Chapter 5
Principles for Gas Separation

With a good understanding of the properties of gaseous and particulate air pollutants, this chapter starts with basic principles for the separation of unwanted gases from the air. It is divided into two major sections as adsorption and absorption. Topics covered in this chapter include adsorbate and adsorbent, adsorption affinity, adsorption isotherm, adsorption wave, absorption, absorption equilibrium, and chemical assisted absorption. Condensation is not covered because it applies mainly to gases with very high concentration, which do not happen often in air emission control.

5.1 Adsorption

5.1.1 General Consideration

Adsorption is a process by which gas molecules are attracted to the surfaces of a solid or liquid and consequently separated from the main gas stream. The adsorbing material is called adsorbent, and the gas molecules to be adsorbed is called adsorbate.

Adsorption can be classified as physisorption and chemisorption. The differences between these two types of adsorptions are summarized in Table 5.1. The former is caused by van der Waals forces and the latter involves chemical reactions between the adsorbent and the adsorbate. Thereby the mechanisms and models for chemical adsorption are more complicated than physical adsorption.

Physioadsorption is a surface phenomenon where the adsorbate will stay on the surface of the adsorbent. The attractive force normal to the surface tends to grab adjacent molecules of adsorbate. For example, activated carbon has a tendency to adsorb volatile organic compounds (VOCs) from an air stream. Chemisorption is driven by a chemical reaction that takes place at the adsorbate-adsorbent interface. As a result, a new chemical species is generated at the interface.

Both physisorption and chemisorption may occur simultaneously at the same adsorption interface and physical adsorption can continue after the chemical adsorption layer is completed. However, the bonding strength of chemisorption is

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Table 5.1 Physisorption and chemisorption

	Physical adsorption	Chemical adsorption
Driving force	van der Waals force between molecules. No change of properties of either the adsorbent or the adsorbate	Chemical reactions between the adsorbent and adsorbate. Forming new adsorption products
Heat release rate	Low, about 20 kJ/g mol	High due to chemical reaction, 20–400 kJ/g mol
Reversibility	Can be easily reversed by reducing the pressure at the temperature at which the adsorption took place	Difficult to reverse. Requires very high temperature or positive ion bombardment to remove the adsorbate
Equilibrium pressure	Physical adsorption of a gas is related to liquefaction or condensation, it only occurs at pressures and temperatures close to those required for liquefaction. Low-pressure adsorptions take place mainly in fine porous adsorbents by capillary effect	Chemisorption can take place at much lower pressures and much higher temperatures than physical adsorption
Thickness of reaction layers	A physical adsorption layer at equilibrium can be several molecules thick	A chemisorption layer can only be one molecule thick, because the newly formed compound layer prevents the further reaction of the adsorbent and the adsorbate

stronger than that of physisorption. A description of the chemisorption bond requires a detailed understanding of molecules outside surfaces and the electronic structure of atoms. The author of this book does not intend to extend the scope of this book to interfacial chemistry; readers interested in this topic are directed to specialized books devoted to chemisorption.

Common physioadsorbents include

- activated carbon,
- silica gel,
- activated alumina, and
- aluminosilicates (molecular sieves).

Activated carbon is a char-like material with a great surface area. Silica gel is a hard, granular, and porous material made by precipitation from sodium silicate solutions treated with an acid. Activated alumina is an aluminum oxide activated at high temperature and used primarily for moisture adsorption. Aluminosilicates are made of porous synthetic zeolites and are used primarily in gas separation processes.

Activated carbon is the most common adsorbent for air emission control. Activated carbon is made by the carbonization of carbon rich coal or biomass (wood, fruit pits, or coconut shells) followed by activation with hot air or steam. It is produced by a two-step process. First, pyrolysis of raw material with a high carbon source such as coal, wood and nutshells results in charred highly carbonaceous solid residue. Then activation of the charred residue by oxidation forms pores and passages

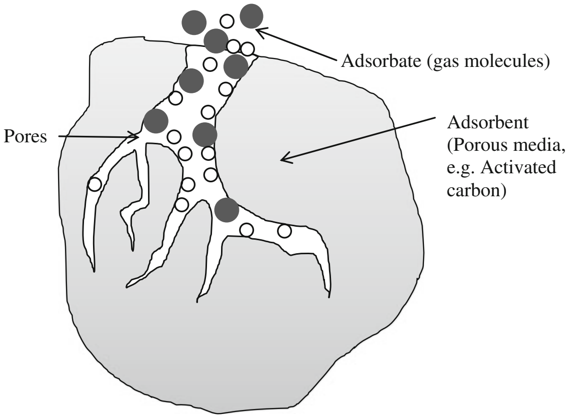


Fig. 5.1 Schematic diagram of pores in adsorbent

with high surface area and different polarities for different air pollutants. Chemical treatment is also necessary to further improve its performance. The final properties of activated carbon depend on the treatment of the activated carbon (e.g., [7]).

Activated carbons can be made in many forms, depending on the need: pellet and granular forms are common for adsorption beds; fibrous structures are common for air filters, for example, activated carbon cloth can be used for removal of water vapor [3].

Most engineered adsorbents are characterized with many pores and consequent large surface areas and low bulk density. If an adsorbent is porous, then its actual surface area is much greater than external area.

Figure 5.1 illustrates how adsorbate molecules are adsorbed on the surfaces of the pores in an adsorbent. The bulk sizes of activated carbon particles can be up to a few millimeters in form of granules or in micrometers for powder.

For most adsorbents, the sizes of the pores are sufficiently small and the corresponding surface area is enormous. The pore diameter of a molecular sieve can be 30 or 40 Angstrom (Å) (1 Å = 0.1 nm). Pore sizes in activated carbon range from 10–10,000 Å in diameter. Those larger than 1,000 Å are called macropores and the pores smaller than 1,000 Å are micropores. The surface areas of the pores can be 500–1,500 m^2/g of activated carbon [1, 7]. Large amount of internal pores in an adsorbent greatly reduces its bulk density. Bulk densities of dry granular activated carbon are 220–500 kg/m^3, and those of powders are 340–740 kg/m^3. The real density of the granular activated carbon itself may be about 2,000 kg/m^3.

5.1.2 Adsorption Affinity

Adsorbent affinity is the attraction between the adsorbent and the adsorbate and it is critical to successful adsorption. Affinities can be designed by adjusting the pore diameters of the adsorbent. For example, silica gel is used for adsorbing water vapor from the air because it has an affinity for water. In air pollution control, activated carbon is an ideal adsorbent for many VOCs because it has an affinity for hydrocarbon gases. Both the surface area of the adsorbent and the affinity of the adsorbent for the adsorbate affect adsorption efficiency. Adsorption efficiency increases with the increase in surface area of adsorbent. Bulk sizes of the porous adsorbent particles do not affect maximum adsorption capabilities, but they affect the time to achieve equilibrium significantly.

Affinities can also be designed by adjusting the pore diameters of the adsorbent. For example, a molecular sieve with a pore diameter of 30 Å can adsorb light gases, such as NH_3 and H_2O. However, when the diameter of the pores is increased to 40 Å, the sorbent is more effective on larger molecules, such as CO_2 and SO_2. Further increasing the pore diameters can enable the adsorption of large organic molecules, such as benzene, phenol, and toluene.

5.1.3 Adsorption Isotherm

Physical and thermodynamic properties of different gases are particularly useful for engineers who design adsorption systems, and analysis of isotherms can yield important data. Adsorption equilibrium is reached when a stable relationship exists between the concentration of the species in air and the amount of adsorbate adsorbed per unit mass of adsorbent. The adsorption equilibrium is a function of temperature.

An adsorption isotherm is a relationship of equilibrium adsorbent capability versus the adsorbate concentration at a given temperature. Note that equilibrium absorption is rarely achieved in real engineering operations. Factors that can reduce the adsorption capacity include moisture in the air, heat waves, or residue moisture in the adsorbent. This actual adsorption capacity is sometimes called working adsorption capacity.

$$M_{\mathrm{eq}} = f(C) \tag{5.1}$$

M_{eq} is the adsorbate to adsorbent mass ratio at equilibrium (kg adsorbate/kg adsorbent), while C is adsorbate concentration in gas phase (kg/m^3, ppmv, etc.)

There are several models for this relationship described in Eq. (5.1), of which Langmiur and Freundlich isotherms are widely used [11]. Both are introduced below.

5.1.3.1 Langmuir Isotherm

Irving Langmuir was awarded the Nobel Prize in 1932 for his investigations concerning surface chemistry. Langmuir model is an empirical model and it was developed in the 1910s based on the following assumptions:

- The adsorbed layer is made up of a single layer of molecules.
- Adsorption is a reversible process.
- The process is dynamic: the adsorbed molecules do not move on the surface of the adsorbent, but they may reenter the air stream.
- The enthalpy of adsorption is the same for all molecules independently of how many have been adsorbed.

At equilibrium the number of molecules being adsorbed equals to the number of molecules leaving the adsorbed state, i.e., *Rate of adsorption = Rate of desorption*

$$k_1 C\left(M_{\max} - M_{\mathrm{eq}}\right) = k_2 M_{\mathrm{eq}} \tag{5.2}$$

where C = the gas concentration (kg/m^3); M_{eq} = equilibrium loading capacity with a unit of kg/kg, $M_{\max}$ = the maximum loading potential of adsorbate that can be loaded to per mass of adsorbent with same unit as M_{eq}. k_1 and k_2 are mass transfer coefficients, and their unit changes with that of $M_{\max}$ and M_{eq}.

Solving Eq. (5.2) leads to the description of $M_{\mathrm{eq}}/M_{\max}$, which stands for the ratio of equilibrium loading to maximum loading potential.

$$\frac{M_{\mathrm{eq}}}{M_{\max}} = \frac{k_1 C}{k_1 C + k_2} \tag{5.3}$$

With a new constant $K_L = k_1/k_2$, Eq. (5.3) becomes

$$M_{\mathrm{eq}} = \frac{M_{\max} K_L C}{1 + K_L C} \tag{5.4}$$

$M_{\max}$ is a constant for a fixed design with fixed amount of known adsorbent; the mass transfer coefficients can also be treated as constants for certain operating conditions. Then K_L and $M_{\max}$ are both constants in the Langmuir model; they are to be determined experimentally. To make sure $K_L C$ is dimensionless, the unit of K_L is the same as that of $1/C$.

The Langmuir isotherm can be rearranged as

$$\frac{1}{M_{\mathrm{eq}}} = \frac{1}{M_{\max}} + \left(\frac{1}{K_L M_{\max}}\right)\frac{1}{C} \tag{5.5}$$

It shows that $1/M_{\mathrm{eq}}$ versus $1/C$ is a linear relationship.

In a typical experiment, one can continuously monitor the up- and down-stream adsorbate concentrations. When they are approaching each other it means that an equilibrium state is reached. Then the amount of adsorbate can be determined by measuring the mass of the adsorbent before and after the experiment.

We can plot the experimental data with $1/C$ as x-axis and $1/M_{\mathrm{eq}}$ as y-axis. By linear regression, the slope of the straight line is $1/K_L M_{\max}$ and the intercept is $1/M_{\max}$.

Table 5.2 Langmuir isotherm constants measured at 25 °C by linear regression

$M_{\mathrm{eq}} = \frac{M_{\max} K_L C}{1 + K_L C}$

Adsorbate	AC type	$M_{\max}$ (g/g)	K_L (1/ppmv)
Acetone	A	0.401	0.00067
	B	0.389	0.00057
	D	0.330	0.000520
	E	0.391	0.000491
Benzene	A	0.389	0.00492
	C	0.393	0.00157
	D	0.124	0.00379
Carbon tetrachloride	A	0.959	0.00206
	D	0.677	0.00177
Chloroform	D	0.631	0.000685
Dichloromethane	A	0.298	0.000716
Diethylamine	A	0.461	0.00139
Ethanol	C	0.353	0.00145
	D	0.333	0.00133
Hexane	A	0.337	0.00924
Isopropanol	A	0.456	0.00185
Methylacetate	A	0.304	0.00170
Methylchloroform	A	0.666	0.00443
Methanol	B	0.394	0.000349
	C	0.334	0.000446
	D	0.334	0.000317
	E	0.396	0.00027
Nitrobenzene	D	0.518	0.140
o-xylene	D	0.378	0.0238
Toluene	B	0.447	0.00686
	C	0.384	0.00873
	D	0.681	0.00371
	E	0.441	0.00629
Trichloroethylene	B	0.703	0.00265
	C	0.650	0.00331
	D	0.625	0.00242
	E	0.708	0.00204

Some of the Langmuir constants for coconut-based activated carbon are available in Table 5.2 [14]. The properties of the coconut-based activated carbon materials are listed in Table 5.3. The constants depend on the adsorbate–adsorbent combination.

Table 5.3 Coconut-based activated carbon reported [14]

AC type	Density (g/cm^3)	Surface area (m^2/g)	Pore volume (cm^3/g)
A	0.38–0.44	1,500–1,625	0.9–1
B	0.44	1,270	0.7
C	0.41	1,090	0.94
D	0.45	1,098	0.57
E	0.43	1,240	0.65

5.1.3.2 Freundlich Isotherm

Freundlich isotherm is also the empirical model and is described as

$$M_{\mathrm{eq}} = K_F C^{\frac{1}{n}} \tag{5.6}$$

where K_F and n are constants for a specific adsorbate–adsorbent system at certain condition. A logarithm conversion on both side transforms this equation into a linear one as

$$\log_{10} M_{\mathrm{eq}} = \log_{10} K_F + \frac{1}{n} \log_{10} C \tag{5.7}$$

Again this linear relationship allows the coefficients to be determined by linear regression of a few experimental data points. $M_{\mathrm{eq}} = K_F$ when $C = 1$, and the slope of the straight line is $1/n$.

Although both Langmuir and Freundlich models are empirical, there are some differences. The Langmuir isotherm is a model with some theoretical analyses and assumptions. It assumes reversible adsorption and desorption of the adsorbate molecules. The Freundlich isotherm is an empirical model without assumption. In general, the Langmuir isotherm works well for typical single component and high adsorbate concentration. The Freundlich isotherm can be used for mixtures of compounds and it agrees well with experimental data.

Freundlich is more relevant to air emission studies where air pollutants are diluted. With $a = \log_{10} K_F$ and $b = 1/n$, Eq. (5.7) becomes

$$\log_{10} M_{\mathrm{eq}} = a + b \log_{10} C \tag{5.8}$$

For a greater accuracy, Yaws et al. [16] refined the model with one more term

$$\log_{10} M_{\mathrm{eq,g/100\,g}} = a + b \log_{10} C_{\mathrm{ppmv}} + d\left(\log_{10} C_{\mathrm{ppmv}}\right)^2 \tag{5.9}$$

The values of a, b, and d are pollutant specific. Experimental data obtained using 243 VOCs adsorbed using activated carbon are available in the literature [16]. Some of them are listed in Table 5.4 for training purpose only in this book. Users are reminded that the units have to match on both sides of the above equation. In order

Table 5.4 The values of coefficients a, b, and d for Eq. (5.9) with $M_{eq,g/100\,g}$ in (g adsorbate/100 g adsorbent) and C_{ppmv} in ppmv

Formula	Name	a	b	d
$CBrCl_3$	Bromotrichloromethane	1.39842	0.23228	−0.02184
$CBrF_3$	Bromotrifluoromethane	−1.46247	0.58361	−0.01044
CBr_2F_2	Dibromodifluoromethane	0.82076	0.30701	−0.01384
CBr_3F	Tribromofluoromethane	−1.43748	0.55503	−0.00450
CCl_2F_2	Dichlorodifluoromethane	−0.07350	0.40145	−0.01404
CCl_2O	Phosgene	−0.64469	0.60428	−0.02986
CCl_3F	Trichlorofluoromethane	0.17307	0.40715	−0.01915
CCl_3NO_2	Chloropicrin	1.26745	0.20841	−0.01288
CCl_4	Carbon tetrachloride	1.07481	0.28186	−0.02273
$CHBr_3$	Tribromomethane	1.73184	0.19948	−0.02246
$CHCl_3$	Chloroform	0.67102	0.36148	−0.02288
CHN	Hydrogen cyanide	−4.39245	1.08948	−0.00740
CH_2BrCl	Bromochloromethane	0.61399	0.41353	−0.02531
CH_2BrF	Bromofluoromethane	0.45483	0.36332	−0.01606
CH_2Br_2	Dibromomethane	1.08376	0.37211	−0.03238
CH_2Cl_2	Dichloromethane	−0.07043	0.49210	−0.02276
CH_2I_2	Diiodomethane	1.94756	0.14984	−0.01947
CH_2O	Formaldehyde	−2.48524	0.69123	−0.00375
CH_2O_2	Formic acid	−1.77731	1.09503	−0.06354
CH_3Br	Methyl bromide	−1.23835	0.78564	−0.05521
CH_3Cl	Methyl chloride	−1.91871	0.62053	−0.00549
CH_3Cl_3Si	Methyl trichlorosilane	1.07198	0.24275	−0.01911
CH_3I	Methyl iodide	0.73997	0.32985	−0.01330
CH_3NO	Formamide	1.30981	0.25274	–
CH_3NO_2	Nitromethane	−0.32847	0.70602	−0.05111
CH_4	Methane	−4.31008	0.77883	−0.00628
CH_4Cl_2Si	Methyl dichlorosilane	0.73271	0.29305	−0.01822
CH_4O	Methanol	−1.96739	0.82107	−0.01393
CH_4S	Methyl mercaptan	−1.12288	0.60573	−0.02094
CH_5N	Methylamine	−1.93548	0.64710	−0.01057
CN_4O_8	Tetranitromethane	1.49047	0.18181	−0.01894
CO	Carbon monoxide	−5.18782	0.90121	−0.01358
COS	Carbonyl sulfide	−1.42882	0.51061	0.00028
CO_2	Carbon Dioxide	−3.65224	0.80180	−0.00328
CS_2	Carbon disulfide	−0.18899	0.47093	−0.01481
$C_2Br_2F_4$	1,2-Dibromotetrafluoroethane	0.90388	0.25693	−0.00974
C_2ClF_5	Chloropentafluoroethane	0.08264	0.34756	−0.01343
$C_2Cl_3F_3$	1,1,2-Trichlorotrifluoroethane	1.27368	0.18656	−0.01231

(continued)

Table 5.4 (continued)

Formula	Name	a	b	d
C_2Cl_4	Tetrachloroethylene	1.40596	0.20802	−0.02097
$C_2Cl_4F_2$	1,1,2,2-Tetrachlorodifluoroethane	1.37307	0.17625	−0.01465
$C_2HBrClF_3$	Halothane	0.92405	0.31204	−0.02004
C_2HCl_3	Trichloroethylene	1.02411	0.29929	−0.02539
C_2HCl_3O	Dichloroacetyl chloride	1.23647	0.26219	−0.02596
C_2HCl_3O	Trichloroacetaldehyde	1.17362	0.26971	−0.02513
C_2HCl_5	Pentachloroethane	1.64566	0.13515	−0.01572
$C_2HF_3O_2$	Trifluoroacetic acid	−0.12577	0.59373	−0.03445
C_2H_2	Acetylene	−2.24177	0.82454	−0.03390
$C_2H_2Br_4$	1,1,2,2-Tetrabromoethane	-	-	-
$C_2H_2Cl_2$	1,1-Dichloroethylene	0.48740	0.33282	−0.01622
$C_2H_2Cl_2$	cis-1,2-Dichloroethylene	0.47567	0.39061	−0.02554
$C_2H_2Cl_2$	trans-1,2-Dichloroethylene	0.47567	0.39061	−0.02554
$C_2H_2Cl_2O_2$	Dichloroacetic acid	1.69237	0.09630	–
$C_2H_2Cl_4$	1,1,1,2-Tetrachloroethane	1.44097	0.19166	−0.01995
$C_2H_2Cl_4$	1,1,2,2-Tetrachloroethane	1.52322	0.17848	−0.02019
C_2H_3Cl	Vinyl chloride	−0.98889	0.66564	−0.04320
C_2H_3ClO	Acetyl chloride	0.03627	0.45526	−0.02093
$C_2H_3ClO_2$	Methyl Chloroformate	0.41186	0.42776	−0.02776
$C_2H_3Cl_3$	1,1,1-Trichloroethane	0.97331	0.28737	−0.02277
$C_2H_3Cl_3$	1,1,2-Trichloroethane	1.17163	0.27791	−0.02746
C_2H_3N	Acetonitrile	−0.79666	0.63512	−0.02598
C_2H_3NO	Methyl isocyanate	−1.07579	0.85881	−0.06876
C_2H_4	Ethylene	−2.27102	0.61731	−0.01467
$C_2H_4Br_2$	1,1-Dibromoethane	1.37260	0.25671	−0.02516
$C_2H_4Br_2$	1,2-Dibromoethane	1.44231	0.25500	−0.02666
$C_2H_4Cl_2$	1,1-Dichloroethane	0.54485	0.36091	−0.02192
$C_2H_4Cl_2$	1,2-Dichloroethane	0.55343	0.37072	−0.02161
$C_2H_4Cl_2O$	Bis(chloromethyl)ether	0.95599	0.33784	−0.03200
$C_2H_4F_2$	1,2-Difluoroethane	−3.97902	2.51862	−0.31617
C_2H_4O	Acetaldehyde	−1.17047	0.62766	−0.02475
C_2H_4O	Ethylene oxide	−2.42379	0.94878	−0.04062
$C_2H_4O_2$	Acetic acid	−0.05553	0.68410	−0.06071
$C_2H_4O_2$	Methyl formate	−0.99586	0.61693	−0.01847
C_2H_4S	Thiacyclopropane	0.02258	0.45520	−0.02154
C_2H_5Br	Bromoethane	0.31783	0.43549	−0.03072
C_2H_5Cl	Ethyl chloride	−0.50828	0.50364	−0.02179
C_2H_5ClO	2-Chloroethanol	0.74164	0.46933	−0.05158
C_2H_5I	Ethyl iodide	1.00356	0.32123	−0.02405
C_2H_5N	Ethyleneimine	−1.16912	0.91238	−0.07400

(continued)

Table 5.4 (continued)

Formula	Name	a	b	d
C_2H_5NO	N-Methylformamide	1.23333	0.21723	–
$C_2H_5NO_2$	Nitroethane	0.44968	0.49708	−0.04612
C_2H_6	Ethane	−2.40393	0.68107	−0.01925
C_2H_6O	Ethanol	−0.51153	0.67525	−0.04473
C_2H_6OS	Dimethyl sulfoxide	1.24042	0.31302	−0.04768

Source [16]. More data can be found in Table A.6

to use these values, the unit of $M_{\mathrm{eq,g/100\,g}}$ must be (g adsorbate/100 g adsorbent) and C_{ppmv} in ppmv.

For many engineering processes, the last term $d\left(\log_{10} C_{\mathrm{ppmv}}\right)^2$ is negligible, and a simplified formula can be used for estimation with a reasonable accuracy. For adsorbate concentrations lower than 50 ppmv, the error is less than 5 %.

Example 5.1: VOC adsorption using AC

In an automobile assembling shop, the concentration of n-butanol ($C_4H_{10}O$) in the room air is 5 ppmv. The density of n-butanol is 3.06 kg/m^3 under standard room air conditions. A carbon filter bed is used for air cleaning, and the airflow rate is 0.1 m^3/s through the filter. Determine

a. the adsorption capacity of the activated carbon filter,
b. the total carbon mass needed for the bed, assuming the working adsorption capacity is 40 % of the maximum potential and the bed service life is one year.

Solution

a. From Table 5.4, we have the adsorption constants of $C_4H_{10}O$:

$$a = 0.89881;\ b = 0.32534;\ d = -0.03648$$

Then Eq. (5.9) leads to

$$\begin{aligned}\log_{10} M_{\mathrm{eq,g/100\,g}} &= a + b\log_{10} C_{\mathrm{ppmv}} + d\left(\log_{10} C_{\mathrm{ppmv}}\right)^2\\ &= 0.89881 + 0.32534\log_{10}(5) - 0.03648[\log_{10}(5)]^2 = 1.1084\end{aligned}$$

$$M_{\mathrm{eq,g/100\,g}} = 10^{1.1084} = 12.8\,(\text{gram of } C_4H_{10}O \text{ per 100 gram of carbon})$$

b. The total amount of n-butanol passing through the carbon bed in 1 year is

$$\begin{aligned}m = QC\rho_g t = 0.1\ \frac{\mathrm{m^3 air}}{\mathrm{s}} \times 0.000005\ \frac{\mathrm{m^3 n-bu}}{\mathrm{m^3 air}} \times 3.05\ \frac{\mathrm{kg}}{\mathrm{m^3 n-bu}} \times (365 \times 24 \times 3600)\ \mathrm{s}\\ = 48.1\ \mathrm{kg}\end{aligned}$$

The actual carbon mass needed is

$$m_{\text{carbon}} = \frac{m}{M_{\text{eq.g}/100\,\text{g}}} \times \frac{100}{40} = \frac{48.1 \text{ kg of } C_4H_{10}O}{0.128 \text{ kg of } C_4H_{10}O \text{ per kg of carbon}} \times \frac{100}{40}$$
$$= 939.5 \text{ kg of carbon}$$

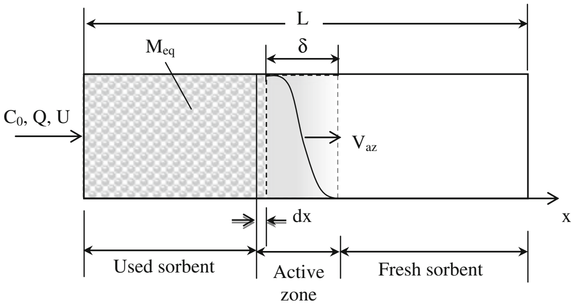
5.1.4 Adsorption Wave

An adsorption wave is used to determine the kinetics of adsorption for an adsorbent column. Consider a gas stream passing through a column packed with adsorbent. The concentration of the adsorbate in the gas before cleaning is denoted as C_0. The adsorption process does not take place uniformly throughout the bed. When the polluted air stream passes through it, three different zones are developed as shown in Fig. 5.2. The dark area near the inlet of the column is the saturated adsorbent because it adsorbs most of the pollutant gas initially and becomes saturated. Immediately downstream is the area where adsorption is active. The remaining portion of the bed adsorbs little pollutant gas and it is considered fresh.

If we zoom in to the entire active zone, the concentration of the adsorbate at the entrance of the active zone can be assumed C_0 because it is adjacent to the saturation zone where there is no loss of adsorbate. In the active adsorption zone, the adsorbate concentration is essentially reduced from C_0 to zero in an S-shape. As more adsorbate enters the adsorption bed, the saturation zone grows longer and longer and it looks as if a wave is propagating within the column. The wave could be steep or quite flat, depending on various factors including the adsorption capacity of the adsorbent, the flow rate and the retention time of the gas stream.

The entire adsorbent bed is nearly saturated as the wave approaches the exit of the column. At this instant, the adsorbent column loses its function and the concentration of the adsorbate at the exit increases. This is referred to as the breakthrough point, or breakpoint. The breakthrough point can also be defined as the ratio of the outlet to inlet concentrations depending on the application and the

Fig. 5.2 Adsorption wave in a stationary adsorption column



emission limits set by emission standards. For many toxic chemicals, a measurable concentration at the exit, even if it is less than 1 % of the inlet concentration, can be defined as the breakthrough point.

The kinetics of adsorption wave can be analyzed as follows. Consider an adsorption column of length L with an adsorption wave width of δ. The concentration of the adsorbate in the gas stream is C_0 (in mass of adsorbate/volume of gas), and the load of the adsorbate in the saturated adsorbent is M_{eq} (in mass of adsorbate per mass of adsorbent). Within the active adsorption zone, the concentration C of adsorbate in the gas varies from C_0 to zero and the load of adsorbate in the adsorbent C_x varies from M_{eq} to zero. While gas moves through the column at a bulk face velocity of U, the saturation zone keeps growing as fresh adsorbent adsorbs the incoming adsorbate, resulting in propagation of active adsorption zone at a speed V_{az}. In practice, $U \gg V_{\mathrm{az}}$, therefore, the relative speed of the gas stream with respect to the active adsorption zone can be assumed as U.

During the process described above, the rate of adsorbate entering adsorbent column is equal to the rate of adsorbate adsorbed by the adsorbent if we ignore other mechanisms for gas separation or leaking. That is,

$$QC_0 = M_{\mathrm{eq}}(\rho_b A V_{\mathrm{az}}) \tag{5.10}$$

where Q = volumetric flow rate of the gas (m^3/s), C_0 = the incoming adsorbate concentration (kg/m^3), ρ_b = bulk density of the adsorbent (kg/m^3), A = cross-sectional area of the adsorption column (m^2), and M_{eq} = equilibrium loading with a unit of kg/kg.

The bulk density of the adsorbent depends on the packing density of the column and it is not the physical density of the adsorbent material itself. Usually the bulk density is much less than the real density of the material and it depends on the packing density.

The left-hand side of Eq. (5.10) stands for the mass flow rate (in kg/s) of the adsorbate into the column, and the term $(\rho_b A V_{\mathrm{az}})$ gives the mass rate of adsorbent used (kg/s). In an engineering practice where the specifications of the adsorption column and operation conditions are known, one can get the values of ρ_s, A, Q and C_0. M_{eq} is required in order to solve Eq. (5.10) for the wave speed V_{az}, and M_{eq} is usually determined experimentally and described using adsorption isotherm.

A simple manipulation of Eq. (5.10) leads to the expression of adsorption wave propagation speed,

$$V_{\mathrm{az}} = \frac{QC_0}{M_{\mathrm{eq}}(\rho_b A)} \tag{5.11}$$

The mathematical description of the relationship between M_{eq} and C_0 depends on the model introduced above or measured data. When using data in Table 5.4, we must pay attention to the units of C_0 and M_{eq}. In Eqs. (5.10) and (5.11) they are different from those of $M_{\mathrm{eq,g/100\,g}}$ and C_{ppmv} listed in Table 5.4. Correct unit conversion is necessary.

$$M_{\mathrm{eq}} = 0.01 M_{\mathrm{eq,g/100\,g}} \tag{5.12}$$

$$C_0 = 10^{-6} \rho_g C_{\mathrm{ppmv}} \tag{5.13}$$

where the factor of 10^{-6} converts adsorbate concentration from ppmv to $\left(\mathrm{m}^3 \text{ adsorbate per } \mathrm{m}^3 \text{ of gas}\right)$. ρ_g is not the density of the entire gas phase, but rather that of the adsorbate ($\mathrm{kg/m^3}$).

Example 5.2: Adsorption wave propagation speed calculation
Same as the parameters given in Example 5.1 above, in an automobile assembling shop, the concentration of n-butanol ($C_4H_{10}O$) in the room air is 5 ppmv. The density of n-butanol is 3.06 $\mathrm{kg/m^3}$ under standard condition. A carbon filter bed is used for air cleaning, and the airflow rate is 0.1 $\mathrm{m^3/s}$ through the bed. The activated carbon bed is manufactured in such a way that its bulk density of the activated carbon is 400 $\mathrm{kg/m^3}$. The cross-sectional area of the bed is 2 $\mathrm{m^2}$. Estimate the propagation speed of the adsorption wave.

Solution
From Example 5.1, we obtained

$$M_{\mathrm{eq,g/100\,g}} = 12.8\,(\text{gram of } \mathrm{C_4H_{10}O} \text{ per 100 gram of A.C.})$$

Unit conversion gives

$$M_{\mathrm{eq}} = 0.01 M_{\mathrm{eq,g/100\,g}} = 0.128(\text{kg VOC/kg AC})$$
$$C_0 = 10^{-6} \rho_g C_{\mathrm{ppmv}} = 10^{-6}(3.06) \times 5 = 1.53 \times 10^{-5}(\text{kg VOC/m}^3)$$

Then we can get the adsorption wave propagation speed as

$$\begin{aligned} V_{\mathrm{az}} &= \frac{QC_0}{M_{\mathrm{eq}} \rho_b A} \\ &= \frac{0.1(\mathrm{m^3/s}) \times 1.53 \times 10^{-5}\left(\text{kg VOC/m}^3\right)}{0.0128(\text{kg VOC/kg AC}) \times \left(400 \text{ kg AC/m}^3\right) \times 2(\mathrm{m^2})} \\ &= 0.01494 \times 10^{-6}(\mathrm{m/s}) = 0.0538(\mathrm{mm/h}) \end{aligned}$$

5.1.5 Breakthrough Time

With the known wave propagation speed, we can easily predict the operating time of a fresh column.

$$t_x = \frac{L - \delta}{V_{\mathrm{az}}} \tag{5.14}$$

where L is the length/height of the column and δ is the width of the adsorption wave (see Fig. 5.2). This is also called the breakthrough time. The lifetime of an adsorbent column bed before the breakthrough point can be estimated using this equation, when regeneration or replacement of adsorbent column is necessary in order to maintain an effective adsorption process.

Although δ can determined by the analysis of gas-solid mass transfer, no single model applies to all gas-solid systems. The exact wave width depends on the packing density, the activated carbon properties and incoming adsorbate concentration. There have been several models developed. One widely used model for breakthrough time t_x is the modified Wheeler equation [8, 14], which is for single adsorbate.

$$t_x = \frac{M_{\mathrm{eq}}}{QC_0}\left[W - \frac{\rho_b Q}{K_x}\ln\left(\frac{C_0}{C_x} - 1\right)\right] \tag{5.15}$$

where t_x = break through time (s), M_{eq} = adsorption capacity (kg/kg), C_0 = inlet concentration (kg/m^3), W = weight of the adsorbent (kg), ρ_b = bulk density of the packed adsorbent (kg/m^3), Q = gas phase volumetric flow rate (m^3/s), K_x = mass transfer rate coefficient (1/s), C_x = exit concentration (kg/m^3). This exit concentration is determined based on local emission standards or air quality requirement.

Note that the last term is related to the breakthrough efficiency, which is the column adsorption efficiency when breakthrough occurs.

$$\eta_x = 1 - \frac{C_x}{C_0} \tag{5.16}$$

Then the breakthrough time Eq. (5.15) can be described in terms of breakthrough efficiency as

$$t_x = \frac{M_{\mathrm{eq}}}{QC_0}\left[W - \frac{\rho_b Q}{K_x}\ln\left(\frac{\eta_x}{1 - \eta_x}\right)\right] \tag{5.17}$$

Example 5.3: Adsorption column breakthrough time

Continuing from Example 5.2 above, we obtained $M_{\mathrm{eq}} = 0.128(\text{kg VOC/kg AC})$, $C_0 = 1.53 \times 10^{-5}(\text{kg VOC/m}^3)$, $Q = 0.1(\text{m}^3/\text{s})$, $\rho_b = 400\,\text{kg AC/m}^3$. Now, the mass transfer coefficient of the adsorbent is $K_x = 20\,\text{s}^{-1}$. The cross-sectional area of the bed is given as 0.1 m^2. The designed adsorption efficiency is $\eta_x = 0.9$. That is, the breakthrough occurs when the outlet n-butanol concentration reaches 10 % of the inlet concentration. Determine the length of the bed if it is to be replaced every 2 months (assuming 60 days).

Solution

First we convert the unit of breakthrough time from months to seconds.

$$t_x = 60 \times 24 \times 3600\,\mathrm{s} = 5{,}184{,}000\,\mathrm{s}$$

From Eq. (5.17) we can get the weight of activated carbon in the filter as

$$\begin{aligned}
W &= \frac{QC_0t_x}{M_{\mathrm{eq}}} + \frac{\rho_b Q}{K_x}\ln\left(\frac{\eta_x}{1-\eta_x}\right)\\
&= \frac{0.1(\mathrm{m}^3/\mathrm{s}) \times (1.53 \times 10^{-5}\ \mathrm{kg/m}^3) \times \left(5.184 \times 10^6\ \mathrm{s}\right)}{0.128(\mathrm{kg/kg})}\\
&\quad + \frac{\left(400\ \mathrm{kg/m}^3\right) \times 0.1(\mathrm{m}^3/\mathrm{s})}{20\ \mathrm{s}^{-1}}\ln\left(\frac{0.9}{0.1}\right)\\
&= 61.965(\mathrm{kg}) + 4.39(\mathrm{kg}) = 66.3\ \mathrm{kg}
\end{aligned}$$

So, the required length of the filter bed is

$$L = \frac{W}{A\rho_b} = \frac{66.3\ \mathrm{kg}}{0.1\ \mathrm{m}^2 \times 400\ \mathrm{kg/m}^3} = 1.66\ \mathrm{m}$$

Breakthrough curves for binary mixtures on a solid adsorbent are more complicated than those for pure compounds. Mixed compounds compete for the same adsorption sites, weakly adsorbed compound may also be replaced with more strongly adsorbed compound. As a result, there may be more than one adsorption wave propagating in the adsorption column, the stronger one moves slower than the weaker one. More in-depth analysis can be found in the literature (e.g. [14]).

With the development of numerous similar theories for adsorption phenomena, few of them generally agreed with a wide range of experimental data. The measurements have shown that increasing the partial pressure of the adsorbate at a given temperature results in increase in adsorption capacity of the adsorbent, while an increase of the temperature of the adsorbate in the air at a certain partial pressure results in decrease in adsorption capacity. Therefore, heating can regenerate many saturated adsorbent. In addition, gases or vapors with heavier molecules can be more effectively adsorbed than the lighter ones.

5.1.6 Regeneration of the Adsorbent

When breakthrough occurs, adsorbent in an adsorption column can be regenerated instead of being disposed of. Regeneration of an adsorbent is a process that drives the adsorbate out of the saturated adsorbent, which can be referred to as desorption. It is done by passing the regeneration fluid, which often is steam or hot air, through the saturated adsorbent column.

As a result, there is a desorption wave in the column but it propagates in the opposite direction of the adsorption wave. The propagation speed of desorption wave can be determined by similar analysis. Readers are referred to the literature for in-depth analysis.

5.2 Absorption

Absorption is a volumetric process where gases penetrate into the structure of the solid or liquid, most likely by diffusion. Similar to the classification of adsorption, absorption can also be classified into physioabsorption and chemioabsorption. A physioabsorption involves negligible chemical reactions, for example solution of oxygen in water. The physical absorption process involves a mass transfer by means of molecular and turbulent diffusion governed by Henry's law (see Sect. 2.3.1). A chemioabsorption process results in new substances from the chemical reactions. For example, when a flue gas passes through a water spray, the droplets will capture the gaseous SO_2 molecules by absorption. Captured SO_2 molecules dissolve in the body of a water droplet and produces H_2SO_3.

An absorption-based process is also commonly referred to as wet scrubbing. However, one has to be careful that wet scrubbing of particles is based on the principles of impaction and coagulation, whereas wet scrubbing of gaseous pollutants is based on absorption. In this section, we explain the basics using counter flow absorption tower.

5.2.1 *Counter Flow Absorption Tower*

Consider a single-stage counter flow gas-liquid system as shown in Fig. 5.3. The gas enters from the bottom and exits at the top; the liquid enters from the top and

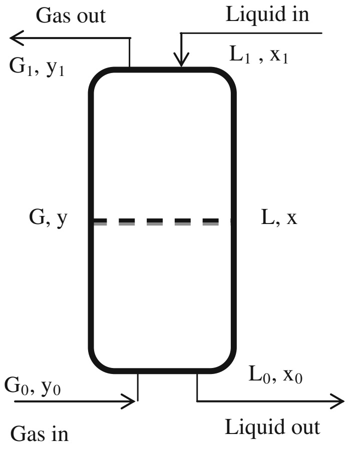


Fig. 5.3 Schematic diagram of a counter-flow absorption tower

exits at the bottom. At any cross section within the absorption tower, all the molecules removed from the gas phase enter the liquid phase, then the mass balance at any cross section within the tower gives

$$\mathrm{d}(Gy) = \mathrm{d}(Lx) \tag{5.18}$$

where L and G are the mole flow rates of the liquid and the gas, respectively (mole/s). y and x are mole fractions of the target pollutant in gas and liquid, respectively. Note that both the gas phase and liquid phase mole flow rates (G and L) are variables within the tower, because gas molecules leave the gas phase enter the liquid phase.

Integration of Eq. (5.18) from any point to top (1) leads to

$$yG - y_1 G_1 = xL - x_1 L_1 \tag{5.19}$$

The gas phase contains the adsorbate molecules and the inert carrier gas (mostly air), and their mole fractions are, respectively, y and $1 - y$. The liquid phase also contains inert liquid and the pollutants absorbed from the gas phase, and their mole fractions are, x and $1 - x$, respectively. The liquid phase without contamination is called solute free liquid.

Denote the mole flow rates of the carrier gas and solute fee liquid as $\bar{G}$ and $\bar{L}$, respectively, which remain constant throughout the process.

$$G = \frac{\bar{G}}{1 - y} \qquad L = \frac{\bar{L}}{1 - x} \tag{5.20}$$

In reality, there may be some evaporation of liquid phase, and extra liquid is added as make up liquid to keep the mass balance, but we have to ignore this in the following analysis. With Eq. (5.20), Eq. (5.19) can be rewritten in terms of $\bar{G}$ and $\bar{L}$ as

$$\left(\frac{y}{1 - y}\right)\bar{G} + \left(\frac{x_1}{1 - x_1}\right)\bar{L} = \left(\frac{x}{1 - x}\right)\bar{L} + \left(\frac{y_1}{1 - y_1}\right)\bar{G} \tag{5.21}$$

Applying this equation to the entire tower from bottom (0) to top (1) leads to:

$$\left(\frac{y_0}{1 - y_0} - \frac{y_1}{1 - y_1}\right)\bar{G} = \left(\frac{x_0}{1 - x_0} - \frac{x_1}{1 - x_1}\right)\bar{L} \tag{5.22}$$

If we define the mole ratio of target gas to that of the corresponding fluid as

$$X = \frac{x}{1 - x} \qquad Y = \frac{y}{1 - y} \tag{5.23}$$

then the mass balance Eqs. (5.21) and (5.22) above can be simplified as

$$(Y - Y_1)\bar{G} = (X - X_1)\bar{L} \tag{5.24}$$

$$(Y_0 - Y_1)\bar{G} = (X_0 - X_1)\bar{L} \tag{5.25}$$

where *Y* and *X* are the mole ratio of pollutant to the corresponding fluid with unit of (mole of pollutant per mole of solute free fluid). They are different from *y* and *x*. *y* and *x* must be less than one but *Y* and *X* can be any values, although most often they are also less than one.

Equation (5.25) can be rewritten as

$$\frac{\bar{L}}{\bar{G}} = \frac{(Y_0 - Y_1)}{(X_0 - X_1)} \tag{5.26}$$

The term on the left-hand side is called liquid to gas mole flow rate ratio. In a design process, the mole ratio of the pollutant in gas phase, Y_0, the carrier gas flow rate $\bar{G}$ are likely known from the source of the air emission. The mole ratio of the pollutant in liquid phase at the inlet, X_1, is usually provided by the solvent supplier. The two unknown parameters are the mole ratio of pollutant in the liquid phase X_0 and that is determined by the mole flow rate of the solute-free liquid ($\bar{L}$).

Example 5.4: Liquid to gas ratio in absorption tower

A mixture of air and H_2S is forced to pass through a single-stage counter flow water absorption scrubber. The inlet mole fraction of H_2S in air is 50 ppmv and outlet being 10 ppmv. Outlet H_2S in water is 20 ppmv. The total pure air flow rate into the scrubber is 80 mol/s. What is the pure water flow rate into the scrubber?

Solution

From the problem description, we can get the following known parameters. For the gas phase, the incoming mole fraction of H_2S in the air is $y_0 = 50 \times 10^{-6}$ (mole H_2S/mole air) and the exiting mole fraction of H_2S in the air is $y_1 = 10 \times 10^{-6}$ (mole H_2S/mole air). Then we can get the corresponding mole ratios as

$$\text{Bottom/gas:} Y_0 = \frac{y_0}{1 - y_0} = \frac{50 \times 10^{-6}}{1 - 50 \times 10^{-6}} \approx 50 \times 10^{-6}$$

$$\text{Top/gas:} Y_1 = \frac{y_1}{1 - y_1} = \frac{10 \times 10^{-6}}{1 - 10 \times 10^{-6}} \approx 10 \times 10^{-6}$$

Similarly for the liquid phase, the mole fraction of H_2S in the incoming liquid phase is $x_1 = 0$ (mole H_2S/mole water) and exiting pollutant mole fraction in the liquid is $x_0 = 20 \times 10^{-6}$ (mole H_2S/mole water). The corresponding mole ratios are

$$X_0 = \frac{x_0}{1 - x_0} = \frac{20 \times 10^{-6}}{1 - 20 \times 10^{-6}} \approx 20 \times 10^{-6}$$
$$X_1 = \frac{x_1}{1 - x_1} = 0$$

Substitute the mole ratios and the carrier gas mole flow rate of $\bar{G}$ = 80 (mole/s) into the mass balance Eq. (5.26), and we have:

$$\frac{\bar{L}}{\bar{G}} = \frac{(Y_0 - Y_1)}{(X_0 - X_1)} \to \frac{\bar{L}}{80} = \frac{(50 - 10)}{(20 - 0)} = 2$$

So the solute-free water flow rate is 160 mol/s. Assuming water molar weight of 18 g/mole, we can calculate the water mass flow rate and it is 2.88 kg/s.

This example also shows quantitatively that for the cases with very low mole fractions of y and x, $1 - y \approx 1$ and $1 - x \approx 1$, then $X = x$ and $Y = y$. Then the mass balance Eq. (5.22) becomes

$$\frac{\bar{L}}{\bar{G}} = \frac{y_0 - y_1}{x_0 - x_1} \quad (\text{for } x \ll 1, y \ll 1) \tag{5.27}$$

5.2.2 Absorption Equilibrium Line and Operating Line

Equation (5.24) can be rewritten as

$$Y = \frac{\bar{L}}{\bar{G}}(X - X_1) + Y_1 \tag{5.28}$$

This equation implies that the gas phase mole ratio Y is a linear function of liquid phase mole ratio X if $\frac{\bar{L}}{\bar{G}}$, X_1, and Y_1 are constant. Therefore, it describes the relationship between the gas phase mole ratio and liquid phase mole ratio at any elevation in an operating tower. If we plot a Y versus X in a figure, it is thereby called the absorption operating line.

5.2.2.1 Absorption Equilibrium Line

A special operating line is *equilibrium line*. If the absorption tower operates in such a manner that the gas-liquid system at any elevation reaches equilibrium, then for any gas mole ratio Y, there is a corresponding equilibrium liquid mole ratio X*. And Y can be related to X* according to the Henry's law. The corresponding linear function defines the absorption equilibrium line.

The equilibrium line can be determined as follows. Equation (5.23) gives

$$x = X/(1+X) \text{ and } y = Y/(1+Y)$$

Substituting them into the Henry's law Eq. (2.76)

$$Py = Hx$$

We can describe the Henry's Law in terms of the mole ratios (X and Y) instead of the mole fractions (x and y),

$$\frac{Y}{1+Y} = \frac{H}{P}\left(\frac{X}{1+X}\right) \tag{5.29}$$

Manipulation of the equation gives the mole ratio in liquid phase as

$$Y = \frac{H}{P}\left(\frac{1+Y}{1+X}\right)X \tag{5.30}$$

For most air emission control by absorption, the concentration of the target gas in air is usually very low, which means $X \ll 1$; $Y \ll 1$. With this critical assumption, which is justified in most applications, Eq. (5.30) can be simplified as

$$Y = \frac{H}{P}X \tag{5.31}$$

In order to differentiate the equilibrium line from the operating line, we put forward two more terms, hypothetical or equilibrium mole ratio: Y* and X*. They are defined as

$$Y^* = \frac{H}{P}X \quad Y = \frac{H}{P}X^* \tag{5.32}$$

A line can be drawn from this equation on X-Y axes. Since this equation is derived from the equilibrium assumption, it is called equilibrium line (see Fig. 5.4). The slope of this line is

$$m = \frac{H(1+Y)}{P(1+X)} \approx \frac{H}{P} \tag{5.33}$$

5.2.2.2 Absorption Operating Line

In operating an absorption tower in engineering practice, the equilibrium between gas and liquid phase cannot be established because of the short residence time when they encounter each other. Therefore, for a given gas mole ratio Y, the corresponding liquid mole ratio X should be always less than the equilibrium mole ratio.

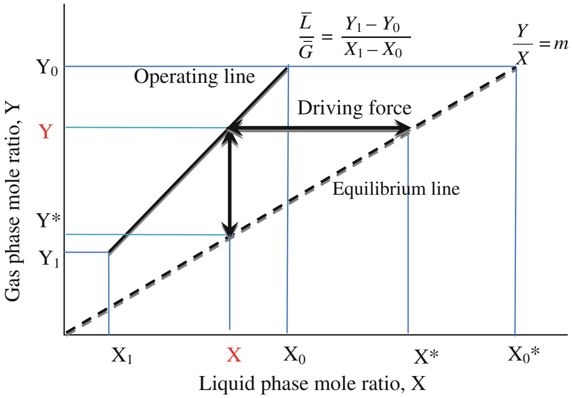


Fig. 5.4 Absorption equilibrium line and operating line

$$Y = \frac{\bar{L}}{\bar{G}}(X - X_1) + Y_1 \tag{5.34}$$

In Fig. 5.4, we also can see the driving force of absorption is the gas phase mole ratio difference Y-Y* or liquid phase mole ratio difference X*-X. Note that (X_1, Y_1) are usually fixed in Fig. 5.4.

5.2.2.3 Absorption Minimum Operating Line

Depending on the engineering design, the driving force of the absorption can be changed by adjusting the operating line. The slope of each line is the corresponding liquid to gas ratio $\frac{\bar{L}}{\bar{G}}$. As seen in Fig. 5.5, there is a minimum operating line where equilibrium is reached at the bottom of the tower, and it corresponds to the lowest operating line right above the equilibrium line in Fig. 5.5. A practical term is the minimum liquid to gas

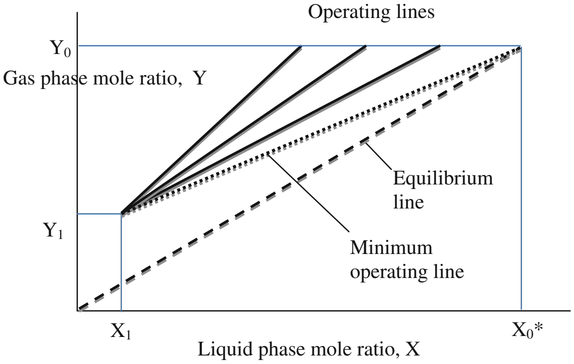


Fig. 5.5 Absorption equilibrium line and different operating lines

ratio defined by the minimum operating line. Once it is determined, the actual operating liquid-to-gas ratio is set higher than this minimum ratio.

The minimum liquid-to-gas flow ratio can therefore be determined using the above Eq. (5.26) based on the equilibrium value of X_0^*,

$$\left(\frac{\bar{L}}{\bar{G}}\right)_{\min} = \frac{Y_0 - Y_1}{X_0^* - X_1} \tag{5.35}$$

$$X_0^* = \frac{x_0^*}{1 - x_0^*} \tag{5.36}$$

and X_0^* would be the maximum possible mole ratio of the target gas in the liquid phase if it were allowed to come to equilibrium with the gas entering the tower in the gas phase. x_0^* can be taken from the equilibrium line with the inlet gas inlet y_0 or determined using Eq. (5.37).

$$x_0^* = Py_0/H \tag{5.37}$$

Example 5.5: Absorption minimum operating line

A mixture of air and H_2S is force to pass through a single-stage counter flow water absorption scrubber. The inlet mole fraction of H_2S in air is 50 ppmv. The total gas flow rate into the scrubber is 80 mol/s and the pure water flow rate into the scrubber is 10 mol/s. Assuming that the gas-water system is at equilibrium state at 30 °C, and the atmospheric pressure is 101,325 Pa. Find the mole fraction of H_2S in gas phase at the exit. Assume that the system within the tower is air-H_2S for gas and water-H_2S for liquid phases.

Solution

Since the air pollutant concentration in the air is very low and the consequent concentration in the liquid phase should also be very low, the simplified mass balance equation can be used to solve this problem. Substitute $\bar{L}$ = 10 mol/s, $\bar{G}$ = 80 mol/s, x_1 = 0 mol H_2S/mole water, y_0 = 0.00005 mol H_2S/mole air into the simplified mass balance equation (5.27) gives

$$y_1 = 5 \times 10^{-5} - \frac{10}{80}(x_0 - 0)$$

The inlet mole fraction of H_2S in the air can be determined from the assumption of equilibrium state. Applying Henry's law to the equilibrium state to the bottom of the system gives

$$Py_0 = Hx_0$$

where the Henry's Law constant can be found from Table 2.4 as H = 609 × 1.1 × 10^5 Pa/mole fraction in water at 30 °C and P = 1.013 × 10^5 Pa with y_0 = 50 × 10^{-6}, x_0 can be determined as

$$x_0 = 8.32 \times 10^{-8} \quad \text{(mole of H}_2\text{S/mole of water)}$$

Then the outlet H_2S mole fraction in the air is

$$y_1 \approx 50 \text{ ppmv} = y_0$$

This result indicates that the wet scrubber that operates at equilibrium governed by Henry's law is basically useless in absorbing the air pollutant into the liquid phase. This is calculated based on the assumption of equilibrium at the bottom of the system. This actually makes sense because that is what equilibrium implies—no net mass transfer between gas and liquid phases. Practically speaking, this system works along the minimum operating line, but it is not that effective in gas absorption. In practice, the operating line must be different from this line.

Example 5.6: Absorption operating line

A packed bed wet scrubber is designed to remove high concentration SO_2 from the exhaust of a sulfuric acid plant. It is expected to achieve a removal efficiency of 95 %. The incoming SO_2 concentration is 10 %. Pure water is used as an absorbent and the solute-free liquid to gas ratio is 1.5 times the minimum ratio. Assume that the system operates at an average temperature of 30 °C and 1 atm. The equilibrium data for SO_2 in air and water at this temperature are as follows [18]

Partial pressure p_{SO_2} (mmHg)	0.6	1.7	4.7	8.1	11.8	19.7	36	52	79
SO_2 concentration in water c_{SO_2} (g SO_2/100 g water)	0.02	0.05	0.1	0.15	0.2	0.3	0.5	0.7	1

Plot the equilibrium line, the minimum operating line and the operating line in the same figure.

Solution

To determine the equilibrium line Y versus X, we need to determine the mole fraction changes in liquid and gas phases in the scrubber.

Step 1: Determine the equilibrium line by the mole fraction in gas by Dalton's law, Eq. (2.40) and liquid phases, respectively

$$y = y_{SO_2} = \frac{P_{SO_2}}{P}$$

$$x = x_{SO_2} = \frac{\dfrac{c_{SO_2}}{64 \text{ g/mole}}}{\dfrac{c_{SO_2}}{64 \text{ g/mole}} + \dfrac{100 \text{ g}}{18 \text{ g/mole}}}$$

Table 5.5 SO_2 solubility data at 30 °C and 1 atm

Partial pressure	Solubility	SO_2 mole fraction in gas	Mole fraction in liquid	Mole ratio	Mole ratio
p_{SO_2} (mmHg)	c_{SO_2} (g SO_2/100 g water)	$y = \frac{p_{SO_2}}{760\ \text{mmHg}}$	x_{SO_2}	$Y = \frac{y}{1-y}$	$X = \frac{x}{1-x}$
0.6	0.02	0.000789	0.00005625	0.00079	0.000056
1.7	0.05	0.00224	0.00014	0.00224	0.00014
4.7	0.1	0.00618	0.000281	0.00622	0.000281
8.1	0.15	0.01066	0.000422	0.01077	0.000422
11.8	0.2	0.0155	0.000562	0.01577	0.000563
19.7	0.3	0.0259	0.000843	0.0266	0.000844
36	0.5	0.04737	0.00140	0.0497	0.00141
52	0.7	0.06841	0.001965	0.07345	0.00197
79	1	**0.104**	**0.0028**	0.1160	0.00281

where 64 and 18 are the molar weights of SO_2 and water, respectively, with the unit of g/mole. Using these equations, we can calculate the SO_2 mole fractions in gas phase and liquid phase (Table 5.5).

And the corresponding the equilibrium line by linear regress is

$$Y = 41.69X - 0.006 \quad \left(R^2 = 0.994\right) \tag{1}$$

The equilibrium line Y versus X is plotted in Fig. 5.6.

We also can get the linear regression of y versus x as

$$y = 37.747x - 0.0043 \quad \left(R^2 = 0.998\right) \tag{2}$$

The minimum water flow rate can be determined using Eq. (5.21) with the inlet SO_2 mol fraction $y_0 = 10\ \% = 0.10$, and exit SO_2 mol fraction $y_1 = 0.10 \times (1–95\ \%) = 0.005$. In the pure water entering the top of the tower, $x_1 = 0$, and at the bottom of tower, the SO_2 mol fraction in the air is $y_0 = 0.01$ and

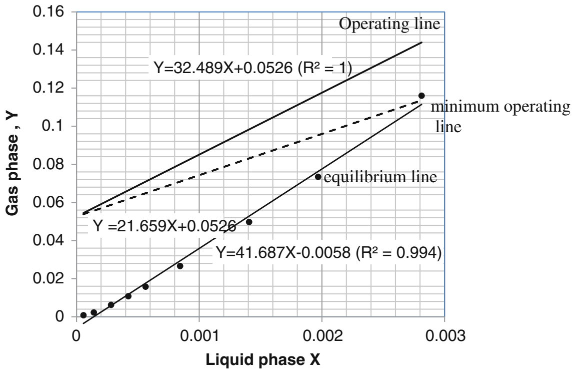


Fig. 5.6 SO_2-equilibrum-line and operation line

the corresponding equilibrium mole fraction in the water exiting the bottom of the tower is determined from the equilibrium line, Eq. (2)

$$x_0^* = 0.0028$$

Then the corresponding minimum liquid-to-gas ratio is determined by substituting these values into Eq. (5.35), together with $x_1 = 0$, $y_1 = 0.05$,

$$\left(\frac{\bar{L}}{\bar{G}}\right)_{\min} = \frac{\frac{y_0}{1-y_0} - \frac{y_1}{1-y_1}}{\frac{x_0^*}{1-x_0^*} - \frac{x_1}{1-x_1}} = 21.67$$

Then the minimum operating line can be determined using Eq. (5.21)

$$\left(\frac{y}{1-y}\right) + \left(\frac{x_1}{1-x_1}\right)\left(\frac{\bar{L}}{\bar{G}}\right)_{\min} = \left(\frac{x}{1-x}\right)\left(\frac{\bar{L}}{\bar{G}}\right)_{\min} + \left(\frac{y_1}{1-y_1}\right)$$

In Fig. 5.6, the minimum operating line is defined as

$$Y = 21.66X + 0.053 \tag{3}$$

The actual operating liquid to gas ratio is 1.5 times of this liquid flow rate

$$\frac{\bar{L}}{\bar{G}} = 1.5 \times \left(\frac{\bar{L}}{\bar{G}}\right)_{\min} = 32.49$$

Then we can determine the actual operating line using Eq. (5.21) again, with $x_1 = 0$, and $y_1 = 0.05$, and $\left(\frac{\bar{L}}{\bar{G}}\right)_{\min} = 32.49$

$$\left(\frac{y}{1-y}\right) + \left(\frac{x_1}{1-x_1}\right)\left(\frac{\bar{L}}{\bar{G}}\right) = \left(\frac{x}{1-x}\right)\left(\frac{\bar{L}}{\bar{G}}\right) + \left(\frac{y_1}{1-y_1}\right)$$

Which leads to, in Fig. 5.6,

$$Y = 32.49 + 0.053 \tag{4}$$

All the three lines defined by Eqs. (1), (3) and (4) are shown in Fig. 5.6.

5.2.3 *Height of the Packed Absorption Tower*

Another engineering interest is the height of the tower, where the minimum liquid flow rate is known. Referring to the same schematic diagram in Fig. 5.3, and the

Table 5.6 Packing data (Adapted from Bhatia [2])

Packing type	Material	Nominal size (in.)	Area per volume (m^2/m^3)
Berl saddle 	Ceramic and porcelain	¼	899
		½	509
		1	259
		2	105
Intalox saddle 	Plastic	1	207
		2	108
		3	89
	Ceramic	¼	984
		½	623
		1	256
		2	118
Raschin ring 	Ceramic and porcelain	½	374
		1	190
		1½	118
		2	92
		3	62
Pall ring 	Metal	5/8 × 0.018 thick	341
		1½ × 0.03 thick	128
Tellerette 		1	180
		2	125
		3	98

two-film model (see Chap. 2), the mass transfer in the liquid phase within the elemental height, dz, in the tower is

$$d(Lx) = k_x(x_i - x)dA_i \tag{5.38}$$

where dA_i is the gas–liquid interfacial surface area over the height of dz, and it depends on the packing material property, a (m^2/m^3 of tower), which is the surface area per bulk volume in the tower.

Typical packing materials and the corresponding surface areas are summarized in Table 5.6 [2]. The packing materials are designed to maximize the gas-liquid interfacial area with low resistance to the flow. Nonetheless, these values are only for guide purpose only. Users are strongly recommended to get updated data from packing suppliers if needed.

Consider a tower with a cross-sectional area A_c filled with packing materials characterized with a (m^2/m^3). The interfacial surface area over the height of dz is

$$\mathrm{d}A_i = aA_c\mathrm{d}z \tag{5.39}$$

where A_c is the cross section area (m^2) of the tower that is normal to the flow direction. The liquid mole flow rate L (mole/s) is generally a variable and it is $L = \bar{L}/(1-x)$. Introducing this variable into Eq. (5.38) leads to

$$\mathrm{d}\left(\frac{x}{1-x}\right) = \frac{k_x}{\bar{L}}(x_i - x)aA_c\mathrm{d}z \tag{5.40}$$

It gives

$$\mathrm{d}z = \frac{\bar{L}}{k_x aA_c(x_i - x)}\mathrm{d}\left(\frac{x}{1-x}\right) = \frac{\bar{L}}{k_x aA_c(x_i - x)}\frac{\mathrm{d}x}{(1-x)^2} \tag{5.41}$$

Manipulation of the equation gives

$$\mathrm{d}z = \left(\frac{\bar{L}}{k_x aA_c}\right)\frac{\mathrm{d}x}{(x_i - x)(1-x)} \tag{5.42}$$

Integration of the above equation leads to the total height of the tower

$$Z = \int_{x_1}^{x_0}\left(\frac{\bar{L}}{k_x aA_c}\right)\frac{\mathrm{d}x}{(x_i - x)(1-x)} \tag{5.43}$$

Rigorously speaking, $\bar{L}/(k_x aA_c)$ is a variable in that the single phase mass transfer coefficients (k_x) increases as the liquid flows downward. For the simplicity of calculation, we can use the mean values of $\bar{L}/(k_x aA_c)$ and it can be treated as a constant. Then

$$Z = \frac{\bar{L}}{k_x aA_c}\int_{x_1}^{x_0}\frac{\mathrm{d}x}{(x_i - x)(1-x)} \tag{5.44}$$

When the total mass transfer coefficient K_x is available, we can use the equilibrium mole fraction x^*, for calculation

$$Z = \frac{\bar{L}}{K_x aA_c}\int_{x_1}^{x_0}\frac{\mathrm{d}x}{(x^* - x)(1-x)} \tag{5.45}$$

By similar analysis for the gas phase, we also can get

$$Z = \frac{\bar{G}}{k_y aA_c}\int_{y_1}^{y_0}\frac{\mathrm{d}y}{(y - y_i)(1-y)} \tag{5.46}$$

$$Z = \frac{\bar{G}}{K_y a A_c} \int_{y_1}^{y_0} \frac{\mathrm{d}y}{(y - y^*)(1 - y)} \tag{5.47}$$

Let us continue with our analysis by liquid phase. In design practice, the terms in front of the integration sign in Eq. (5.44) is often referred to as height of transfer unit (HTU) calculated using liquid phase mass transfer coefficient. For example, the HTU based on liquid phase mass transfer is

$$\mathrm{HTU}_x = \frac{\bar{L}}{k_x a A_c} \tag{5.48}$$

The corresponding term by integration in Eq. (5.44), is called number of transfer unit (NTU),

$$\mathrm{NTU}_x = \int_{x_1}^{x_0} \frac{\mathrm{d}x}{(x_i - x)(1 - x)} \tag{5.49}$$

By the same approach we can get the HTU_y and NTU_y for gas phase. They all can be described using the overall mass transfer coefficients K_x, K_y as well. Nonetheless, the packed tower height is

$$H = \mathrm{HTU} \times \mathrm{NTU} \tag{5.50}$$

5.2.3.1 Packed Tower Diameter and Flooding Velocity

Body diameter is another important parameter of a packed tower. It is mainly limited by the gas velocity at which liquid droplets become entrained in the exiting gas stream.

$$D = \left(\frac{4Q}{\pi \bar{u}_g}\right)^{1/2} \tag{5.51}$$

where the diameter D is in m, Q is the volumetric gas flow rate in (m^3/s) and $\bar{u}_g$ is the mean gas face speed in m/s. When the gas flow rate reaches a point that the liquid is held in the void spaces between the packing materials, the corresponding gas-to-liquid ratio is termed as **loading point**. A further increase in gas flow rate (or gas velocity) will prevent the liquid from moving downward causing the liquid to fill up the void spaces in the packing. As a result, the gas–liquid interface surface area drops substantially and thereby the absorption efficiency decreases dramatically. And, the pressure drop increases greatly too. This condition is referred to as flooding, and the corresponding gas velocity is called flooding velocity. As a typical engineering practice, the diameter of a packed tower should enable the operation at 50–75 % of the flooding velocity.

A common and relatively simple procedure for estimating flooding velocity and minimum column diameter is to use a generalized flooding and pressure drop correlation. One version of the flooding and pressure drop relationship for a packed tower is the Sherwood Chart [12]. Readers are referred to literature for in-depth understanding on this topic in engineering design of a packed bed wet scrubber.

5.2.4 Chemical Absorption

In many engineering applications, the resistance in the liquid phase mass transfer is reduced by converting the dissolved gas into other materials. This reduction in the solute concentration in the liquid allows more gases to be absorbed at a much lower consumption of the liquid absorbent. For example, base solvents are used for the capture of acidic gases. The most common acid gases include sulfur dioxide (SO_2), hydrogen chloride (HCl), and hydrogen fluoride (HF). Nitric oxides and carbon dioxide formed in most combustion processes are also mildly acidic. Common alkalis include lime, soda ash, and sodium hydroxide. Sodium hydroxide is usually fed in solution. One classic example is de-SO_2 by spray of limestone or sodium hydroxide. The alkali requirements are usually calculated based on the quantities of acidic gases captured and the molar ratios necessary for the corresponding chemical reactions.

Consider the packed-bed wet scrubber again and assume that the fresh liquid solvent contains little dissolved gas of concern. At steady state, the mass transfer rate (in mole/s) within the liquid phase is

$$N = k_x a V (x_i - x_{\mathrm{ss}}) \tag{5.52}$$

where V the total reactor volume (m^3) and aV together is the interfacial contact area for mass transfer (m^2); x and x_{ss} are the mole fraction of the target gas at gas–liquid interface and that in the bulk liquid at steady state, respectively.

The target gas transferred into the liquid is either physically stored in the liquid or consumed by chemical reactions:

$$N = \bar{L}\left(\frac{x_{\mathrm{ss}}}{1 - x_{\mathrm{ss}}}\right) + k x_{\mathrm{ss}} \tag{5.53}$$

Again $\bar{L}$ is the mole flow rate (in mole/s) of the solute free liquid entering the tower. k (mole/s) is the chemical reaction coefficient corresponding to x_{ss}. When k is available based on the mass concentration c_{ss} rather than x_{ss}, a conversion between units is needed. The first term on the right-hand side of Eq. (5.53) stands for amount of physically dissolved gas; the last term for chemically absorbed gas.

Combine Eq. (5.52) and (5.53), we have:

$$N = k_x aV(x_i - x_{ss}) = \bar{L}\left(\frac{x_{ss}}{1 - x_{ss}}\right) + kx_{ss} \tag{5.54}$$

For cases where $x_{ss} \ll 1$, $1 - x_{ss} \approx 1$, then

$$k_y aV(y_i - y_{ss}) = \bar{L}y_{ss} + ky_{ss} \tag{5.55}$$

Solving this equation we can get the steady state concentration of the target gas in the liquid phase

$$\frac{x_{ss}}{x_i} = \frac{k_x aV}{k_x aV + \bar{L} + k} \tag{5.56}$$

This equation indicates that there are three factors that affect the steady state absorption ratio, which is defined as x_{ss}/x_i, and they are $k_x aV, \bar{L}$ and k. They stand for the effects of interfacial mass transfer, liquid flow rate, and kinetic rate of chemical reaction, respectively. Practically, it is challenging to determine the mole fraction at the interface, x_i, although it could be estimated by extensive theoretical analysis.

5.2.4.1 Enhanced Absorption Factor, e

A more practical approach to this problem is to employ an enhanced absorption factor, *e*. It is defined as the ratio of extra amount of target gases absorbed into the liquid by chemical absorption to that by physical absorptions.

$$e = \frac{x'}{x} \tag{5.57}$$

where x' stands for the extra absorption resulted from chemical absorption. The theoretical enhanced absorption factor could be very high, but the actual value depends on the design and operation of the tower. Then, with chemical absorption considered, Eq. (5.19) becomes

$$yG - y_1G_1 = (x + x')L - x_1L_1 = x(1 + e)L - x_1L_1 \tag{5.58}$$

It indicates that the amount of liquid flow rate is decreased by a factor of $(1 + e)$. Then all results obtained by the analysis for physical absorption can be applied to chemical absorption, by multiply $\bar{L}$ with a factor of $(1 + e)$. For example, Eq. (5.21) leads to

$$\frac{y}{1-y} - \frac{y_1}{1-y_1} = \left(\frac{x}{1-x} - \frac{x_1}{1-x_1}\right)\left(\frac{\bar{L}}{\bar{G}}\right)(1+\mathrm{e}) \tag{5.59}$$

This equation also indicates that the amount of liquid to gas ratio is reduced by enhanced chemical absorption.

5.3 Practice Problems

1. The concentration of acetone (C_3H_6O) in a machine shop is 3 ppmv. The density of acetone vapor is 2.01 kg/m^3 under standard conditions. A carbon filter bed is used for air cleaning. The airflow rate through the filter is 0.05 m^3/s. Determine

    a. The adsorption capacity of the activated carbon filter using Yaws data (1995).
    b. The total amount of carbon needed for the bed, assuming the working adsorption capacity is 75 % of the saturated adsorption and the bed service life is 1 year.

2. In a machine shop, the concentration of acetone (C_3H_6O) in the room air is 0.00001 kg/m^3. An activated carbon filter is used in an air recirculation system to remove the acetone. The bulk density of the activated carbon is 400 kg/m$^{3\cdot}$ The airflow rate of the recirculation system is 20 l/s. The cross-sectional area of the bed is 1.5 m^2. Determine

    a. The speed of the adsorption wave
    b. The length of the bed if the bed is to be replaced every 30 days.

3. A carbon adsorption unit is designed to control the emission from an air stream having 250 ppmv of toluene flowing through the bed at a rate of 1,500 m^3/min. The process works 24 h/day at 27 °C temperature and 1 atm pressure. Assume the working capacity of the carbon is 0.15 kg toluene/kg of carbon. Determine the amount of carbon needed in all beds of a 4-bed adsorber if two beds are online for 4 h and then regenerated while the other two working.
4. A carbon adsorption unit is designed to control the emission from an air stream having 250 ppmv of toluene is flowing through the bed at a rate of 1,500 m^3/min. Calculate the cross sectional area of a bed if maximum allowable superficial velocity through the bed is 20 m/min.
5. A carbon adsorption unit is designed to control the emission from an air stream having 2,500 ppmv of ethylene glycol vapor is flowing through the bed at a rate of 1,500 m^3/min at a temperature of 27 °C and pressure of 1 atm. Calculate the working adsorption capacity of the carbon. Assume that the working adsorption capacity of the bed is 50 % of the adsorption capacity, and that the bed is filled

with 200 kg of activated carbon. The expected breakthrough efficiency is 90 %. Estimate its breakthrough time. Assume $K_x = 20\ \mathrm{s}^{-1}$ and packing density of 400 kg/m^3.

6. An activated carbon column is used to remove tribromomethane (2.89 g/cm^3) from the air at standard condition. The mass flow rate of air is 2.5 kg/s and the concentration of the pollutant in the inlet air stream is 0.0025 kg/m^3. The bulk density of the activated carbon is 500 kg/m^3, and the mass transfer coefficient of the adsorbent $K_x = 25\ \mathrm{s}^{-1}$. The adsorption bed is 2 m deep and 1.5 m^2 in cross-sectional area. The designed adsorption efficiency is $\eta_x = 0.95$. That is, the breakthrough point of the bed is considered to be when the outlet concentration reaches 5 % of the inlet concentration. Estimate the life time of this column.
7. A packed bed is designed to remove SO_2 by pure water absorption from a sulfuric acid plant. The incoming SO_2 concentration is 10 %. The water flow rate is 1.5 times the minimum water flow rate and the inert gas flow rate $\bar{G}$ = 500 kg/hr. The tower operates at an average temperature of 30 °C and 1 atm. The equilibrium data for SO_2 in air and water at this temperature.

Partial pressure p_{SO_2} (mmHg)	Solubility c_{SO_2} (g SO_2/100 g water)
0.6	0.02
1.7	0.05
4.7	0.10
8.1	0.15
11.8	0.20
19.7	0.30
36.0	0.50
52.0	0.70
79.0	1.00

If the corresponding mass transfer coefficients are

$$k_y a = 0.6634 L^{0.82}$$

$$k_x a = 0.09944 L^{0.25} G^{0.70}$$

where L and G are the liquid and gas flow rates in kg/(m^{2}h)

(a) determine minimum water flow rate,
(b) the equilibrium line,
(c) the operating line is the same figure,
(d) the gas phase mass transfer coefficient at the gas inlet,
(e) the gas phase mass transfer coefficient at the gas outlet,
(f) the liquid phase mass transfer coefficient at the liquid inlet,
(g) the liquid phase mass transfer coefficient at the liquid outlet.

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