component i, which would be exerted if it had occupied the whole volume of the solution, and P is the static pressure of the fluid.

From equations (2-1) and (2-2) and the definitions of fractions the following properties of the fractions follow

$$\sum_{i=1}^{n} b_i = \sum_{i=1}^{n} x_i = 1 \tag{2-7}$$

From equations (2-1), (2-3) and (2-5) we have the relation between mass density of the solution ρ and its molar density C

$$\rho = M C \tag{2-8}$$

where

$$M = \sum_{i=1}^{n} x_i M_i \tag{2-9}$$

is the mean molecular weight.

There is an explicit interrelationship between mass and mole fractions

$$b_i = \frac{x_i M_i}{M} \qquad (i = 1,\dots,n) \tag{2-10}$$

$$x_i = \frac{b_i / M_i}{\sum_{i=1}^{n} b_i / M_i} \qquad (i = 1,\dots,n) \tag{2-11}$$

Usually, the symbol y_i is used to denote mole fractions of components in the gas phase and x_i in the liquid phase.

In systems with inert gas components and nonvolatile solvents it is convenient to use mole ratios instead of mole fractions x_i and y_i. These ratios express the number of kilomoles of a particular component i refered to one kilomole of inert or nonvolatile solvent component. The symbol Y_i is used to denote mole ratio in the gas phase, X_i in the liquid phase.

Sometimes molality is used for aqueous solutions. Molality m_i

denotes the number of kilomoles of component i per kilogram of water.

When considering multicomponent solutions, besides the concept of such quantities as mass concentration or molar concentration of a component, the concept of partial quantities is used.

Partial specific quantities $\tilde{z}_i$ concerning particular components i are defined by means of the partial derivative of a given extensive value with respect to the mass of the i-th component at a constant amount of other components, constant pressure and temperature. Quantities specific to the fluid are calculated from partial quantities using the formula

$$z = \sum_{i=1}^{n} b_i \tilde{z}_i \tag{2-12}$$

The molar values for the whole fluid are calculated from partial molar quantities according to the formula

$$Z = \sum_{i=1}^{n} x_i \tilde{Z}_i \tag{2-13}$$

2.2. MODEL OF THE INTERFACIAL REGION

Absorption is a diffusional operation in which some components of the gas phase are absorbed by the liquid. Before discussing the law governing mass transfer, it is useful to consider interfacial equilibria, and first of all a model of the interfacial region.

The region separating two fluid phases is called the interfacial region. (It should not however be confused with hydrodynamic films in transfer theories.) Physically, each phase is not a continuous medium and, therefore, the phase boundary is not a surface in the geometrical sense. In fact, the interfacial region is a thin layer of thickness equal to at least several molecular diameters. Unlike the main bulk of the liquid, this region often reveals non-Newtonian rheological properties, due to which it can influence the behaviour of a two-phase system as a whole.

There are several simplified models of the interfacial region: surface discontinuity, singular surface, stratum zone and others. For the calculation of mass transfer in which the change of the transfer mechanism due to surface tension effects (e.g. Marangoni's phenomena) can be neglected, the simplest model, the so-called

model of surface discontinuity, appears to be satisfactory (Fig. 2-1). In this model the interfacial region is replaced by a hypothetical surface, called the interface, which has no physical properties (e.g. it has no surface tension). This surface cannot accumulate mass, energy and momentum in any form, and consequently the continuity conditions for mass and energy (eventually momentum)
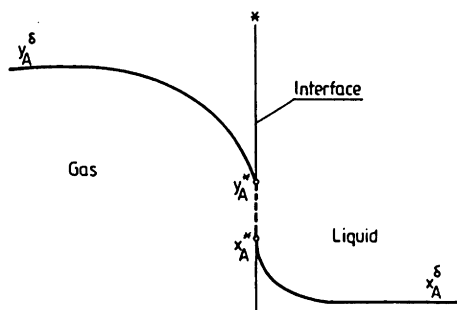
Fig. 2-1. Model of interface

fluxes are satisfied on it. The indeterminancy of the system properties at the interface causes their step-wise changes in transition from one phase to another. In the case of components present in both phases of a gas-liquid system, the discontinuous change of their concentrations is determined by the conditions of absorption equilibrium.

2.3. THERMODYNAMICS OF GAS-LIQUID EQUILIBRIA

For multicomponent mixtures consisting of n components at a temperature T and pressure P, the gas-liquid equilibrium is known if the quantitative relationship between the gas and liquid composition is strictly determined. The existence of an equilibrium in this system can be written using the formulae

$$T_G = T_L \tag{2-14}$$

$$P_G = P_L \tag{2-15}$$

$$f_{iG} = f_{iL} \quad (i = 1,...,n) \tag{2-16}$$

where f_{iG} is the fugacity of component i in the gas phase and f_{iL} is the fugacity of component i in the liquid phase.

The condition necessary for equilibrium in a gas-liquid

multicomponent system is that temperatures and pressures, as well as the fugacities of particular components, be equal in the two phases.

Equations (2-14) to (2-16) describe the equilibrium not only in a gas-liquid system but also in vapour-liquid system. The absorption equilibrium (the gas-liquid system) occurs when the critical temperature of at least one component of the multicomponent mixture is lower than the temperature of the system. Otherwise, a distillation equilibrium exist.

The fugacity of component i in a gas mixture depends on the gas composition, temperature and pressure. To make the fugacity dependent on the mixture composition the fugacity coefficient is introduced. For the gas phase the following relation holds

$$f_{iG} = \phi_{iG} y_i P \qquad (i = 1,...,n) \tag{2-17}$$

The fugacity coefficient ϕ_{iG} depends on temperature, pressure and gas composition. For gases obeying the ideal gas law, the fugacity coefficient is equal to 1.

$$\phi_{iG} = 1 \qquad (i = 1,...,n) \tag{2-18}$$

For nonpolar mixtures it may usually be assumed that for pressures not exceeding 2×10^6 Pa the fugacity coefficient is close to unity. In general, the fugacity coefficient is connected to the volumetric properties of a gas by the following relation

$$\ln \phi_{iG} = \frac{1}{RT} \int_{V_G}^{\infty} \frac{\left[\left(\frac{\partial P}{\partial C_i} \right)_{T, V_G, C_j \neq C_i} - RT \right]}{V_G} dV_G - \ln \frac{P}{CRT}$$

$$(i = 1,...,n) \tag{2-19}$$

where V_G is the volume of the gas phase.

Similarly, for the liquid phase the following equation holds.

$$f_{iL} = \phi_{iL} x_i P \qquad (i = 1,...,n) \tag{2-20}$$

The relation describing the liquid fugacity coefficient ϕ_{iL} is the same as equation (2-19), the only change being substitution of subscript G by L.

To use equation (2-19) to calculate the fugacity coefficient it is necessary to know the equation of state for a given phase. Every book on thermodynamics gives many such equations; they will therefore not be quoted here.

In the case of the liquid phase, besides equation (2-20) there is another method of describing the fugacity of an individual component f_{iL} using the concept of an activity coefficient and the fugacity of component i in some standard state. It is assumed in the literature that calculations for nonpolar systems is different from that for electrolytes and systems undergoing chemical reaction. Below, we shall discuss a method for nonpolar systems.

The fugacity of component i in the liquid phase is given by the relation

$$f_{iL} = \gamma_i x_i f_{iL}^o \qquad (i = 1,\ldots,n) \qquad (2\text{-}21)$$

where γ_i is the activity coefficient of component i in the mixture and f_{iL}^o is the fugacity of component i in some standard state. Usually the standard state is taken as a pure liquid component i at the same temperature.

$$f_{iL}^o = f_L^o \qquad (i = 1,\ldots,n) \qquad (2\text{-}22)$$

It should be kept in mind that the product $\gamma_i x_i$ is equal to the activity of component i in the mixture.

$$a_i = \gamma_i x_i \qquad (i = 1,\ldots,n) \qquad (2\text{-}23)$$

The fugacity of a pure liquid component i at temperature T and pressure P is equal to

$$f_L^o = P_i \phi_L \exp \int_{P_i}^{P} \frac{V_L}{RT} \, dP \qquad (i = 1,\ldots,n) \qquad (2\text{-}24)$$

where P_i is the vapour pressure of component i at temperature T, ϕ_L is the fugacity coefficient of pure component i and V_L is the molar volume of pure component i.

The fugacity coefficient ϕ_L depends on temperature and pressure. However, for a nonassociated liquid it is close to unity. The exponential term in the last equation is called the Poynting

factor. Only for very high pressures, when the compressibility of a liquid should be taken into account, does the Poynting factor differ significantly from unity. In most cases of absorption it can be neglected and assumed to equal 1.

Substituting equations (2-24), (2-22) into (2-21) we have

$$f_{iL} = \gamma_i x_i P_i \phi_L \exp \int_{P_i}^{P} \frac{V_L}{RT} \, dP \qquad (i = 1,...,n) \qquad (2\text{-}25)$$

In such an approach the burden of the calculation lies with calculation of activity coefficients γ_i. There are many equations which allow us to determine this value, the most important ones being the Wilson, NRTL and UNIQUAC equations, and many others. As with the equation of state, they will not be discussed here and the reader may find them in the literature quoted.

Upon substitution of equation (2-17) and (2-25) into equation (2-16) the most general equation describing the gas-liquid equilibrium is obtained.

$$y_i P = \frac{\phi_L P_i \gamma_i}{\phi_{iG}} x_i \exp \int_{P_i}^{P} \frac{V_L}{RT} \, dP \qquad (i = 1,...,n) \qquad (2\text{-}26)$$

This equation may be simplified in many ways. As mentioned earlier, for pressures below 2×10^6 Pa the Poynting factor is close to unity. Also under these conditions it can be assumed that the gas phase behaves like an ideal gas. So equation (2-26) simplifies to the form

$$y_i P = P_i \gamma_i x_i \qquad (i = 1,...,n) \qquad (2\text{-}27)$$

or

$$p_i = P_i \gamma_i x_i \qquad (i = 1,...,n) \qquad (2\text{-}28)$$

The latter relation is often written as follows

$$p_i = He_i x_i \qquad (i = 1,...,n) \qquad (2\text{-}29)$$

where He_i is the Henry constant equal to

$$He_i = P_i \gamma_i \qquad (i = 1,...,n) \qquad (2\text{-}30)$$

Equation (2-29) shows that the higher the Henry constant, the lower the solubility of the gas in the liquid.

If the liquid phase is also an ideal solution, equation (2-27) is reduced to Raoult's law

$$y_i P = P_i x_i \qquad (i = 1,\ldots,n) \qquad (2\text{-}31)$$

Usually, in absorption systems the nonideality of the liquid phase cannot be neglected and the basic relationship describing the absorption equilibrium is equation (2-29). The Henry constant is a function of temperature. Table 2-1 presents the dependence of the Henry constant on temperature for several gases soluble in water.

Table 2-1. Henry constant for a few gases (gas-water systems), $[\text{He}_i \times 10^8 \text{ Pa}]$

Component	Temperature, K			
	273.15	288.15	303.15	318.15
H_2	58.6	66.9	73.8	76.9
N_2	53.6	74.8	93.6	110.5
CO	35.6	49.6	62.8	73.8
CO_2	0.74	1.24	1.87	2.60
H_2S	0.27	0.43	0.62	0.82
CH_4	22.7	34.1	45.5	55.7
C_2H_6	12.7	22.9	34.7	46.9

In general, for moderate temperatures, gas solubilities decrease with an increase in temperature. Only in the region of the critical solvent temperature does the solubility increase. This is illustrated in Figure 2-2.

Besides Henry's law in the form of equation (2-29), other forms are encountered in the literature. For instance,

$$y_i = m_i x_i \qquad (i = 1,\ldots,n) \qquad (2\text{-}32)$$

$$p_i = H_i C_i \qquad (i = 1,\ldots,n) \qquad (2\text{-}33)$$

or

$$x_i = H_i' p_i \qquad (i = 1,\ldots,n) \qquad (2\text{-}34)$$

Hence, attention should always be paid to the form of this law so as to avoid mistakes in calculations. There are simple converters of one Henry constant to another.
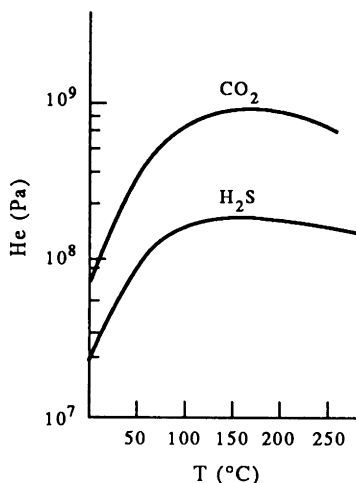
Fig. 2-2. Henry's constant for H_2S and CO_2 in water vs. temperature

Two more problems should be mentioned
- the solubility of gases in a mixture of two different solvents
- the solubility of gases in an electrolyte solution.
In the case of a mixture of n solvents it may be assumed as a crude rule that the Henry constant for component A is given by the equation

$$\ln H_{A,mix} = \sum_{i=1}^{n} x_i \ln H_{Ai} \qquad (2-35)$$

Equilibria in electrolyte solutions are called ionic equilibria. General properties and laws of phase equilibria presented for nonpolar systems also hold in the case of equilibria in which ions are present [6, 7, 8]. The specificity of ionic equilibria is connected mainly with the thermodynamic interpretation of the activity of electrolyte ions in the solution. As a result, slightly different equations describing the activity coefficient in electrolyte solutions from those determining this coefficient in nonpolar solutions are obtained. Electrolyte solutions are normally classified as "weak electrolytes" and "strong electrolytes". Gas molecules on their passage to the liquid solution react chemically with solution molecules and as a result ions are formed. Such a chemical reaction is called dissociation. Dissociation may only be partial (as a result "weak electrolytes" are formed) or total (when "strong electrolytes" are produced). The "weak electrolytes" are normally gases such as NH_3, CO_2, SO_2 or H_2S dissolved in various,

usually aqueous, solvents. An example of a strong electrolyte is hydrogen chloride dissolved in water (hydrochloric acid). For weak electrolytes the phase equilibrium equations must be completed with additional relationships which cover mass balance of the weak electrolyte in the liquid phase, a dissociation equilibrium equation and the electroneutrality principle of the solution. In the description of phase equilibrium in electrolyte solutions by Henry's law, the Henry constant can be determined on the basis of the equations presented by van Krevelen and Hoftijzer [9]. The following relations hold here

$$\log_{10} \frac{He_{i,el}}{He_i} = hI \qquad (2\text{-}36)$$

where I is the ionic strength calculated from the formula

$$I = \frac{1}{2} \sum_i C_i z_i \qquad (2\text{-}37)$$

$He_{i,el}$ is the Henry constant of gas in the electrolyte solution,

He_i is the Henry constant of gas in water,

C_i is the concentration of ions of valency z_i

and

$$h = h_+ + h_- + h_G \qquad (2\text{-}38)$$

where h_+, h_- and h_G are the contributions of positive and negative ions present and the gas. The values of h can be found in various publications [10, 11].

Example 2-A. On the basis of the phase equilibrium equations and relations following from the theory of weak electrolytes, Edwards et al. [12, 13] described analytically the liquid-gas equilibrium for solutions containing one or more volatile electrolytes: ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide. Using the equilibrium equations given by these authors, calculate the pressures of ammonia (1), and water vapour (2) in the gas phase over a solution of ammonia. The system is under a pressure $P = 1.013 \times 10^5$ Pa at temperature $T = 293.15$ K, 313.15 K, 323.15 K. The composition of the liquid phase is such