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Air and Steam Stripping  
of Toxic Pollutants  
Volume I

by

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## SUMMARY

A compilation has been made showing the Henry's Law constant (H) as a function of temperature for all the organic pollutants on the toxic pollutant list. Henry's Law is

$$\frac{(\text{concentration in the vapor})(\text{total pressure})}{(\text{concentration in water solution})(H)} =$$

so that H is a measure of the apparent vapor pressure over a solution in water. For poorly soluble compounds the water molecules try to expel the organic molecules and H is much higher than the vapor pressure over the pure organic. The ratio (H/vapor pressure) is called the activity coefficient. The activity coefficient is inversely proportional to solubility for poorly soluble compounds and often has a value in the thousands or higher.

Most values of H have been determined from data on the effect of temperature on vapor pressure and from a knowledge of the solubility at one temperature. The solubility has been converted to an activity coefficient and the activity coefficient has been extrapolated to other temperatures. This procedure is believed to be the most reliable available. When H has been measured at one temperature it is still the activity coefficient, and not H, which has been extrapolated to other temperatures.

For the few toxic pollutants which are miscible with water the activity coefficient has been estimated from the vapor-liquid equilibrium data or from the azeotrope data (azeotropes are common) using the technique of van Laar.

We believe the estimates of H to be reasonably satisfactory for all except 33 of the 186 listed pollutants.

A brief development of the theory of stripping is given with the intent of classifying pollutants by the ease with which they can be stripped. A classification proved possible and will be found on Table 5-2 which is reproduced at the end of this summary. Compounds which are "very easily stripped" can be reduced to about 1/1,000th of the feed concentration by low vapor rates in columns which are quite short (5 to 10 ft), rather like small cooling towers. Sixty-eight of the 186 listed pollutants are very easily stripped. "Intermediate" and "difficult to strip" compounds may require columns up to twenty times as high and will also need high steam

or air rates. "Very easily stripped" compounds have a half life in a still body of water on the order of 12 hours.

We compared air and steam stripping at vapor rates which gave approximately the same cost for the vapor. Air rates were taken at about eight times the steam rate. On this basis most compounds can be stripped as easily with air as with steam because the Henry's Law constants tend to be multiplied by about eight when the temperature is raised from 20°C to 100°C. In general air stripping will be used when the contaminant can be released to the atmosphere and steam stripping will be used when the contaminant must be recovered.

When air is the stripping vapor, water will also evaporate and the water stream will cool down which decreases  $H$ . Procedures for calculation are given. It is suggested that a good control is to add steam to the air to saturate it, particularly on cold, dry winter days.

A brief discussion on available equipment and on the comparison of predictive calculations to stripping data at low concentration. As expected and supported by predictive calculations, most stripping data indicated significant removal of compounds with high Henry's Law Constant ( $H @ 100^\circ\text{C} > 20 \text{ atm}$ ). Deviations from this behavior were observed for certain compounds.

In case of packed towers stripping a waste stream consisting of compounds with Henry's Law Constant higher than 100 atm, the height of packing or the removal efficiency was found to be nearly independent of the magnitude of Henry's Law Constants. Liquid-phase resistance (diffusivity) was found to be affecting the performance. Developing better contacting devices in terms of reducing liquid-phase resistance through more efficient packing and better liquid distribution in plate columns seems to be the probable solution to improving the performance of strippers.

Available data on stripping and stripping equipment is so limited that meaningful comparisons between predictive calculations and operating data are very difficult to make, particularly when there is so much uncertainty in making on-site analyses of organic compounds at low concentrations.

Table 5-2 TOXIC POLLUTANTS CLASSIFIED BY EASE OF STRIPPING

Very easily stripped

H(100°C) > 100 atm

H(20°C) > 13 atm

5-4 <sup>+</sup>	2-Chloroethyl vinyl ether
7-13	Triethylamine
9-1	Benzene
9-2	Chlorobenzene
9-3	1,2-Dichlorobenzene
9-4	1,3-Dichlorobenzene_____
9-5	1,4-Dichlorobenzene
9-6	1,2,4-Trichlorobenzene
9-7	Hexachlorobenzene
9-8	Ethylbenzene
9-10	Toluene
9-15	Benzyl chloride
9-16	Styrene
9-18	Xylenes
10-1	2-Chloronaphthalene
**	10-3 Benzo(b)fluoranthene
**	10-4 Benzo(k)fluoranthene
**	10-5 Benzo(a)pyrene
	10-9 Acenaphthene
**	10-12 Chrysene
**	10-13 Fluoranthene
	10-15 Naphthalene
	10-17 Pyrene

+ the left hand column are the code numbers used in the Treatability Manual and in Appendix 3.

\*\* probably, but data is poor

(very easily stripped - continued)

11-1 Aroclor 1016  
11-2 Aroclor 1221  
11-3 Aroclor 1232  
11-4 Aroclor 1242  
11-5 Aroclor 1248  
11-6 Aroclor 1254  
11-7 Aroclor 1260  
12-1 Methyl chloride  
12-2 Methylene chloride  
12-3 Chloroform  
12-4 Carbon tetrachloride  
12-5 Chloroethane  
12-6 1,1-Dichloroethane  
12-7 1,2-Dichloroethane  
12-8 1,1,1-Trichloroethane  
12-9 1,1,2-Trichloroethane  
12-10 1,1,2,2-Tetrachloroethane  
12-11 Hexachloroethane  
12-12 Vinyl chloride  
12-13 1,2-Dichloropropane  
12-14 1,3-Dichloropropene  
12-15 Hexachlorobutadiene  
12-16 Hexachlorocyclopentadiene  
12-17 Methyl bromide  
12-18 Dichlorobromomethane  
12-19 Chlorodibromomethane  
12-20 Bromoform  
12-21 Dichlorodifluoromethane  
12-22 Trichlorofluoromethane  
12-23 Trichloroethylene

(very easily stripped - continued)

- 12-24 1,1-Dichloroethylene
- 12-25 1,2-Trans-dichloroethylene
- 12-26 Tetrachloroethylene
- 12-27 Allyl chloride
- 12-30 Ethylene dibromide
- 13-20 Heptachlor
- 13-25 Toxaphene
- \*\* 13-37 Isoprene
- 13-46 Carbon disulfide
- 14-4 Amyl acetate
- 14-5 n-Butyl acid
- 14-13 Vinyl acetate
- 15-1 Methyl mercaptan
- 15-3 Cyclohexane

Easily stripped

H(100°C) 20 to 100 atm.

H(20°C) 2 to 13 atm.

- 5-3 Bis(2-chloroisopropyl) ether
- 7-7 Acrylonitrile
- 9-19 Nitrotoluene
- 10-10 Acenaphthylene
- 10-14 Fluorene
- 10-16 Phenanthrene
- 13-8 Aldrin
- 13-9 Dieldrin
- 13-24 Chlordane
- \*\* 13-26 Captan
- 14-1 Acetaldehyde
- \*\* 14-16 Acrolein
- 14-18 Propylene oxide

\*\* probably, but data is poor



Intermediate

H(100°C) 8 to 20 atm.

H(20°C) 1 to 2 atm.

5-2. Bis(2-chloroethyl) ether

8-5 Pentachlorophenol

8-6 2-Nitrophenol

9-9 Nitrobenzene

9-11 2,4-Dinitrotoluene

9-12 2,6-Dinitrotoluene

10-11 Anthracene

12-31 Epichlorohydrin

\*\* 13-12 4,4'-DDD

13-21 Heptachlor epoxide

Difficult to strip

H(100°C) 4 to 8 atm..

H(20°C) 0.5 to 1 atm.

\* 8-2 2-chlorophenol

\* 8-3 2,4-Dichlorophenol

\* 8-4 2,4,6-Trichlorophenol

14-15 Crotonaldehyde

15-4 Isophorone

\* this is for air; a higher category for steam

\*\* probably, but data is poor

Very difficult to strip

H(100°C) 2 to 4 atm.

- 6-2 Diethyl phthalate
- 8-1 Phenol
- \* 8-10 2,4-Dimethylphenol
- 8-13 4,6-Dinitro-o-cresol
- 8-14 Cresol
- \* 9-17 Quinoline
- \* 14-3 Allyl alcohol

Cannot be stripped

- 5-7 Bis(2-chloroethoxy) methane
- 6-1 Dimethyl phthalate
- 7-10 Ethylenediamine
- 8-7 4-Nitrophenol
- 8-8 2,4-Dinitrophenol
- 8-9 Resorcinol
- 9-13 Aniline
- 9-14 Benzoic acid
- 10-8 Benzo(ghi) perylene
- 13-2 Endosulfan sulfate
- 13-13 Endrin
- \*\* 13-18 Diurone
- 13-22 Carbofuran
- \*\* 13-28 Coumaphos
- 13-29 Diazinon
- 13-30 Dicamba
- 13-31 Dichlobenil
- 13-32 Malathion
- 13-33 Methyl parathion
- 13-34 Parathion

\* this is for air; a higher category for steam

\*\* probably, but data is poor

(cannot be stripped - continued)

13-35 Guthion  
13-38 Chlorpyrifos  
13-39 Dichlorvos  
13-41 Disulfoton  
13-43 Mexacarbate  
13-44 Trichlorfon  
14-2 Acetic acid  
14-6 Butyric acid  
14-7 Formaldehyde  
14-8 Formic acid  
14-12 Propionic acid  
14-14 Adipic acid  
15-2 Dodecyl benzenesulfonic acid  
15-5 Strychnine  
15-7 Zinc phenol sulfonate

Poor data, but probably difficult to strip

5-5 4-Chlorophenyl phenyl ether  
6-3 Di-n-butyl phthalate  
6-5 Bis(2-ethylhexyl) phthalate  
7-1 N-nitrosodimethylamine  
7-2 N-nitrosodiphenylamine  
7-5 3,3'-Diphenylhydrazine  
7-6 1,2-Diphenylhydrazine  
13-11 4,4'-DDT  
13-17 Kepone  
13-40 Diquat  
13-42 Mevinphos  
14-9 Fumaric acid  
14-10 Maleic acid

Poor data; better data worth obtaining as may be strippable

5-6 4-Bromophenyl phenyl ether  
6-4 Di-n-octyl phthalate  
6-6 Butyl Benzyl phthalate  
7-3 N-nitrosodi-n-propylamine  
7-4 Benzydine  
7-9 Diethylamine  
8-12 p-Chloro-m-cresol  
10-2 Benz(a)anthracene  
10-6 Indeno(1,2,3-cd)pyrene  
10-7 Dibenzo(ah)anthracene  
13-10 4,4'-DDE  
13-27 Carbaryl  
14-17 Furfural  
15-6 2,3,7,8-Tetrachlorodibenzo-p-dioxin

Data inadequate for comment

7-8 Butylamine  
7-11 Monoethylamine  
7-12 Monomethylamine  
7-14 Trimethylamine  
12-28 2,2-Dichloropropionic acid  
13-1  $\alpha$ -Endosulfan  
13-3  $\beta$ -Endosulfan  
13-4  $\alpha$ -BHC  
13-5  $\beta$ -BHC  
13-6  $\delta$ -BHC  
13-7  $\gamma$ -BHC  
13-14 Kelthane  
13-15 Naled  
13-16 Dichlone  
13-19 Endrin aldehyde

(data inadequate for comment - continued)

13-23 Mercaptodimethur

13-36 Ethion

13-45 Propargite

14-11 Methyl methacrylate

Decompose in water

5-1 Bis(chloromethyl) ether

12-29 Phosgene

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## 1. INTRODUCTION AND OUTLINE

The transference of toxic pollutants from solution in water to the vapor phase or to the atmosphere is of interest for several reasons.

(1) It will occur naturally. Many pollutants have a half life in solution in a slowly flowing river, pond or lake which is controlled by the rate at which they vaporize into the atmosphere. Bubbling air through the water or a waterfall will greatly enhance the rate of vaporization.

(2) Stripping can be used as a deliberate method of cleaning the water. If the contaminant is considered to be harmless in the atmosphere, air stripping can be used. Air stripping is particularly useful for removing small amounts of chlorinated hydrocarbons from drinking water. Air stripping is used at Lake Tahoe to remove dilute ammonia from treated sewage effluent. When recovery of the contaminant is required, such as when stripping high concentrations of ammonia or hydrogen sulfide from industrial wastewaters, steam stripping is usually used.

The ease with which a particular compound is stripped or naturally volatilizes depends on the volatility, which in turn depends on two properties of the contaminant - its vapor pressure and its solubility in water. That compounds with high vapor pressures are easily stripped is expected. The effect of solubility can also be explained quite simply. A compound which is not much soluble in water is a compound whose molecules are not compatible with water molecules. In dilute solution each molecule of organic is surrounded by water molecules which want to push the organic molecule away. The apparent vapor pressure of a poorly soluble organic can be thousands of times higher over an aqueous solution than over the pure organic.

The measure of the apparent vapor pressure over solution is called the Henry's Law constant. Explanations and techniques for determining the Henry's Law constant are given in Section 4. A compilation of Henry's Law constants for all listed organic toxic pollutants is given in Appendix 3. Appendix 3 is the single most important contribution of this report.

In Section 5 the theory of batch and continuous stripping is given and the ease with pollutants can be stripped is determined. Pollutants will be found ranked by ease of stripping on Table 5-2. Of 185 listed toxic pollutants, 68 are very easily strippable; that is, not much vapor is needed



and the period of contact or height of contacting tower between vapor and liquid is small. For these 68 pollutants, stripping is a useful treatment. Forty-eight compounds cannot be stripped and the rest can either be stripped with varying degrees of difficulty or information is lacking to make a judgment.

When air is used as the stripping vapor, water will also evaporate. This cools the water and decreases the volatility of the organic relative to water. Approaches for allowing for this effect are also given in Section 5.

This report is not a design manual. A brief introduction to the choice of equipment is given in Section 6 and the reader is referred to manufacturers' manuals for details of design.

Comparison of predictive calculations to stripping data at low concentration is discussed in Section 7. Also presented in this section is the development of a correlation for the effect of liquid diffusivity on tower sizing and organic removal efficiency.

## 2. CONCLUSIONS

The Henry's Law constant is known or can be reasonably estimated for all except 33 of the 185 toxic organic pollutants listed. About 68 pollutants can be very easily stripped; they have a half life in a lake of the order of 12 hours and can be reduced to 1/100th or 1/1,000th of their original concentration by stripping with air in a single stage device such as a small cooling tower.

An additional 36 pollutants can be stripped with more difficulty. Design of air stripping equipment for these compounds is difficult because the water temperature falls on dry, winter days when water is evaporated by the stripper. The addition of enough steam to saturate the air is a possible method of control. Stripping with pure steam may also be used. Although steam is much more expensive than air, the increased temperature so increases volatility that less steam than air is required for the same job. Steam stripping is cheapest when the water stream is already hot.

About 48 compounds cannot be stripped or probably cannot.

### 3. RECOMMENDATIONS

The following compounds, for which volatility data is inadequate, are probably sufficiently volatile that measurement of Henry's Law constant is of interest.

5-6	4-Bromophenyl phenyl ether
6-4	Di-n-octyl phthalate
6-6	Butyl benyl phthalate
7-3	N-nitrosodi-n-propylamine
7-4	Benzidine
7-9	Diethylamine
8-12	p-Chloro-m-cresol
10-2	Benz(a)anthracene
10-6	Indeno(1,2,3-cd)pyrene
10-7	Dibenzo(ah)anthracene
13-10	4,4'-DDE
13-27	Carbaryl
14-17	Furfural
15-6	2,3,7,8-Tetrachlorodibenzo-p-dioxin

The following compounds, for which volatility data is inadequate, are probably not sufficiently volatile that measurement of Henry's Law constant is of interest.

5-5	4-Chlorophenyl phenyl ether
6-3	Di-n-butyl phthalate
6-5	Bis(2-ethylhexyl) phthalate
7-1	N-nitrosodimethylamine
7-2	N-nitrosodiphenylamine
7-5	3,3'-Diphenylhydrazine
7-6	1,2-Diphenylhydrazine
13-11	4,4'-DDT
13-17	Kepone
13-40	Diquat
13-42	Mevinphos
14-9	Fumaric acid
14-10	Maleic acid

For the following compounds there is insufficient data to judge whether or not they are likely to be volatile.

7-8 Butylamine  
7-11 Monoethylamine  
7-12 Monomethylamine  
7-14 Trimethylamine  
12-28 2,2-Dichloropropionic acid  
13-1  $\alpha$ -Endosulfan  
13-3  $\beta$ -Endosulfan  
13-4  $\alpha$ -BHC  
13-5  $\beta$ -BHC  
13-6  $\delta$ -BHC  
13-7  $\gamma$ -BHC  
13-14 Kelthane  
13-15 Naled  
13-16 Dichlone  
13-19 Endrin aldehyde

#### 4. VAPOR LIQUID EQUILIBRIA

##### 4.1 Introduction to the Theory of Vapor-Liquid Equilibria of Organic Molecules in Dilute Aqueous Solution.

In order to design a stripper one must have information on the volatility of the material to be stripped. In this section we discuss whether the volatility (more correctly the vapor-liquid equilibrium compositions) can be estimated from properties of the pure components. In fact, estimates cannot be made for most organic molecules in water and some experimentally determined information is required. Very occasionally one has direct measurements at the pressure, temperature and concentration of interest. Sometimes there is distillation data at concentrations much higher than those of interest and one needs to extrapolate to low concentrations. Usually the only data available is the vapor pressure of the pure organic and its solubility in water. This data can also be used to approximate the vapor-liquid equilibrium relationship.

The theory and estimation of vapor-liquid equilibria is given in many texts; for example, by Lewis and Randall<sup>1</sup>, Gilliland<sup>2</sup> and Reid, Prausnitz and Sherwood<sup>3</sup>. The discussion given here is limited to a brief introduction to nomenclature and estimation of the equilibria for dilute solutions of organics in water at close to atmospheric pressure and in the temperature range of liquid water.

The property which describes the "escaping tendency" of a compound was called "fugacity" by G. N. Lewis<sup>1</sup>. At equilibrium, and by definition of fugacity, the fugacity of every component,  $i$ , in the liquid equals the fugacity in the vapor:

$$f_i^L = f_i^V$$

Fugacity is logically defined so that at the given temperature and at such a low total pressure that the vapor is an ideal gas, the fugacity equals the vapor pressure. Thus, fugacity has the units of pressure and may be regarded as an "ideal" or "corrected" vapor pressure.

##### Gas Phase

The "mole fraction" of a component,  $i$ , in the gas phase, written  $y_i$ , equals the vapor pressure divided by the total pressure and is, therefore, a convenient expression of concentration. Since the pressure of interest

to us is low, the fugacity equals the vapor pressure and we have

$$f_i^V = \text{Vapor Pressure} = y_i P$$

where  $P$  is the total pressure.

This equation is called Dalton's law and it can be used for all cases of interest to us here.

#### Liquid Phase

The fugacity of a compound in the liquid phase must be related to the vapor pressure of the pure liquid, written  $p_i^*$ . Also, the fugacity is generally a function of pressure, temperature and concentration. However, the pressure of interest to us is low and it is customary, for low pressures, to define an "activity coefficient",  $\gamma_i$ , and to write

$$f_i^L = \gamma_i x_i P_i^*$$

In writing this equation several decisions have been made. The correction necessary for high pressure has been omitted. This correction is called the "Poynting effect" in some texts. The activity coefficient, which is a function of composition and temperature, has been defined. The expression of concentration,  $x_i$ , has been chosen to be the mole fraction. This is so that the ratio  $y_i/x_i$  (concentration in the vapor divided by concentration in the liquid) shall be dimensionless. In dilute solutions

$$x = \text{moles/l} \times 0.018$$

and 
$$x = \text{mg/l} \times 18 \times 10^{-6} / \text{MW}$$

where MW = molecular weight of the organic.

A solution is called "ideal" if  $\gamma_i = 1$ . In this case

$$f_i^L = x_i P_i^*$$

which equation is called Raoult's law. In solutions of interest to us Raoult's law holds for water but not for the organic (see, for example, Gilliland<sup>2</sup>). We cannot use Raoult's equation and  $\gamma_i$  must be determined experimentally.

### The Form of the Vapor-Liquid Equilibrium Relationship.

The equations introduced so far give

$$y_i = \gamma_i x_i p_i^*/P$$

In this equation  $P$  is total pressure and  $p_i^*$  is the vapor pressure of the pure organic (a function of temperature). The activity coefficient, which is dimensionless, is a function of concentration and temperature.

An alternative nomenclature is to write

$$f_i^L = x_i H_i$$

This equation is called Henry's Law and  $H$  is called Henry's Law constant.  $H$  is a function of temperature and concentration except that  $H$  is independent of concentration at low concentrations.  $H$  has the units of pressure and the two usual units for reporting  $H$  are mm Hg and atmospheres. In reading the literature one will find reports in which the concentration unit (for which we use the mole fraction,  $x$ , which is dimensionless) is not dimensionless. In this case  $H$  has the units of pressure divided by concentration. Furthermore, some authors report the reciprocal of our  $H$ . The vapor-liquid equilibrium relationship is

$$y_i = x_i H_i/P$$

and

$$H_i = \gamma_i p_i^*$$

Yet another nomenclature is to write

$$y_i = x_i K_i$$

so

$$\begin{aligned} K_i &= H_i/P \\ &= \gamma_i p_i^*/P \end{aligned}$$

$K_i$  is dimensionless.

To use any of the forms of the vapor-liquid relationship we must know  $\gamma$  and  $p^*$ , or  $H$ , or  $K$ .

#### 4.2 Activity Coefficients for Slightly Soluble Compounds.

Most of the organic compounds of interest to us are only slightly soluble in water and this is much the most important method of determining activity coefficients. This is the principal method used by all authors that we have found (see, for examples, Hwang and Fahrenthold<sup>4</sup>, Kavanaugh and Trussel<sup>5</sup>, Dilling et al<sup>6</sup>).

When a sparingly soluble compound is dissolved in water to saturation, ( $x_i = x_i$  (saturated)) there will be two liquid phases in equilibrium (or one liquid and one solid phase) - the water phase and the organic phase. If, in addition, no vapors other than water and the organic are present (particularly if air is not present), there will be three phases in equilibrium. With two components present, there is one degree of freedom and if the temperature is chosen, the total pressure is specified. When complete information on two components with three phases in equilibrium is available, Henry's law constant can be determined accurately. It can be shown that if Henry's law holds for the organic in the water phase, then Raoult's law must hold for the water in the water phase (see, for example, Smith and Van Ness, Ref. 44, page 347). In this case, for equilibrium between the vapor and water phases,

$$\begin{aligned} y_o P &= \gamma_o x_o p_o^* = x_o H_o \\ y_w P &= x_w p_w^* \end{aligned}$$

where the suffix w means "water" and the suffix o means "organic". Since  $y_o + y_w = x_o + x_w = 1$ , adding these two equations gives

$$\begin{aligned} P &= \gamma_o x_o p_o^* + (1 - x_o) p_w^* \\ &= x_o H_o + (1 - x_o) p_w^* \\ \text{or, } H_o &= \frac{P - (1 - x_o) p_w^*}{x_o} \end{aligned} \tag{1}$$

$$\gamma_o = H_o / p_o^* = \frac{P - (1 - x_o) p_w^*}{p_o^* x_o}$$

Complete equilibrium data is very seldom available. Solubility is usually measured at pressures below the equilibrium pressure and, in addition, air is present in the vapor phase. (Expressed another way, we



may say that solubilities are usually measured at one atmosphere and at temperatures below the equilibrium temperature, with air present in the vapor phase). The approximation usually made is

$$y_o P = p_o^*$$

In this case

$$\begin{aligned} H_o &= p_o^*/x_o \text{ (satd)} \\ \gamma_o &= 1/x_o \text{ (satd)} \end{aligned} \quad (2)$$

Equation (2) is the approximation used throughout this report and by all the authors quoted who have made similar estimates. In using Equation (2) we assume that the fugacity of the organic phase is the vapor pressure of the pure organic at the prevailing temperature. We thus neglect the solubility of water in the organic phase and assume that the fugacity of the liquid organic is independent of pressure.

Often the solubility of water in the organic phase in equilibrium with the water phase is given. In this case another approximation, which we have never seen used, is possible. Assume that Raoult's law holds for the organic in the organic phase. Then

$$x_{o,w} H_o = x_{o,o} p_o^*$$

where  $x_{o,w}$  is the mole fraction of organic in the water phase and  $x_{o,o}$  is the mole fraction of organic in the organic phase.

$$H_o = x_{o,o} p_o^*/x_{o,w} \quad (3)$$

Smith and Van Ness (Ref. 44 page 361) give complete data for ethyl-ether and water. Calculations are presented on the table below. Compared to Equation (1), which is exact, the approximate Equations (2) yields a maximum error of 4.4%. Equation (3), which requires more data than Equation (2), yields the same error and does not seem to be preferable.

### Ethyl-ether and Water System

t (°C)	P (atm)	Satd. Water Phase $x_o$	Satd. Ether Phase $x_o$	$P_w^*$ (atm)	$P_o^*$ (atm)	$H_o$ (atm)		
						Eqn. (1)	Eqn. (2)	Eqn. (3)
34	1.000	0.0123	0.9456	0.053	0.983	77.0	79.9	75.6
50	1.744	0.0103	0.9348	0.121	1.679	158	163	152
70	3.195	0.0075	0.9212	0.306	3.018	386	402	370
90	5.514	0.0058	0.9107	0.691	5.040	832	869	791

These equations require a knowledge of the vapor pressure of the pure organic and its solubility as a function of temperature. They then give us  $H$  or  $\gamma$  at one concentration. The concentration at which we know  $H$  and  $\gamma$  is the highest concentration obtainable and we must assume that  $H$  and  $\gamma$  remain constant with respect to concentration at concentrations below saturation. Now it is experimentally true that if the concentration is low enough  $H$  and  $\gamma$  are independent of concentration. For example, for such sparingly soluble gases as oxygen and nitrogen, Henry's law applies with  $H$  constant. In a later section we extrapolate phenol-water equilibrium data to show that  $\gamma$  is constant at low enough concentrations. In using the above technique to obtain  $H$  or  $\gamma$  we have no way of knowing if the organic is sufficiently insoluble for accuracy; we just assume it is and this technique is less reliable the more soluble the organic.

An example follows. At 25°C Hwang and Fahrenthold<sup>4</sup> give, for 1, 1, 1-trichloroethane

<u>M.wt</u>	<u>solubility (mg/l)</u>
133.4	4,400

Dilling et al<sup>6</sup> give (at 25°C),

<u>solubility (mg/l)</u>	<u>vapor pressure (mm Hg)</u>
1,300	123

The Chem. Eng. Handbook<sup>16</sup> gives

"insoluble" 125

The two different solubilities are

$$X = 4,400 \times 18 \times 10^{-6} / 133.4 = 5.9 \times 10^{-4}$$

or

$$X = 1.75 \times 10^{-4}$$

The Henry's law constant is

$$H = 123 / 5.9 \times 10^{-4} = 2.08 \times 10^5 \text{ mm Hg} = 274 \text{ atm}$$

or

$$H = 925 \text{ atm.}$$

Kavanaugh and Trussel<sup>5</sup>, who did not give the base data, calculated  $H = 400 \text{ atm.}$

The numbers used illustrate not only the calculation but also the discrepancies that frequently are found.

The use of this method will require a correlation of vapor pressure and solubility (or activity coefficient) as a function of temperature.

#### 4.3 Vapor Pressure as a Function of Temperature

Reid, Prausnitz and Sherwood<sup>3</sup> (Chapter 6) have considered the many correlating equations available. We are only interested in temperatures between about 0° and 100°C (273° to 373°K). We are not interested in compounds with very low vapor pressures because they will not be stripped. For our purposes the preferred correlating equation is

$$\text{Log } p^* = A + B / (C + T)$$

which is called Antoine's equation. An alternative equation, less satisfactory at low temperatures, is the Clapeyron equation

$$\text{Log } p^* = A + B/T$$

where T is in °K.

#### 4.4 Activity Coefficient as a Function of Temperature

Reid, Prausnitz and Sherwood<sup>3</sup> (Page 307) state that the effect of temperature on the activity coefficient is a particularly troublesome question. They suggest using

$$\text{Log } \gamma \text{ (constant composition)} = c + d/T$$

where T is in °K.

Since we are working at concentrations so low that  $\gamma$  is independent of concentration, the limitation of constant concentration can be ignored.

If only one point is available, the constant, c, should be taken as zero so

$$\text{Log } \gamma = d/T$$

This is the form of the equation that we most often use. It is the way that Hwang and Farenthold<sup>4</sup> extrapolate from 25°C to 100°C. Fortunately the effect of temperature on  $\gamma$  is very much less than the effect of temperature on  $p^*$  so the fact that we cannot correlate  $\gamma$  very well is not of extreme importance. Tsonopoulos and Prausnitz<sup>21</sup>, working with aromatic molecules in the range 0-50°C found it best to assume  $\gamma$  independent of temperature.

We return to our example on 1, 1, 1 - trichloroethane. As we have seen, Hwang and Farenthold<sup>4</sup> give, at 25°C, a solubility of 4,400 mg/l or a mole fraction of  $5.9 \times 10^{-4}$ . Thus at 25°C (298°K)  $\gamma = 1/5.9 \times 10^{-4} = 1,700$ . At 100°C (373°K)  $\gamma$  is given by

$$\frac{\text{Log } 1,700}{\text{Log } \gamma} = \frac{273}{298} = 1.25$$

$$\text{so } \gamma \text{ (373°K)} = 384.$$

At 100°C Hwang and Fahrenthold give

$$p^* = 213 \text{ kPa} = 2.1 \text{ atm},$$

so, at 1 atm,

$$K = y/x = \gamma p^*/P = 384 \times 2.1 = 806 \text{ atm}$$

The value given by Hwang and Fahrenthold is 796 and they may have had other solubility data. Note that from 25°C to 100°C we assumed that  $\gamma$  changed by 4.4 time and  $p^*$  changed by 13 times. The change in  $p^*$  is much the most important effect of temperature.

#### 4.5 Extrapolation of Activity Coefficients Measured at High Concentration - Activity Coefficient as a Function of Concentration

The vapor-liquid equilibrium of phenol in water has been measured by several authors. Gilliland<sup>2</sup> quotes a 1933 thesis and the lowest concentration at which he gives information is  $x = 0.001$ ,  $y = 0.002$  at 1 atmosphere. If we assume that at this concentration  $\gamma$  is independent of concentration we would have

$$K = y/x = 2$$

$$H = Py/x = 2 \text{ atm}$$

$$\gamma = Py/p^* x = 37$$

where  $p^* (100^\circ\text{C}) = 0.054 \text{ atm}$  (see below).

Note that  $\gamma$  is very much greater than one and Raoult's law does not apply. We will now suggest ways of extrapolating equilibrium data that are preferable to linear extrapolation from the lowest point and show that the value of  $\gamma$  obtained above is accurate.

Many relationships have been proposed between  $\gamma$  and concentration for binary mixtures. All the relationships must satisfy the Gibbs-Duhem equation and summaries have been given by Gilliland<sup>2</sup>, Reid, Prausnitz and Sherwood<sup>3</sup> (page 300, Table 8-3), Holmes and Van Winkle<sup>4</sup> and in other texts.

It seems that van Laar's equations, which are among the simplest to use, are adequate for our purposes. We have not made a detailed comparison with other equations.

The van Laar equations are

$$\begin{aligned}\log \gamma_1 &= A/[1 + Ax_1/(Bx_2)]^2 \\ \log \gamma_2 &= B/[1 + Bx_2/(Ax_1)]^2\end{aligned}$$

where 1 and 2 are the two components of a binary mixture. If we have any one experimental point, we know  $\gamma_1$ ,  $\gamma_2$ ,  $x_1$  and  $x_2$  ( $= 1 - x_1$ ) and the two equations can be solved for A and B. The equations can then be used to explore the variation of  $\gamma$  with  $x$ .

The following manipulations give expressions specific in A and B which are useful when a single point is available.

$$x_1 \log \gamma_1 = \frac{Ax_1}{(1 + Ax_1/Bx_2)^2} = \frac{1/Ax_1}{(1/Ax_1 + 1/Bx_2)^2}$$

$$x_2 \log \gamma_2 = \frac{1/Bx_2}{(1/Ax_1 + 1/Bx_2)^2}$$

$$x_1 \log \gamma_1 / x_2 \log \gamma_2 = Bx_2 / Ax_1$$

From the first Van Laar equation

$$\begin{aligned}A &= \log \gamma_1 [1 + Ax_1/Bx_2]^2 \\ &= \log \gamma_1 [1 + x_2 \log \gamma_2 / x_1 \log \gamma_1]^2\end{aligned}$$

and similarly

$$B = \log \gamma_2 [1 + x_1 \log \gamma_1 / x_2 \log \gamma_2]^2$$

As a first example consider again phenol (component 1 or A) and water (component 2 or B). A single point that is often known is the azeotrope. At 1 atmosphere the azeotrope is

$$x_1 = 0.0195, \quad x_2 = 0.9805$$

The boiling point is 99.8°C so

$$p_1^* = 0.054 \text{ atm (see correlation below)}$$

$$p_2^* = 0.993 \text{ atm.}$$

We calculate

$$\gamma_1 = 1/0.054 = 18.5, \gamma_2 = 1/0.993 = 1.007$$

$$A, \text{ phenol} = 1.59$$

$$B, \text{ water} = 0.262$$

(It is worth remembering the  $p_1^*$  and  $p_2^*$  are the vapor pressures of the pure components and do not add to one atmosphere). If A and B as calculated above are used to calculate  $\gamma_1$  when  $x_1 = 0.001$ , we obtain

$$\begin{aligned} \log \gamma_1 &= 1.59/[1 + (0.001)(1.59)/(0.999)(0.262)]^2 \\ &= 1.57 \end{aligned}$$

$$\gamma_1 = 37.2$$

which is an unusually good agreement with value found by linear extrapolation from the point  $x = 0.001$ ,  $y = 0.002$ .

The van Laar equations are not useful when the single data point is at a very low concentration. At a low concentration of organics  $\gamma_2$  (for water) approaches one and  $\log \gamma_2$  is very small. But  $x_1$  (the organic) is also small and  $x_1/\log \gamma_2$  tends to become indeterminate. An error of one tenth of a degree centigrade in the boiling point can drastically alter the calculation. When data is available at low concentrations, linear extrapolation is the preferred extrapolation.

Any extrapolation will be better if many points are available. To extrapolate, the equations may be linearized so that the data can be conveniently plotted to obtain A and B. One way to plot the data is to plot  $x_1/x_2$  against  $1/(\ln \gamma_1)^{1/2}$ . From the first van Laar equation

$$1 + Ax_1/Bx_2 = (A/\ln \gamma_1)^{1/2}$$

so

$$x_1/x_2 = \frac{B}{A^{1/2}} \left( \frac{1}{\ln \gamma_1} \right)^{1/2} - \frac{B}{A}$$

Another way is to plot  $\frac{x_1 x_2}{x_1 \ln \gamma_1 + x_2 \ln \gamma_2}$  against  $x_1$ . The following manipulations explain this plot.

$$\begin{aligned}
 x_1 \ln \gamma_1 + x_2 \ln \gamma_2 &= \frac{\frac{1/Ax_1}{(1/Ax_1 + 1/Bx_2)^2}}{\frac{1/Bx_2 + 1/Ax_1}{(1/Bx_2 + 1/Ax_1)^2}} \\
 &= \frac{1}{(1/Ax_1 + 1/Bx_2)} \\
 \frac{x_1 x_2}{x_1 \ln \gamma_1 + x_2 \ln \gamma_2} &= \frac{x_2}{A} + \frac{x_1}{B} \\
 &= \frac{1}{A} + x_1 \left( \frac{1}{B} - \frac{1}{A} \right)
 \end{aligned}$$

In plotting to obtain van Laar coefficients it must be remembered that A and B are functions of temperature and isothermal plots are required. When, as frequently happens, the available data is at constant pressure and variable temperature, van Laar's equations may be written

$$\begin{aligned}
 T \log \gamma_1 &= A/(1 + Ax_1/Bx_2)^2 \\
 T \log \gamma_2 &= B/(1 + Bx_2/Ax_1)^2
 \end{aligned}$$

and  $T \log \gamma_1$ ,  $T \log \gamma_2$  used instead of  $\log \gamma_1$  and  $\log \gamma_2$  in all the equations. T is in °K.

Hicks et al<sup>7</sup> have fitted van Laar's equations to data given in references 2 and 8 to 11 and found

$$\begin{aligned}
 A, \text{ phenol} &= 1.941 - 0.00352 \, t^\circ\text{C} \\
 B, \text{ water} &= 0.324 - 0.00052 \, t^\circ\text{C} \\
 55 &< t^\circ\text{C} < 240
 \end{aligned}$$

The effect of temperature on A and B was found by simply putting the best straight line through the available values. From these equations we have calculated  $\gamma_1$ , for phenol, as shown below (we have ignored the temperature limitation on the correlation).



Temp	$x_1$		$\gamma_1$
<u>°C</u>	<u>A</u>	<u>B</u>	<u>(<math>x_2 = 1 - x_1</math>)</u>
30	1.835	0.308	0.01
			0.001
			0.0001
			$10^{-5}$
			$10^{-6}$
100	1.589	0.272	$10^{-2}$
			$10^{-3}$
			$10^{-4}$
			$10^{-5}$
			$10^{-6}$

At 100°C and  $x_1 = 10^{-3}$  (5,200 ppm)  $\gamma_1$  (=37) is as calculated from the low concentration data point and  $\gamma_1$  is independent of concentration within about 3%.  $\gamma_1$  is independent of concentration within 1% when  $x_1 < 10^{-4}$  (= 520 ppm) and is independent of concentration within 0.05% when  $x_1 < 10^{-5}$  (52 ppm).

The vapor pressure of phenol has been correlated by the equation

$$\text{Log } p^* \text{ (mm Hg)} = A + B/(C + t^\circ\text{C})$$

where

	<u>A</u>	<u>B</u>	<u>C</u>	<u>Reference</u>
1.	7.50	-1724	192	Hicks et al <sup>7</sup>
2.	7.14	-1518	175	Dean <sup>13</sup>
3.	7.13	-1516	174	Reid et al <sup>3</sup>
4.	6.93	-1383	159	Gnehling <sup>12</sup>

These equations give very similar results and numbers 2 and 3 seem to be a good average set of constants.

At low concentrations, for phenol

$$\begin{aligned} \text{Log } E(\text{mm Hg}) &= \text{Log } \gamma + \text{Log } p^* = A + \text{Log } p^* = \\ &1.941 - 0.00352 t + 7.13 - 1517/(174 + t) = \\ &9.071 - 0.00352 t^\circ\text{C} - 1517/(174 + t^\circ\text{C}) \end{aligned}$$

#### 4.6 Direct Measurement of Henry's Law Constant

The solubility of gases is usually expressed in the form of a Henry's Law constant. It is quite easy to vary the partial pressure of a gas and measure its solubility which gives H directly. Most toxic pollutants of interest are not gases and solubility measurements of H are not usually available.

However, Mackay, Shiu and Sutherland<sup>30</sup> have devised a most useful stripping technique to measure H which has been used extensively by Warner, Cohen and Ireland<sup>20</sup>. Nitrogen is bubbled through a column of water in which the organic was dissolved. The water column is held at constant temperature and a record is kept of the concentration of the organic in the water as a function of time. It is experimentally demonstratable that the organic is in equilibrium between the water and the nitrogen so that the rate of removal of organic by stripping,

$$- V \frac{dc}{dt} = (pp) \frac{G}{RT}$$

where

V is the volume of the water, m<sup>3</sup>

c is the concentration of the organic, moles/m<sup>3</sup>

t is time, hours

G is the nitrogen rate, m<sup>3</sup>/hr

R is the gas constant, (m<sup>3</sup>) (atm) / (mole) (°K)

T is the temperature, °K

and

$$\begin{aligned} (pp) & \text{ (the partial pressure of organic over the solution)} \\ & = yP = Hx = Hc \times 18 \times 10^{-6} \end{aligned}$$

so,

$$\text{if } c = c_0 \text{ at } t = t_0$$

$$\ln (c/c_0) = (18 \times 10^{-6} \text{ HG/VRT}) t$$

and a plot of  $\ln c$  against  $t$  has a slope of  $18 \times 10^{-6} \text{ HG/VRT}$  from which H can be determined.

We should mention here that we are not concerned with stripping contaminants that react with water such as  $\text{NH}_3$  and  $\text{CO}_2$ . Since it is  $\text{NH}_3$ , not  $\text{NH}_4^+$ , which is volatile, and  $\text{CO}_2$ , not  $\text{HCO}_3^-$ , which is volatile, stripping calculations involve simultaneous calculations of chemical equilibrium in solution. The basis for these calculations has been given by Hicks et al.<sup>7</sup>

Henry's Law constants have been given for the single contaminants for  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{HCN}$ , which are of interest. Some calculations from the formulae given in the references are presented on Table 4-1. For single contaminants we suggest using the newest reference which is Edwards et al<sup>18</sup>. The formulae are

$$\begin{aligned}\ln H (\text{ammonia}) &= -149.006 - 157.552/T + \\ &\quad 28.1001 \ln T - 0.049227 T \\ \ln H (\text{H}_2\text{S}) &= 342.595 - 13,236.8/T - \\ &\quad 55.0551 \ln T + 0.0595651 T \\ \ln H (\text{HCN}) &= 1446.005 - 49,068.8/T - \\ &\quad 241.82 \ln T + 0.315014 T\end{aligned}$$

where T is in °K

and H is in (atm) (kg)/mole = H atm x  $18 \times 10^{-6}$ .

Formulae given by the API<sup>19</sup> show that H (ammonia) is altered by 100% if the acid gases  $\text{CO}_2 + \text{H}_2\text{S}$  total about 160 mg/l and that H ( $\text{H}_2\text{S}$ ) is altered by 100% if the alkaline gas  $\text{NH}_3$  is present at about 80 mg/l. In most cases the simple formulae for H given above are not useful and chemical equilibrium must be taken into account.

TABLE 4-1. HENRY'S LAW CONSTANTS FOR GASEOUS CONTAMINANTS

$t^\circ\text{C}$ <u><math>T^\circ\text{K}</math></u>	H in (atm - kg/mole)		
	15 <u>288</u>	50 <u>323</u>	100 <u>373</u>
<u><math>\text{NH}_3</math></u>			
Ref. 17	0.0101	0.0472	0.246
Ref. 18	0.0100	0.0478	0.248
Ref. 19	0.0104	0.0478	0.248
<u><math>\text{H}_2\text{S}</math></u>			
Ref. 17	7.24	16.55	28.9
Ref. 18	7.49	15.87	27.45
Ref. 19	8.79	17.95	30.13
<u><math>\text{HCN}</math></u>			
Ref. 17	0.0571	0.258	2.93
Ref. 18	0.0466	0.269	0.997

## 5. THE THEORY OF STRIPPING

### 5.1 Organization of the Section, Batch and Continuous Stripping, Isothermal and Adiabatic.

If contaminated water is placed in a vessel, a pond or a lake and air or other vapor is passed through it, the contaminants may be slowly vaporized and, as time passes, the water is cleaned. This is a realistic situation; contamination may have been due to a spill or other one-time discharge. Vapor bubbling through a vessel or pond is described by the equation for a batch stripper given in Section 5-3.

A volatile contaminant will vaporize from a lake even if air is not bubbled through the water. In this case the rate of removal depends on the rate of diffusion to the water surface, as well as on the volatility (Henry's Law constant) of the contaminant. A description of this situation has been given by Mackay and Leinonen<sup>31</sup> and is discussed in the next Section (5.2).

Now consider a continuous stripper; that is, the water as well as the vapor is flowing. The passage of vapor through the vessel will normally mix the water. The cleanest water we can hope to get from a simple vessel is when vapor and water reach equilibrium and then the water cleanliness will depend on the Henry's Law constant of the organic contaminant and the vapor to water ratio. The only way to obtain cleaner water is to pass more vapor. Usually increasing the vapor rate is not economical and the practice is to pass water down a tower counter-current to the vapor flowing up. This means that the cleanest vapor is put in contact with the cleanest water and that as the vapor rises it comes into contact with dirtier and dirtier water until vapor leaves the top of the tower with a high load of contaminant.

The tower is usually full of some sort of packing designed to encourage contact between liquid and vapor. An empty tower, called a spray tower, can also be used, but the results will be much the same as a single simple vessel with vapor bubbled through. The choice of tower packing is discussed in Section 6.

The designer of a stripping tower has the job of determining the height of the tower and the vapor/liquid ratio required to reach the wanted degree of stripping. (The diameter of the tower is controlled by the throughput rate). There are two approaches to determining tower height. The first approach, which is mostly used when the tower packing is continuous from

bottom to top, is to write an equation for rate of transfer of contaminant from the water to the vapor phase. The rate equation is integrated to determine the tower height. This procedure needs the rate coefficient of mass transfer which must be determined experimentally.

When the stripping tower contains discrete trays or plates rather than a continuous packing, it is usually more convenient to think in terms of equilibrium stages (see Figure 5-1.). The vapor and liquid are assumed to thoroughly mix and reach equilibrium on a plate. The liquid then falls to the next equilibrium plate below and the vapor rises to the equilibrium plate above. The height of the tower is expressed as the number of equilibrium plates to do the job.

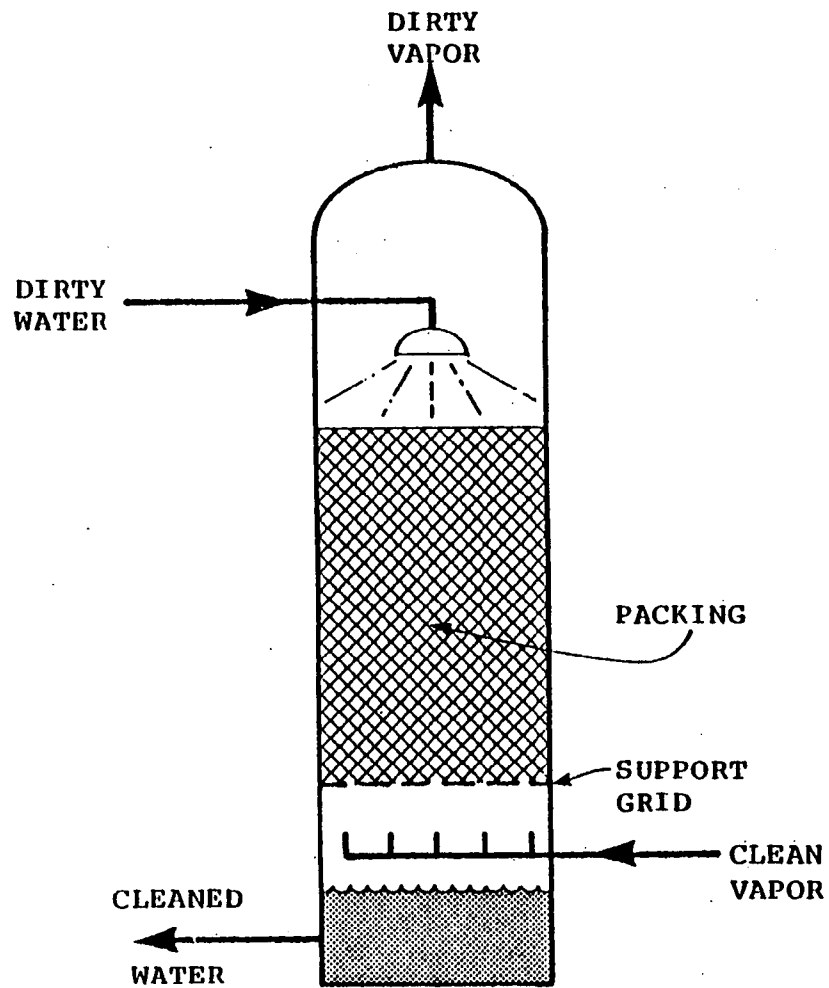
Equilibrium is not reached on real plates and an experimentally determined efficiency is needed to tell how many real plates are required when the number of equilibrium (or theoretical) plates has been calculated.

We find it simpler to work in terms of equilibrium plates. (The words "equilibrium" and "theoretical" are interchangeable and the words "plates" and "stages" are interchangeable.) In Section 5.5 we briefly describe the rate of mass transfer approach and show how the height of packing equivalent to a theoretical plate (HETP) can be found by taking measurements on an operating tower. In Section 5.6 we give the complete equations for the equilibrium stages approach and use the results to classify organic pollutants by the ease with which they can be stripped.

The simplest equations to write apply to isothermal stripping. In isothermal stripping, when steam is the vapor, the water must enter the tower preheated to the boiling point; when air is in the vapor, the water must enter at the wet bulb temperature of the air. Air strippers are not usually isothermal; they are adiabatic. Water is usually evaporated and the liquid water is usually cooled.

Adiabatic stripping with air is considered in Sections 5.4 and 5.8. Particularly in the case of a counter-current air stripping it can be difficult to design equipment which will behave satisfactorily as the air conditions change with the seasons. We suggest that the best control of such equipment is to add a little steam to the air when the air is particularly dry. Steam-air mixing is discussed in Section 5.9.

Finally, in Section 5.10, a brief analysis is given of a system in which the water is circulated. This is particularly applicable to cooling towers.



PACKED TOWER

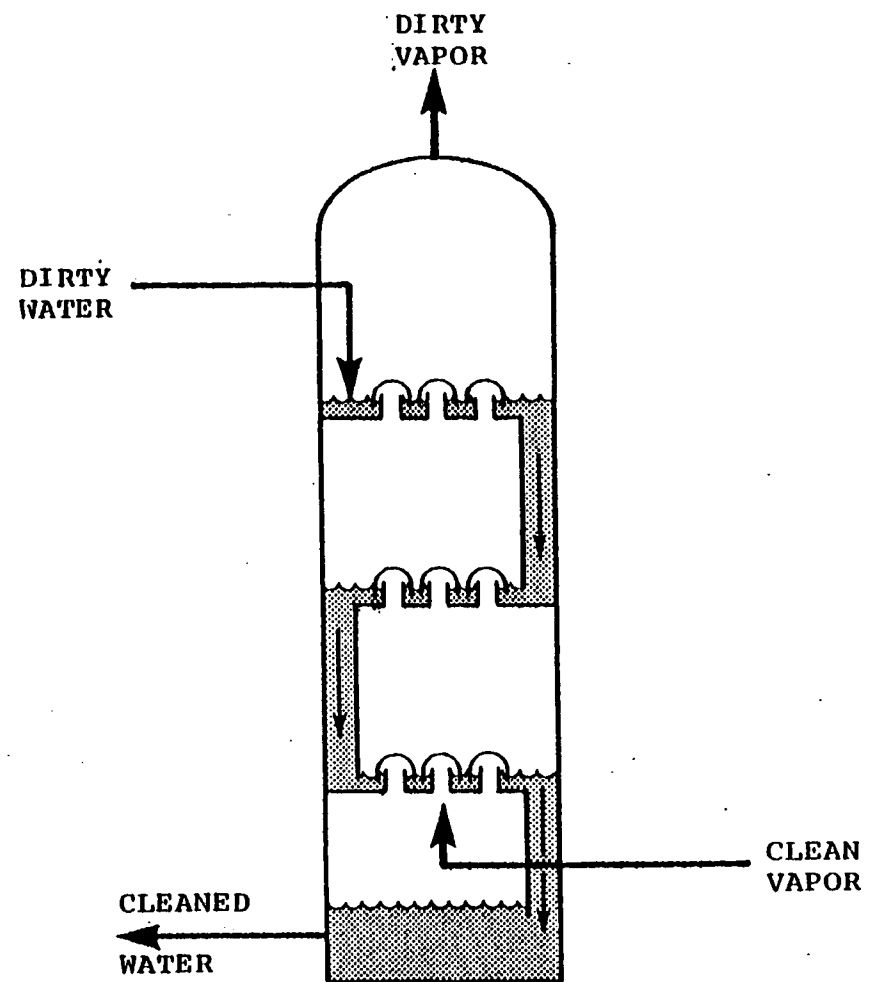


PLATE TOWER

Figure 5-1. Pictorial of packed and plate towers.

## 5.2 Evaporation from a Lake

Mackay and Leinonen<sup>31</sup> have given a formula for the half life of a volatile contaminant in a lake. Their formula is

$$t_{0.5} = 0.69 L/K_L$$

where

$$t_{0.5} = \text{half life in hours}$$

$L$  = depth in meters at which the half life is measured

$K_L$  = overall mass transfer liquid coefficient, m/hr.

also

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{(18 \times 10^{-6}) H k_G/RT}$$

where

$k_L$  = liquid side mass transfer coefficient, = (approx) 0.2 m/hr

$k_G$  = gas side mass transfer coefficient, = (approx) 30 m/hr

$H$  = Henry's Law constant in atm

$18 \times 10^{-6}$  =  $\text{m}^3/\text{mol}$  of water

$R$  = gas constant =  $8.2 \times 10^{-5} (\text{m}^3) (\text{atm})/(\text{mol}) (^\circ\text{K})$

$T$  = temperature in  $^\circ\text{K}$ .

At  $70^\circ\text{F}$  =  $21^\circ\text{C}$  =  $294^\circ\text{K}$ , at a depth of 1 meter,

$$\frac{1}{K_L} = \frac{1}{0.2} + \frac{1}{(2.24 \times 10^{-2}) H}$$

$$\text{and } t_{0.5} = 3.45 + 30.8/H.$$

This equation is graphed on Figure 5-2. It seems reasonable to classify organic molecules as

$H(21^\circ\text{C}) > 10$ , easily stripped

$H(21^\circ\text{C}) = 2 \text{ to } 10$ , intermediate

$H(21^\circ\text{C}) < 2$ , slow to be stripped.

This classification is compatible with another classification given in Section 5.7.

## 5.3 Isothermal Batch Stripping

Consider a solution of  $M_c$  moles of contaminant in  $W$  moles of water at the boiling point. Saturated steam is passed through in such a way that the vapor leaves in equilibrium with the solution. Water does not leave the solution, but when an amount of steam,  $dV$ , is passed an amount of contaminant,  $-dM_c$ , leaves the solution and appears in the vapor. The vapor leaving is  $dV - dM_c$  moles ( $dM_c$  is a negative quantity).

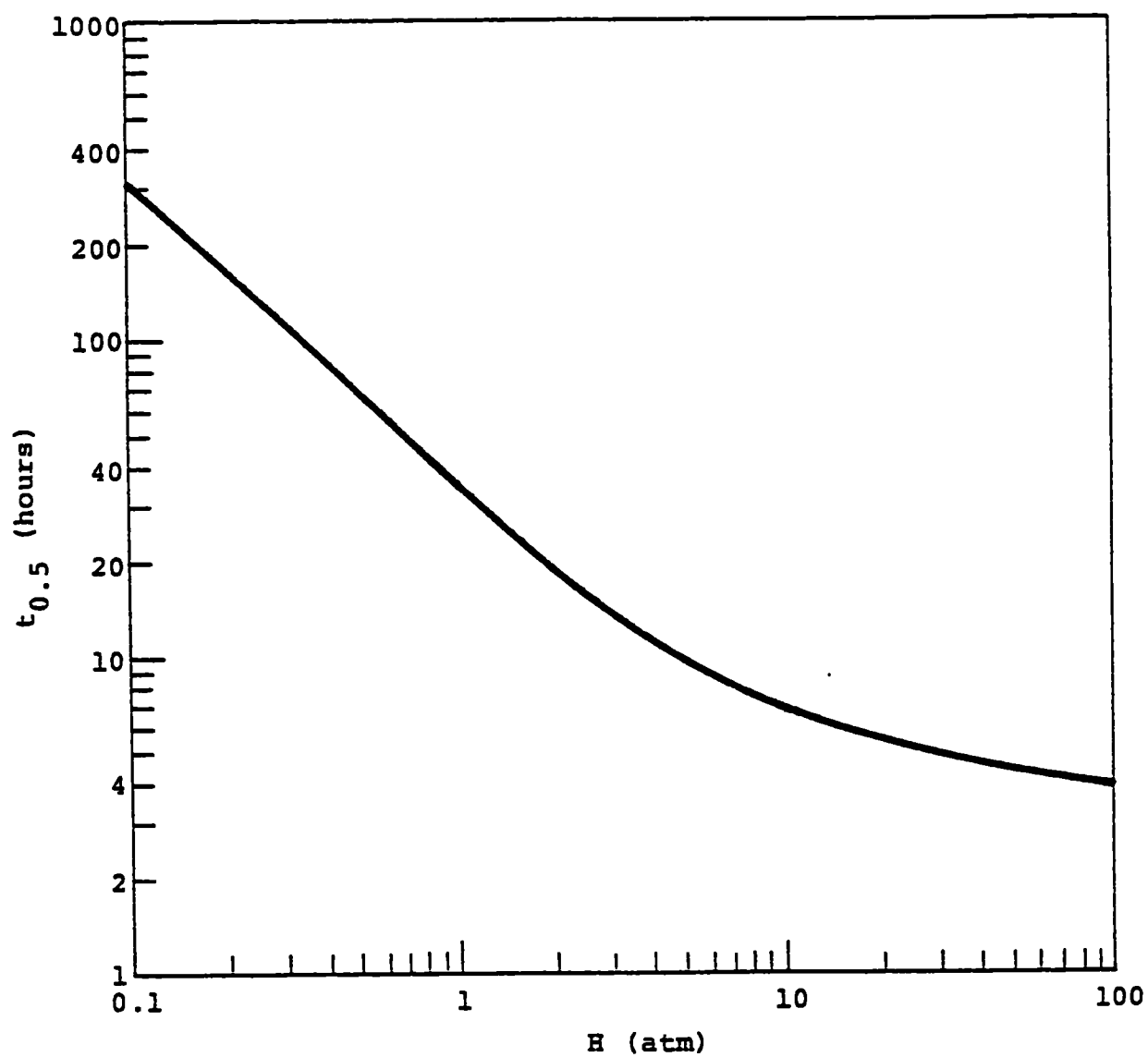


Figure 5-2. Half life in a lake as a function of Henry's Law constant.



(The derivation applies to air as well as to steam so long as the stripper is isothermal or approximately isothermal. The closer the air to being saturated at the water temperature, the closer the system is to isothermal.)

$$y = \frac{-dM_c}{dV - dM_c}$$

is in equilibrium with the solution composition, i.e.

$$y = xH/P = Kx$$

where

$$K = H/P$$

Since

$$x = \frac{M_c}{W + M_c}$$

$$\frac{-dM_c}{dV - dM_c} = \frac{KM_c}{W + M_c}$$

and

$$KdV = \left\{ K-1 - \frac{W}{M_c} \right\} dM_c$$

If this equation is integrated between  $V = 0$  and  $V = V$ , and  $M_c = M_{ci}$  (initial) and  $M_c = M_{cf}$  (final) one obtains

$$KV = (K-1)(M_{cf} - M_{ci}) - W \ln \frac{M_{cf}}{M_{ci}}$$

This can be rewritten as

$$K \frac{V}{W} = (K-1) \frac{M_{ci}}{W} \left\{ \frac{M_{cf}}{M_{ci}} - 1 \right\} - \ln \frac{M_{cf}}{M_{ci}}$$

The preferred nomenclature is to use

$$x_i = \frac{M_{ci}}{M_{ci} + W}$$

so 
$$\frac{M_{ci}}{W} = \frac{x_i}{1-x_i} = (\text{approx}) x_i \text{ for low values of } x_i$$

(and we are interested in  $x_i$  less than  $10^{-3}$  in all cases).

Also 
$$\frac{M_{cf}}{M_{ci}} = 1 - F_R$$

where  $F_R$  is the fraction of contaminant removed.

The final equation is, for low initial concentrations,

$$\frac{KV}{W} = - (K-1) x_i F_R - \ln(1-F_R)$$

In all the cases of interest to us  $x_i$  is so low that the first term on the righthand side can be neglected and

$$\frac{KV}{W} = (\text{approx}) - \ln(1-F_R)$$

Some calculations using this formula have been made for benzene, nitrotoluene and nitrobenzene and are presented on Table 5-1 for a total pressure of 1 atm so that  $K = H$ . Graphs are presented later on Figures 5-3 and 5-5.

#### 5.4 Adiabatic Batch Stripping with Air

The general situation is not isothermal and water evaporates into the air stream. If the tank is adiabatic (heat not supplied), which it will usually be, the water will cool. It is necessary to calculate the rate at which the temperature falls as the air is passed through the water. It is then possible to calculate the rate at which the organic is stripped, taking account of the decrease in Henry's Law constant as the temperature falls.

A procedure for making the calculations is given in Appendix 1. Calculations were made for benzene ( $H(20^\circ\text{C}) = 278 \text{ atm}$ ), o-nitrotoluene ( $H(20^\circ\text{C}) = 6 \text{ atm}$ ) and nitrobenzene ( $H(20^\circ\text{C}) = 0.9 \text{ atm}$ ). Benzene stripped so fast that the calculations were of no interest. The results for o-nitrotoluene are shown on Figures 5-3 and 5-4. The results for nitrobenzene are shown on Figure 5-5. In each case the starting solution was saturated at  $20^\circ\text{C}$ .

TABLE 5-1. ISOTHERMAL BATCH STRIPPING

<u>Compound</u>	<u>Temp.</u> <u>°C</u>	<u>H (atm)</u>	<u>Vapor Passed</u> <u>(V/W)</u>	<u>Fraction Remaining</u> <u>(1-F<sub>R</sub>)</u>
Benzene	10	213	0.011	0.1
			0.022	0.01
			0.032	0.001
	20	278	0.0083	0.1
			0.017	0.01
			0.025	0.001
o-Nitrotoluene	10	4.23	0.54	0.1
			1.1	0.01
			1.6	0.001
	20	6.0	0.38	0.1
			0.77	0.01
			1.15	0.001
Nitrobenzene	10	0.53	1.3	0.5
			3.0	0.2
	20	0.91	0.76	0.5
			1.8	0.2
			2.5	0.1

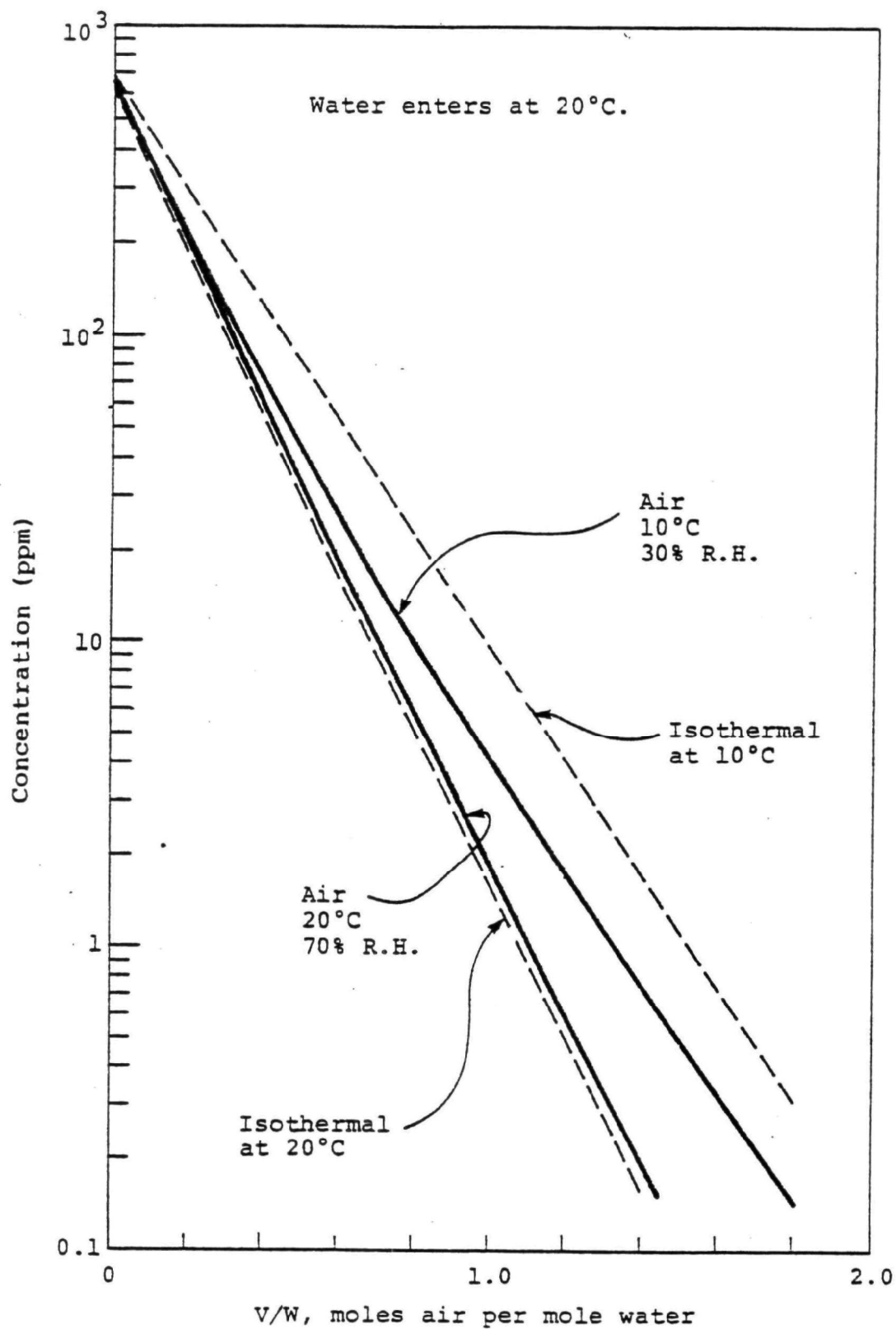


Figure 5-3. Affect of air quantity on residual concentration when stripping o-nitrotoluene.

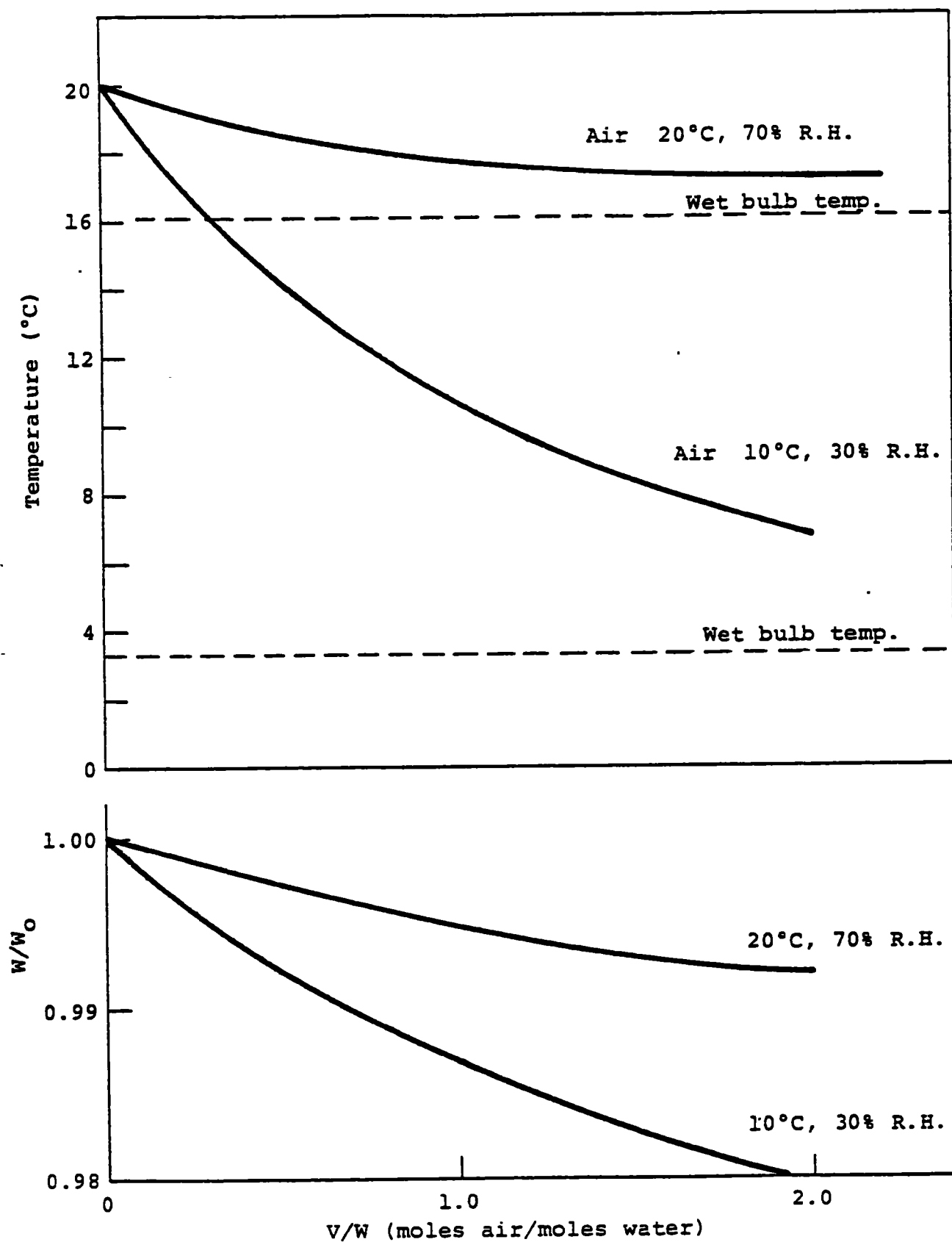


Figure 5-4. Water temperature and water vaporized in batch stripping.

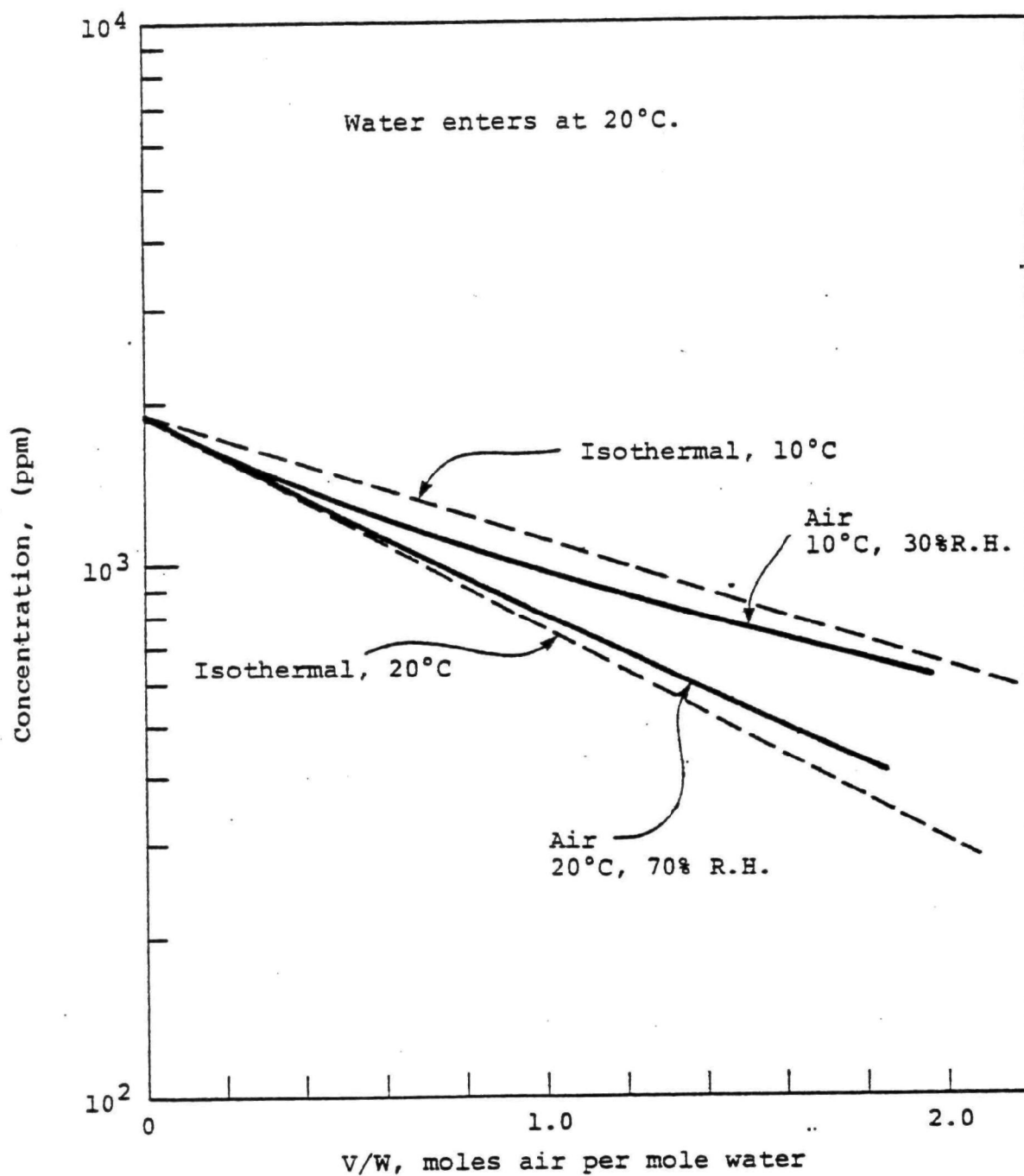


Figure 5-5. Effect of air quantity on residual concentration when stripping nitrobenzene.

o-Nitrotoluene ( $H(20^{\circ}\text{C}) = 6 \text{ atm}$ ,  $H(10^{\circ}\text{C}) = 4.2 \text{ atm}$ ) is moderately easy to strip. The concentration is reduced to 1/1000th of the initial concentration by 1.1 moles air per mole water when the air is warm and quite saturated ( $20^{\circ}\text{C}$  and 70% relative humidity) and by 1.7 moles air per mole water when the air is colder and dryer ( $10^{\circ}\text{C}$  and 30% RH). For comparison benzene ( $H(10^{\circ}\text{C}) = 213 \text{ atm}$ ) is very easy to strip and the concentration is reduced to 1/1,000th of the initial concentration by about 0.3 moles air per mole water. The warm air case for o-nitrotoluene is satisfactorily duplicated by the isothermal calculation at  $20^{\circ}\text{C}$ . However, the cold air case is not really well duplicated by an isothermal calculation at  $20^{\circ}\text{C}$  (the water temperature) nor at  $10^{\circ}\text{C}$  (the air dry bulb temperature). The answer lies in between at about  $15^{\circ}\text{C}$ .

The reason for the  $15^{\circ}\text{C}$  average can be seen from the graph of water temperature on Figure 5-4. Water starts at  $20^{\circ}\text{C}$  and, when the concentration is reduced to 1/1,000th after passing 1.7 moles air per mole water, the water temperature has dropped to  $9^{\circ}\text{C}$ . A temperature of  $15^{\circ}\text{C}$  is a good average.

Nitrobenzene ( $H(20^{\circ}\text{C}) = 0.9 \text{ atm}$  and  $H(10^{\circ}\text{C}) = 0.5 \text{ atm}$ ) is very difficult to strip. The concentration is not even reduced to 1/10th by 2 moles air per mole water (see Figure 5-5). The warm air case is reasonably calculated by a  $20^{\circ}\text{C}$  isothermal calculation and the cold air case is reasonably calculated by a  $10^{\circ}\text{C}$  isothermal calculation. The temperature curve which is independent of the organic pollutant (discussed later), shows why these average temperatures are reasonably satisfactory (see Figure 5-4).

The key to the calculation is to determine the temperature curve. With the temperature known the stripping can be calculated using the isothermal equation with  $H$  evaluated at a reasonable average temperature or  $H$  can be allowed to vary stepwise as the temperature falls.

A general calculational procedure is given in Appendix 1. With a dilute solution stripping the organic has a negligible effect on the temperature of the solution which is overwhelmingly dependent on the amount of water which vaporizes. It is, therefore, possible to illustrate what the computer does by a simple hand calculation.

The one essential formula is a means of calculating the humidity of saturated air,  $H$  moles water per mole dry air.

$$H(\text{satd.}) = \frac{y_w}{1-y_w}$$

where

$$y_w = \frac{P_w}{P_{\text{total}}} = \frac{1}{14.7} \exp \left[ 21.158 - \frac{5920.8}{t^{\circ}\text{C} + 273} - 6.977 \times 10^{-3} (t^{\circ}\text{C} + 273) \right]$$

Now consider water at 20°C. Air enters at 10°C and 30% relative humidity.  
For air saturated at 10°C

$$H(\text{satd.}) = 0.0121 \text{ moles water/moles air}$$

$$\text{so } H(30\%) = 0.00363$$

Suppose we have 1 mole water and allow 0.2 moles air to pass through it. For a first try assume the air leaves at 20°C.

$$H(\text{satd.}, 20^{\circ}\text{C}) = 0.0233$$

so 0.2 moles of air take out

$$0.2 (0.0233 - 0.00363) = 0.003934 \text{ moles water.}$$

The latent heat of water at 20°C is 10,550 cal/mole and the specific heat is 18 cal/(mole)(°C) so the water temperature falls

$$10,500 \times 0.003934 / 18 = 2.31^{\circ}\text{C.}$$

Since the air must leave at the average water temperature we cannot assume that the air leaves at 20°C. We will assume that the air leaves at 19°C.

$$H(\text{satd. } 19^{\circ}\text{C}) = 0.0219$$

so 0.2 moles of air take out

$$0.00365 \text{ moles water}$$

and the water cools by 2.13°C. Since the water starts at 20°C and ends at 17.9°C, our assumption of an average exit air temperature of 19°C is satisfactory. The calculation must now be repeated for the next 0.2 moles of air with the water starting at 18°C.

The calculation is tedious and may not be worthwhile. The discussion of how much detail is needed is deferred to Section 5.8 in which we describe continuous adiabatic stripping.

### 5.5 Isothermal, Counter-Current Stripping and Estimation of Height of an Equivalent Theoretical Plate

The theory of packed towers is given in all chemical engineering texts on mass transfer and only a brief summary is given here.



### Summary of the Theory

A packed tower is pictured on Figure 5-6. The tower is  $Z$  meters high and  $S \text{ m}^2$  in cross section. Dirty water enters at a rate  $W$  moles/hr and, because we assume that water does not evaporate, water leaves at the same rate. The vapor rate (steam or air) is  $V$  moles/hr.  $x$  and  $y$  are mole fractions of the contaminant in the liquid and vapor phases.

The overall rate of mass transfer of contaminant from water to vapor at height  $Z$  of the tower can be described by the equation

$$dJ, (\text{Flux in moles/hr}) = K_L a (x - x^*) S dZ = -W dx = V dy$$

In this equation

- $S dZ$  is the differential volume of the tower,  $\text{m}^3$ ,
- $a$  is the interfacial area caused by the packing,  $\text{m}^2/\text{m}^3$  of tower,
- $K_L$  is the mass transfer coefficient,  $\text{moles}/(\text{hr})(\text{m}^2)$   
(unit mole fraction driving force measured in the water)
- $x$  = mole fraction of contaminant in the water
- $x^*$  = mole fraction that would occur in the water if the water were in equilibrium with the vapor

We consider a tower at atmospheric pressure so

$$x^* = y/H$$

where

- $y$  = mole fraction of contaminant in the vapor at height  $Z$  of the tower
- $H$  = Henry's Law constant expressed in atmospheres

The differential equation for mass transfer can be written in integrated form as

$$\int_{x_{\text{out}}}^{x_{\text{in}}} \frac{dx}{x - y/H} = - \frac{K_L a S Z}{W}$$

Two equations are possible, one based on water concentrations and water flow, the other based on gas concentrations and gas flow. The choice is arbitrary but water concentrations are the more convenient.

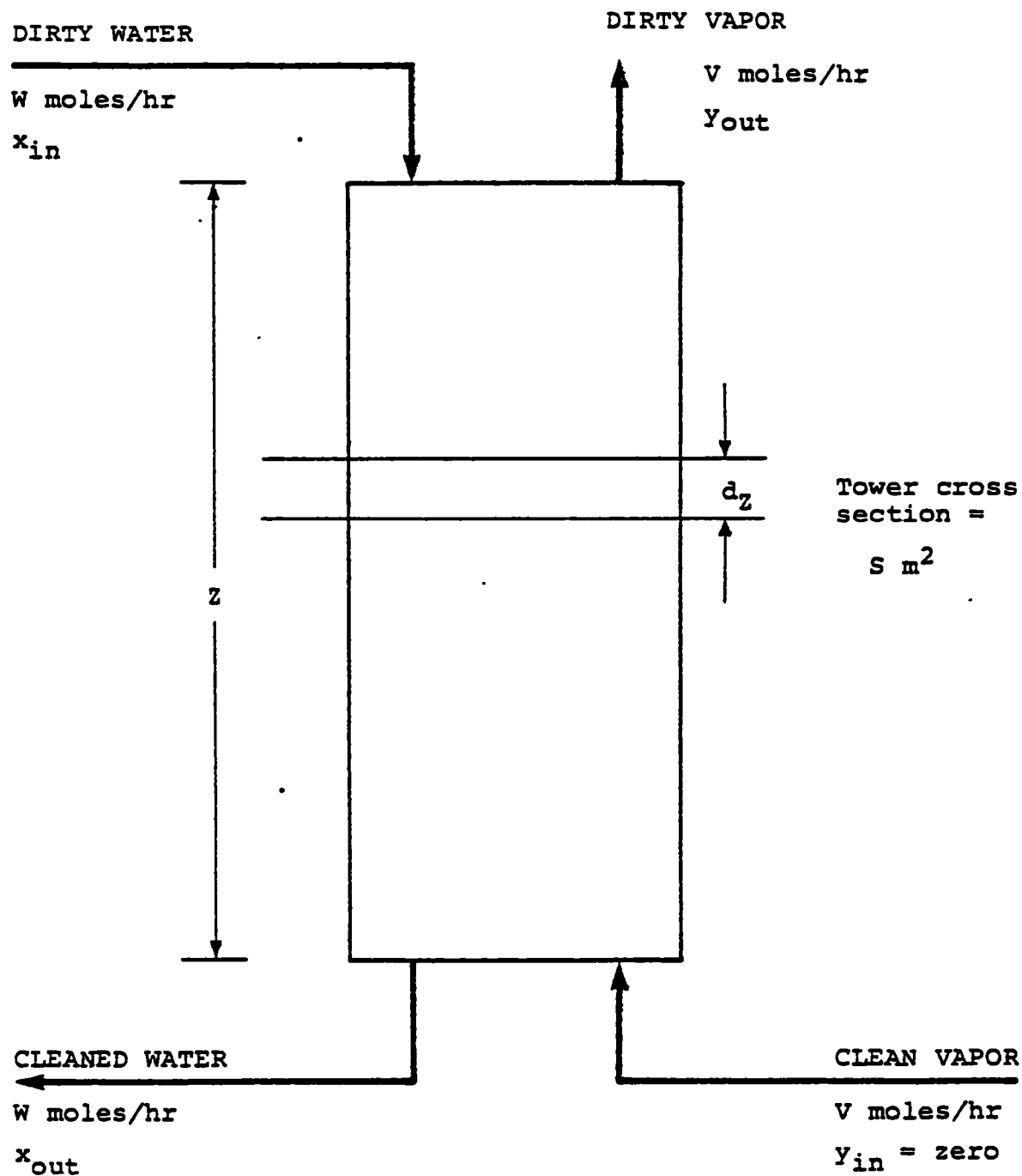


Figure 5-6. Nomenclature for a packed tower.

The integral on the left hand side of the above equation is called the number of transfer units, NTU. The bigger the difference between  $x_{in}$  and  $x_{out}$ , the larger is the number of transfer units needed to perform the stripping. Evaluation of NTU can, in general, be made by numerical integration of concentrations measured in the liquid and vapor at several points in an operating tower. Only a few points are needed and the use of Simpson's rule is usually adequate. However, in the particular case of interest here, where Henry's Law applies, direct integration is possible as discussed below.

The term

$$\frac{W}{K_L a S}$$

which has the dimensions of length, the same as  $Z$ , is called the height of a transfer unit. The larger  $K_L a$  the smaller is the height of packing needed to do a given transfer. The height of the tower is, from our definitions,

$$Z = HTU \times NTU$$

The height of a transfer unit and hence the mass transfer coefficient,  $K_L a$ , is determined experimentally by finding the number of transfer units in a tower of known height at constant water and vapor rates.

#### Direct Integration to Determine the Number of Transfer Units

Since  $Wdx = -Vdy = dJ$

the flux,  $J$ , is a linear function of  $x$  and of  $y$  and, because  $H$  is taken to be constant, of  $(x - y/H)$ . The slope of the line of plotting  $J$  against driving force (see nomenclature on Figure 5-6) is

$$\frac{d(x - y/H)}{dJ} = \frac{(x_{in} - y_{out}/H) - x_{out}}{J_{total}}$$

( $y_{in}$  has been taken as zero)

It is convenient to write

$$\begin{aligned} x_{in} - y_{out}/H &= \Delta_{top} \\ x_{out} &= \Delta_{bottom} \\ x - y/H &= \Delta \end{aligned}$$

Putting  $dJ = \Delta S dz$  gives

$$\frac{d\Delta}{K_L a \Delta S} = \frac{\Delta_{\text{top}} - \Delta_{\text{bot.}}}{J_{\text{tot}}} dz$$

which can be integrated to give

$$\frac{\ln \frac{\Delta_{\text{top}}}{\Delta_{\text{bot}}}}{\Delta_{\text{top}} - \Delta_{\text{bot}}} = \frac{K_L a S Z}{J_{\text{tot}}}$$

The lefthand side is the reciprocal of the logarithmic-mean driving force (LMDF) and we can write

$$J_{\text{tot}} = K_L a S Z (\text{LMDF})$$

Since  $J_{\text{tot}} = W (x_{\text{in}} - x_{\text{out}})$   
we can also write

$$\begin{aligned} Z &= \frac{W(x_{\text{in}} - x_{\text{out}})}{K_L a S (\text{LMDF})} \\ &= \text{HTU} \times \frac{x_{\text{in}} - x_{\text{out}}}{\text{LMDF}} \end{aligned}$$

from which it follows that

$$\text{NTU} = \frac{x_{\text{in}} - x_{\text{out}}}{\text{LMDF}}$$

#### Design of a Packed Tower

For a given job,  $W$ ,  $x_{\text{in}}$ ,  $x_{\text{out}}$  are given. The vapor rate,  $V$ , is chosen and  $y_{\text{out}}$  calculated from the material balance

$$W(x_{\text{in}} - x_{\text{out}}) = Vy_{\text{out}}$$

It is then possible to calculate LMDF and NTU. A suitable packing is chosen for which  $K_L a$  is known for the water and vapor rates chosen. HTU and  $Z$  can then be found. Repeated calculations will give the trade-off between decreasing the vapor rate,  $V$ , and increasing the tower height,  $Z$ . Additional calculations can show the advantage of different packings.

#### Height of an Equivalent Theoretical Plate

We find it easiest to visualize stripping towers in terms of equivalent theoretical plates which are used in the following sections. The number of

theoretical plates to do a given separation does not depend on the equipment. The height of packing to do a given separation depends on the choice of packing. We need, therefore, to find the height of packing equivalent to a theoretical plate (HETP).

The height of a tower ( $Z = \text{HETP}$ ) which is equivalent to a theoretical plate is the height which causes the vapor leaving at the top to be in equilibrium with liquid leaving at the bottom. That is

$$y_{\text{out}}/H = x_{\text{out}}$$

In this case

$$1/\text{LMDF} = \frac{\ln \frac{x_{\text{in}} - y_{\text{out}}/H}{x_{\text{out}} - y_{\text{in}}/H}}{(x_{\text{in}} - x_{\text{out}}) - (y_{\text{out}} - y_{\text{in}})/H}$$

becomes

$$\frac{\ln \frac{x_{\text{in}} - x_{\text{out}}}{x_{\text{out}} - y_{\text{in}}/H}}{(x_{\text{in}} - x_{\text{out}}) - x_{\text{out}} + y_{\text{in}}/H}$$

Now the mass balance is

$$W(x_{\text{in}} - x_{\text{out}}) = -V(y_{\text{in}} - y_{\text{out}})$$

so

$$y_{\text{in}}/H = x_{\text{out}} - \frac{W}{VH}(x_{\text{in}} - x_{\text{out}})$$

If we write

$$R(\text{range}) = x_{\text{in}} - x_{\text{out}}$$

$$1/\text{LMDF} = \frac{\ln \frac{R}{WR/VH}}{R - WR/VH}$$

$$\text{and } \text{NTU} = R/\text{LMDF} = \frac{\ln VH/W}{1 - W/VH} = \frac{\ln W/VH}{W/VH - 1}$$

$$\text{HETP} = \text{HTU} \times \frac{\ln W/VH}{W/VH - 1}$$

### 5.6 Number of Equilibrium Stages in Continuous Isothermal Stripper.

In this section we find the number of equilibrium, or theoretical, stages to do a job of stripping. The theory will then be used to classify pollutants by ease of stripping.

Theoretical stages are very useful for comparing pollutants, but they are not, in any sense, realizable pieces of equipment. A real tower may contain packing, in which case one has to know the height of an equivalent theoretical plate. Or a real tower may contain plates. But a real plate is not an equilibrium stage and one has to know the plate efficiency to find the number of real plates when the number of theoretical plates is known. The difference is large. Efficiencies may be as low as 0.5 and two real plates may be required to do the work of one theoretical plate.

#### The General Formula

A simple stripping tower is shown on Figure 5-7. Dirty water at a rate  $F$  moles/hr and having a mole fraction  $x_{in}$  of contaminant enters at the top. Clean stripping vapor at a rate  $S$  moles/hr enters at the bottom. Cleaned water at a flow rate  $W$  moles/hr and having a mole fraction  $x_{out}$  of contaminant leaves at the bottom.  $x_{out}$  is specified. Dirty vapor at a flow rate  $V$  moles/hr and having a mole fraction  $y_{out}$  of contaminant leaves at the top. For the moment we consider only the cases where

$$F = W \text{ and } V = S$$

That is, the cases in which water is neither evaporated nor condensed. If steam is the stripping vapor the feed enters at the boiling point. If air is the stripping vapor, it enters saturated at the water temperature. Our assumption is an approximation but the concentrations of contaminants are so low that removal of contaminant has negligible effect on the flow rate of the total streams.

A mass balance for the contaminant around the bottom of the tower including the first plate gives

$$\text{Mass IN} = \text{Mass OUT}$$

$$Wx_2 = Wx_1 + Vy_1$$

A similar mass balance including the second plate gives

$$Wx_3 = Wx_1 + Vy_2$$

If the  $(n-1)$ th plate is included

$$Wx_n = Wx_1 + Vy_{n-1}$$

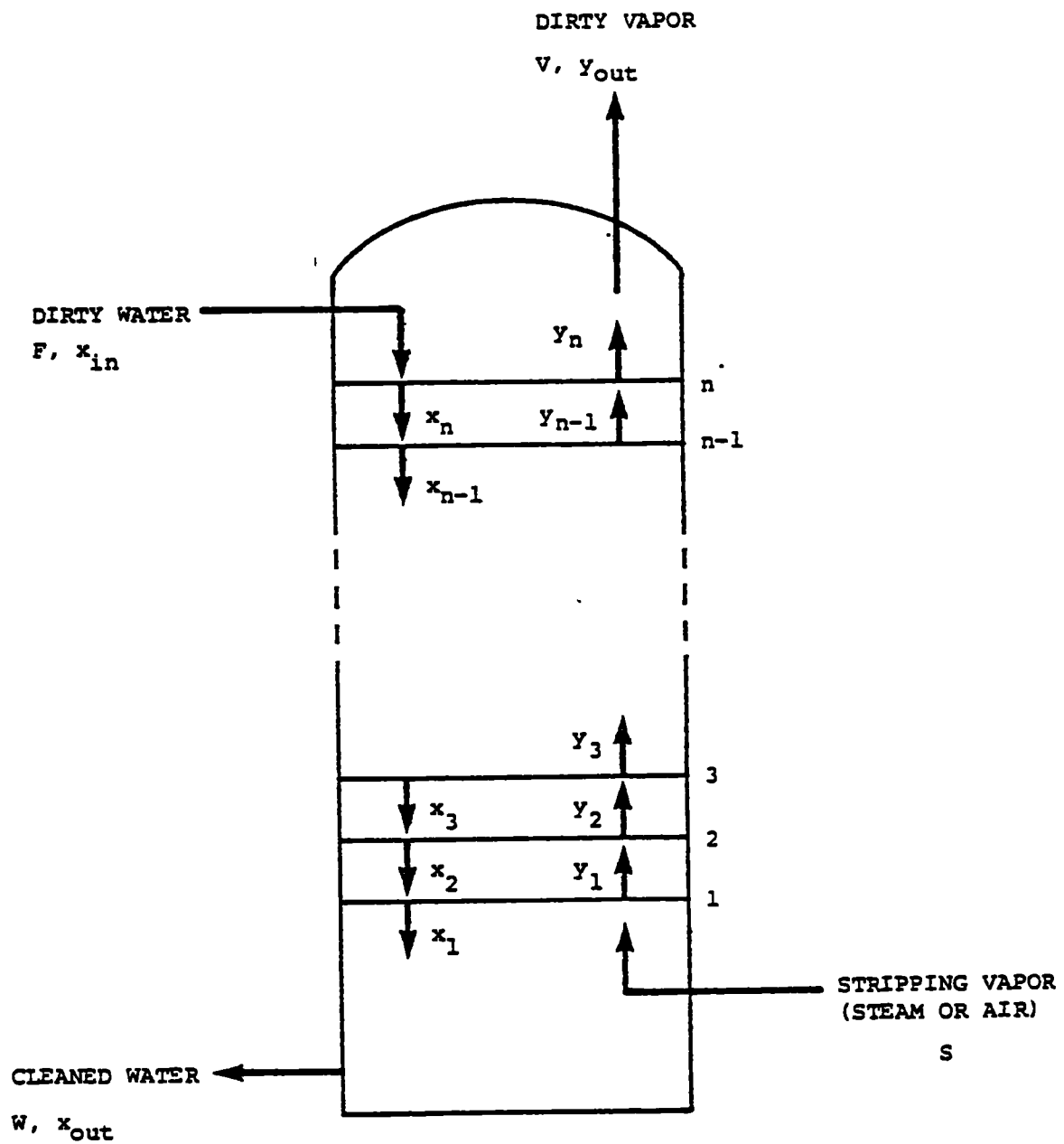


Figure 5-7. Simple stripping tower showing equilibrium stages.

This equation has two unknowns,  $x_n$  and  $y_{n-1}$  and another equation is needed. We assume that the vapor and liquid leaving a plate are in equilibrium so

$$y_n = (H/P) x_n = Kx_n$$

Equilibrium plates are theoretical plates. Actual stripping column plates do not reach equilibrium. The approach to equilibrium is discussed in Section 6.

The calculation of the number of theoretical plates can now be made.

$$x_2 = x_1 + (V/W) y_1 = x_1 + (VK/W) x_1$$

$$\begin{aligned} x_3 &= x_1 + (V/W) y_2 = x_1 + (VK/W) x_2 \\ &= x_1 + (VK/W) x_1 + (VK/W)^2 x_1 \end{aligned}$$

and so on;

$$x_n = x_1 [1 + (VK/W) + (VK/W)^2 + \dots + (VK/W)^{n-1}]$$

To sum the series inside [], let

$$T = 1 + VK/W + (VK/W)^2 + \dots + (VK/W)^{n-1}$$

$$\text{then } (VK/W) T = VK/W + \dots + (VK/W)^n$$

$$\text{and } ((VK/W) - 1) T = (VK/W)^n - 1.$$

so

$$\frac{x_1}{x_n} = \frac{(VK/W) - 1}{(VK/W)^n - 1}$$

If  $n$  is the number of plates to reduce the feed concentration,  $x_{in} = x_{n+1}$ , to the effluent concentration,  $x_{out} = x_1$ , then

$$\begin{aligned} \frac{x_{out}}{x_{in}} &= \frac{(VK/W) - 1}{(VK/W)^{n+1} - 1} \\ n + 1 &= \frac{\ln[(x_{in}/x_{out})(VK/W - 1) + 1]}{\ln(VK/W)} \end{aligned}$$

#### Sample Calculation

Suppose that epichlorohydrin is to be steam stripped at 1 atmosphere.  $H = 20$  atm and  $K = H/P = 20$ . Let the feed concentration be 5,140 mg/l. Since M.W. = 92.53,

$$\begin{aligned} x_{in} &= 5,140 \times 18 \times 10^{-6} / 92.53 = 10^{-3} \\ \text{we choose } x_{out} &= 10^{-6} \text{ (5.14 mg/l)} \end{aligned}$$



Let  $V/W = 0.15$ ;

$VK/W = 3$

$$n + 1 = \frac{\log [(3-1) 10^3 + 1]}{\log 3}, n = 5.9$$

Additional calculations give

$V/W$	$n$
0.1	9
0.125	7
0.15	6
0.2	5
0.3	4

Note that the larger the value of  $V/W$ , that is the more steam used for stripping, the smaller the number of plates. This is always true of stripping columns; the designer has a tradeoff between a lot of plates or a lot of stripping vapor.

#### The Range of Practical Operability

There are practical limits on the number of theoretical plates and the mass of stripping vapor used. For the purposes of this report we will make the following assumptions:

- (1) the column is limited to 20 theoretical plates
- (2) the desired ratio  $x_{out}/x_{in}$  is between  $10^{-2}$  and  $10^{-4}$
- (3) stripping vapor rates will lie on the range

$$0.1 \leq V/W \leq 0.3 \text{ for steam}$$

$$0.75 \leq V/W \leq 2.5 \text{ for air}$$

Assumption number 3 is discussed in the following subsection.

The relationship between  $VK/W$ ,  $n$  and  $x_{in}/x_{out}$  is graphed on Figure 5-8.  $VK/W$  must be greater than one. Given the upper limit on the number of plates of 20 plates a low value of  $VK/W = 1.1$  may just be useful. There is a general lower limit of  $VK/W = 1.2$ . As  $VK/W$  is increased fewer plates are needed. When  $VK/W = 10$  about 3 plates will do the job. Increasing  $VK/W$  above 10 does not give a large decrease in the number of plates and will probably not be worth paying for the extra vapor. In general we will use

$$1.2 \leq VK/W \leq 10$$

with a probable extreme of

$$1.1 \leq VK/W \leq 100.$$

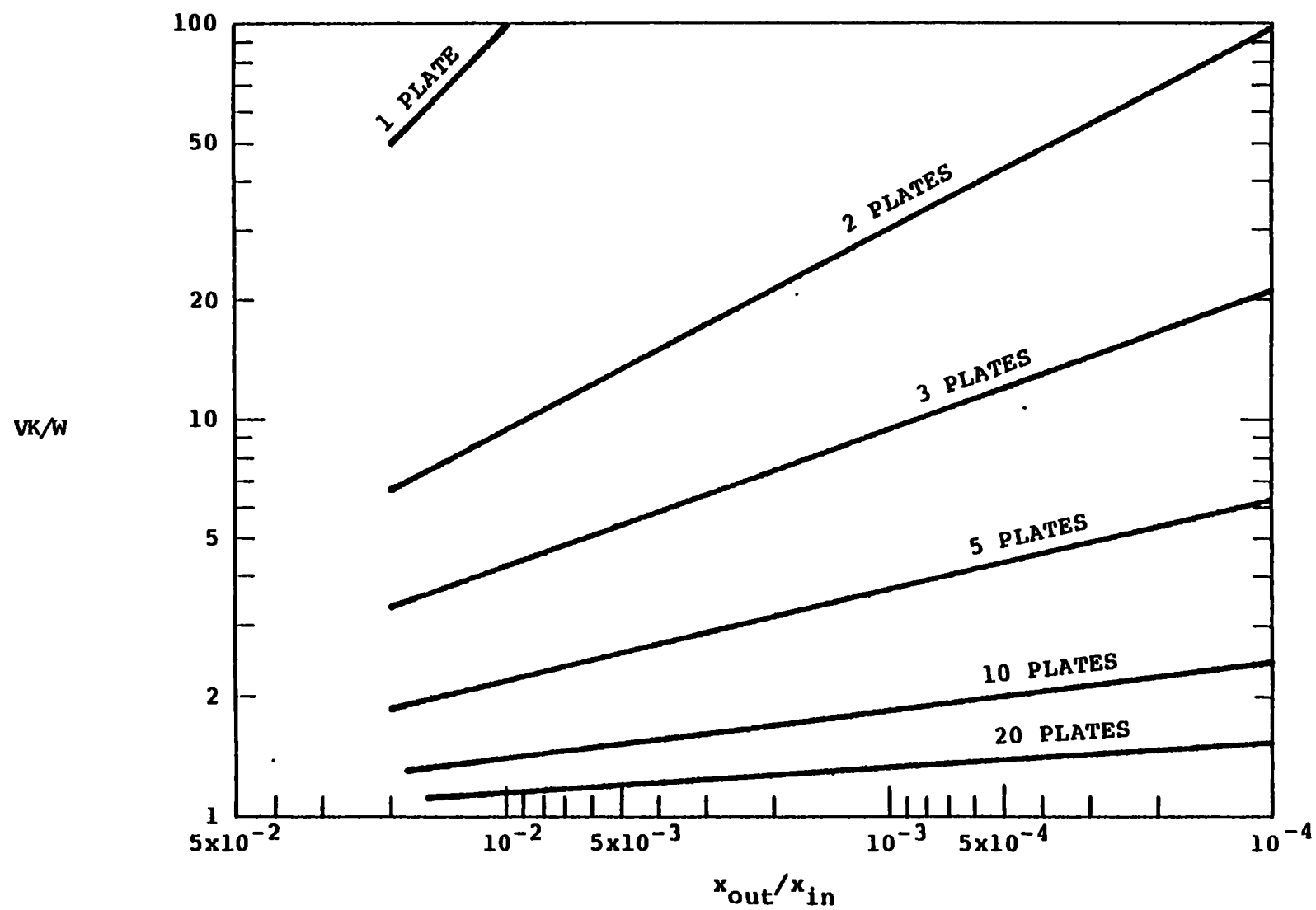


Figure 5-8. Relationship between stripping vapor rate and number of plates.

### Choice of Vapor Rate

To compare air and steam some discussion is necessary. The general equations for the horsepower needed to drive a gas compressor are<sup>32</sup>:

$$HP = WH / (33,000e)$$

$$H = \left( \frac{Z_s + Z_d}{2} \right) \left( \frac{1,545}{M_w} \right) T_i \left[ \frac{r^{(n-1)/n} - 1}{(n-1)/n} \right]$$

$$(n-1)/n = (k-1)/k$$

HP is horsepower = 0.745 KW

W is gas flow in lb/min

H is polytropic head (ft-lb)/lb

e is polytropic efficiency = 0.77

$Z_s, Z_d$  are compressibility factors for suction and discharge, = 1

$M_w$  is molecular weight

$T_i$  is suction temperature, = 530 °R (°R = 460 + °F)

r is the compression ratio = 1.3 for 4.5 psi pressure drop

k is ratio of specific heats = 1.40

(k-1)/k for air = 0.286

From this equation, for a temperature of 70°F and compression ratio of 1.3, the energy to supply S lb moles of air for stripping is 0.11 S kw-hrs.

The energy to supply S lb moles of steam for stripping is about 18,000 S Btu. To compare steam to air one must convert kw-hrs to Btu. The simple energy conversion for generating electricity is 10,000 Btu/kw-hr which makes 1 lb mole of steam equivalent in energy to 16.4 lb moles of air. However, the value of 1 kw-hr is usually closer to the value of 20,000 Btu which makes 1 lb mole of steam of equal value to about 8 lb moles of air. (An example of value is if electricity is worth 4¢/kw-hr and low pressure steam worth \$2/10<sup>6</sup> Btu).

Note that for steam the vapor/liquid ratio is the same for weight rates of flow as for molar rates of flow. For air

$$\text{vapor/liquid weight ratio} = 1.6 \text{ vapor/liquid molar ratio}$$

In practice steam strippers (such as ammonia strippers) usually operate with steam rates between 0.1 and 0.3 times the feed rate, that is

$$V/W = 0.1 \text{ to } 0.3$$

just as we have chosen.

Air strippers, in the form of cooling towers usually operate with gas/liquid weight rates in the range 0.75 to 2, that is molar rates in the range 0.47 to 1.25, so our chosen molar ratios are on the high side and have been chosen to give equal cost between steam and air.

#### 5.7 Pollutants Classified by Ease of Stripping

At this point it is possible to classify compounds by the ease with which they can be stripped. The classification is given on Table 5-2. Consider compounds listed as very easily stripped. These are all compounds for which it is practical and simple to obtain  $VK/W \geq 10$ . For steam we chose  $V/W = 0.1$  so  $K(100^\circ\text{C}) \geq 100$ . For air we chose  $V/W = 0.75$  so  $K(20^\circ) \geq 13$ . Since  $K = H/P$  and we usually are concerned with atmospheric pressure strippers,  $H = K$  if  $H$  is expressed in atmospheres.

The "difficult to strip" compounds have  $VK/W \geq 1.2$ ;  $V/W$  for steam = 0.3 and  $K(\text{steam}) \geq 4$ . A few compounds with  $H(100^\circ\text{C})$  between 2 and 4 atm. have been classified as "very difficult to strip". These compounds require more than 20 plates. Compounds with  $H(100^\circ\text{C}) < 2$  atm have been classified "cannot be stripped".

Of a total of 185 listed toxic pollutants Table 5-2 shows that

68 are very easily stripped or decompose in water.

36 are strippable with various degrees of difficulty.

48 cannot be stripped or probably cannot.

33 lack information.

For most compounds the classification was independent of the choice of stripping vapor (air or steam). A few compounds, marked \*, are classified for air stripping and will be more easily stripped by one category higher if steam stripping is used.

Touhill (Ref. 37 page 235) has compiled a large list of reports on stripping. Our classification is compatible with this list.

#### 5.8 Adiabatic Continuous Stripping with Air

If the water does not enter the top of the column at the wet bulb temperature of the air, then water is stripped and, in the usual case

Table 5-2 TOXIC POLLUTANTS CLASSIFIED BY EASE OF STRIPPING

Very easily stripped

$H(100^{\circ}\text{C}) > 100 \text{ atm}$

$H(20^{\circ}\text{C}) > 13 \text{ atm}$

5-4 <sup>+</sup>	2-Chloroethyl vinyl ether
7-13	Triethylamine
9-1	Benzene
9-2	Chlorobenzene
9-3	1,2-Dichlorobenzene
9-4	1,3-Dichlorobenzene
9-5	1,4-Dichlorobenzene
9-6	1,2,4-Trichlorobenzene
9-7	Hexachlorobenzene
9-8	Ethylbenzene
9-10	Toluene
9-15	Benzyl chloride
9-16	Styrene
9-18	Xylenes
10-1	2-Chloronaphthalene
**	10-3 Benzo(b)fluoranthene
**	10-4 Benzo(k)fluoranthene
**	10-5 Benzo(a)pyrene
	10-9 Acenaphthene
**	10-12 Chrysene
**	10-13 Fluoranthene
	10-15 Naphthalene
	10-17 Pyrene

+ the left hand column are the code numbers used in the Treatability Manual and in Appendix 3.

\*\* probably, but data is poor

(very easily stripped - continued)

11-1	Aroclor 1016
11-2	Aroclor 1221
11-3	Aroclor 1232
11-4	Aroclor 1242
11-5	Aroclor 1248
11-6	Aroclor 1254
11-7	Aroclor 1260
12-1	Methyl chloride
12-2	Methylene chloride
12-3	Chloroform
12-4	Carbon tetrachloride
12-5	Chloroethane
12-6	1,1-Dichloroethane
12-7	1,2-Dichloroethane
12-8	1,1,1-Trichloroethane
12-9	1,1,2-Trichloroethane
12-10	1,1,2,2-Tetrachloroethane
12-11	Hexachloroethane
12-12	Vinyl chloride
12-13	1,2-Dichloropropane
12-14	1,3-Dichloropropene
12-15	Hexachlorobutadiene
12-16	Hexachlorocyclopentadiene
12-17	Methyl bromide
12-18	Dichlorobromomethane
12-19	Chlorodibromomethane
12-20	Bromoform
12-21	Dichlorodifluoromethane
12-22	Trichlorofluoromethane
12-23	Trichloroethylene

(very easily stripped - continued)

- 12-24 1,1-Dichloroethylene
- 12-25 1,2-Trans-dichloroethylene
- 12-26 Tetrachloroethylene
- 12-27 Allyl chloride
- 12-30 Ethylene dibromide
- 13-20 Heptachlor
- 13-25 Toxaphene
- \*\* 13-37 Isoprene
- 13-46 Carbon disulfide
- 14-4 Amyl acetate
- 14-5 n-Butyl acid
- 14-13 Vinyl acetate
- 15-1 Methyl mercaptan
- 15-3 Cyclohexane

Easily stripped

H(100°C) 20 to 100 atm.

H(20°C) 2 to 13 atm.

- 5-3 Bis(2-chloroisopropyl) ether
- 7-7 Acrylonitrile
- 9-19 Nitrotoluene
- 10-10 Acenaphthylene
- 10-14 Fluorene
- 10-16 Phenanthrene
- 13-8 Aldrin
- 13-9 Dieldrin
- 13-24 Chlordane
- \*\* 13-26 Captan
- 14-1 Acetaldehyde
- \*\* 14-16 Acrolein
- 14-18 Propylene oxide

\*\* probably, but data is poor

Intermediate

H(100°C) 8 to 20 atm.

H(20°C) 1 to 2 atm.

- 5-2 Bis(2-chloroethyl) ether
- 8-5 Pentachlorophenol
- 8-6 2-Nitrophenol
- 9-9 Nitrobenzene
- 9-11 2,4-Dinitrotoluene
- 9-12 2,6-Dinitrotoluene
- 10-11 Anthracene
- 12-31 Epichlorohydrin
- \*\* 13-12 4,4'-DDD
- 13-21 Heptachlor epoxide

Difficult to strip

H(100°C) 4 to 8 atm.

H(20°C) 0.5 to 1 atm.

- \* 8-2 2-chlorophenol
- \* 8-3 2,4-Dichlorophenol
- \* 8-4 2,4,6-Trichlorophenol
- 14-15 Crotonaldehyde
- 15-4 Isophorone

\* this is for air; a higher category for steam

\*\* probably, but data is poor



Very difficult to strip

H(100°C) 2 to 4 atm.

- 6-2 Diethyl phthalate
- 8-1 Phenol
- \* 8-10 2,4-Dimethylphenol
- 8-13 4,6-Dinitro-o-cresol
- 8-14 Cresol
- \* 9-17 Quinoline
- \* 14-3 Allyl alcohol

Cannot be stripped

- 5-7 Bis(2-chloroethoxy) methane
- 6-1 Dimethyl phthalate
- 7-10 Ethylenediamine
- 8-7 4-Nitrophenol
- 8-8 2,4-Dinitrophenol
- 8-9 Resorcinol
- 9-13 Aniline
- 9-14 Benzoic acid
- 10-8 Benzo(ghi) perylene
- 13-2 Endosulfan sulfate
- 13-13 Endrin
- \*\* 13-18 Diurone
- 13-22 Carbofuran
- \*\* 13-28 Coumaphos
- 13-29 Diazinon
- 13-30 Dicamba
- 13-31 Dichlobenil
- 13-32 Malathion
- 13-33 Methyl parathion
- 13-34 Parathion

\* this is for air; a higher category for steam

\*\* probably, but data is poor

(cannot be stripped - continued)

13-35 Guthion  
13-38 Chlorpyrifos  
13-39 Dichlorvos  
13-41 Disulfoton  
13-43 Mexacarbate  
13-44 Trichlorfon  
14-2 Acetic acid  
14-6 Butyric acid  
14-7 Formaldehyde  
14-8 Formic acid  
14-12 Propionic acid  
14-14 Adipic acid  
15-2 Dodecyl benzenesulfonic acid  
15-5 Strychnine  
15-7 Zinc phenol sulfonate

Poor data, but probably difficult to strip

5-5 4-Chlorophenyl phenyl ether  
6-3 Di-n-butyl phthalate  
6-5 Bis(2-ethylhexyl) phthalate  
7-1 N-nitrosodimethylamine  
7-2 N-nitrosodiphenylamine  
7-5 3,3'-Diphenylhydrazine  
7-6 1,2-Diphenylhydrazine  
13-11 4,4'-DDT  
13-17 Kepone  
13-40 Diquat  
13-42 Mevinphos  
14-9 Fumaric acid  
14-10 Maleic acid

Poor data; better data worth obtaining as may be strippable

5-6 4-Bromophenyl phenyl ether  
6-4 Di-n-octyl phthalate  
6-6 Butyl Benzyl phthalate  
7-3 N-nitrosodi-n-propylamine  
7-4 Benzidine  
7-9 Diethylamine  
8-12 p-Chloro-m-cresol  
10-2 Benz(a)anthracene  
10-6 Indeno(1,2,3-cd)pyrene  
10-7 Dibenzo(ah)anthracene  
13-10 4,4'-DDE  
13-27 Carbaryl  
14-17 Furfural  
15-6 2,3,7,8-Tetrachlorodibenzo-p-dioxin

Data inadequate for comment

7-8 Butylamine  
7-11 Monoethylamine  
7-12 Monomethylamine  
7-14 Trimethylamine  
12-28 2,2-Dichloropropionic acid  
13-1  $\alpha$ -Endosulfan  
13-3  $\beta$ -Endosulfan  
13-4  $\alpha$ -BHC  
13-5  $\beta$ -BHC  
13-6  $\delta$ -BHC  
13-7  $\gamma$ -BHC  
13-14 Kelthane  
13-15 Naled  
13-16 Dichlone  
13-19 Endrin aldehyde

(data inadequate for comment - continued)

13-23 Mercaptodimethur

13-36 Ethion

13-45 Propargite

14-11 Methyl methacrylate

Decompose in water

5-1 Bis(chloromethyl) ether

12-29 Phosgene

which is adiabatic, the water cools. The Henry's Law constant varies from plate to plate as the temperature varies. It is a simple matter to estimate the fraction stripped on each plate once the temperature is known on each plate. The method for calculating the temperature on each plate is given in Appendix 2 and some results are discussed below. But a word of caution is required.

We calculate the temperature, and hence the fraction of organic stripped, on a theoretical or equilibrium plate. When a real tower is built, it is important to remember that real plate efficiencies may not be the same for water and for the organic. Also, the height of packing equivalent to a theoretical plate is not the same for water and for the organic. The rate of stripping of water is controlled by the rate of diffusion of water vapor from the interface through the air layer and into the main body of the air. The rate of stripping of volatile organics is controlled by the rate of diffusion from the main body of the water to the interface; this is always an order of magnitude slower than the diffusion rate in the gas if the organic is easily strippable. The liquid side resistance for organic stripping has been illustrated in Section 5.2 where evaporation from a lake was described.

Figure 5-9 shows a typical warm water such as might be fed to a cooling tower with typical mid-season air (not the height of summer nor the middle of winter). The feed rates are 0.37 moles air/mole water. In one theoretical plate the water temperature falls by 13°C (24°F) which is about the way that cooling towers are designed. In fact our calculations suggest that the usual cooling tower is close to one theoretical plate. In the next 5 plates the temperature only falls an additional 10°C. For this situation stripping of an organic can reasonably be estimated using the isothermal stripping equation with  $H$  evaluated in the temperature range 30 to 35°C. It is worth pointing out that in this particular application, air is heated as it rises. The hot air near the top of the tower has a much greater capacity for water vapor than the entering air. Thus most of the water which evaporates does so on the top plate and the biggest temperature drop for the water occurs on the top plate.

On Figure 5-10 is shown the effect of stripping a cold water with a rather dry air. Note, as before, that on the top one or two plates the temperature of the water falls rapidly, but that on the lower plates the

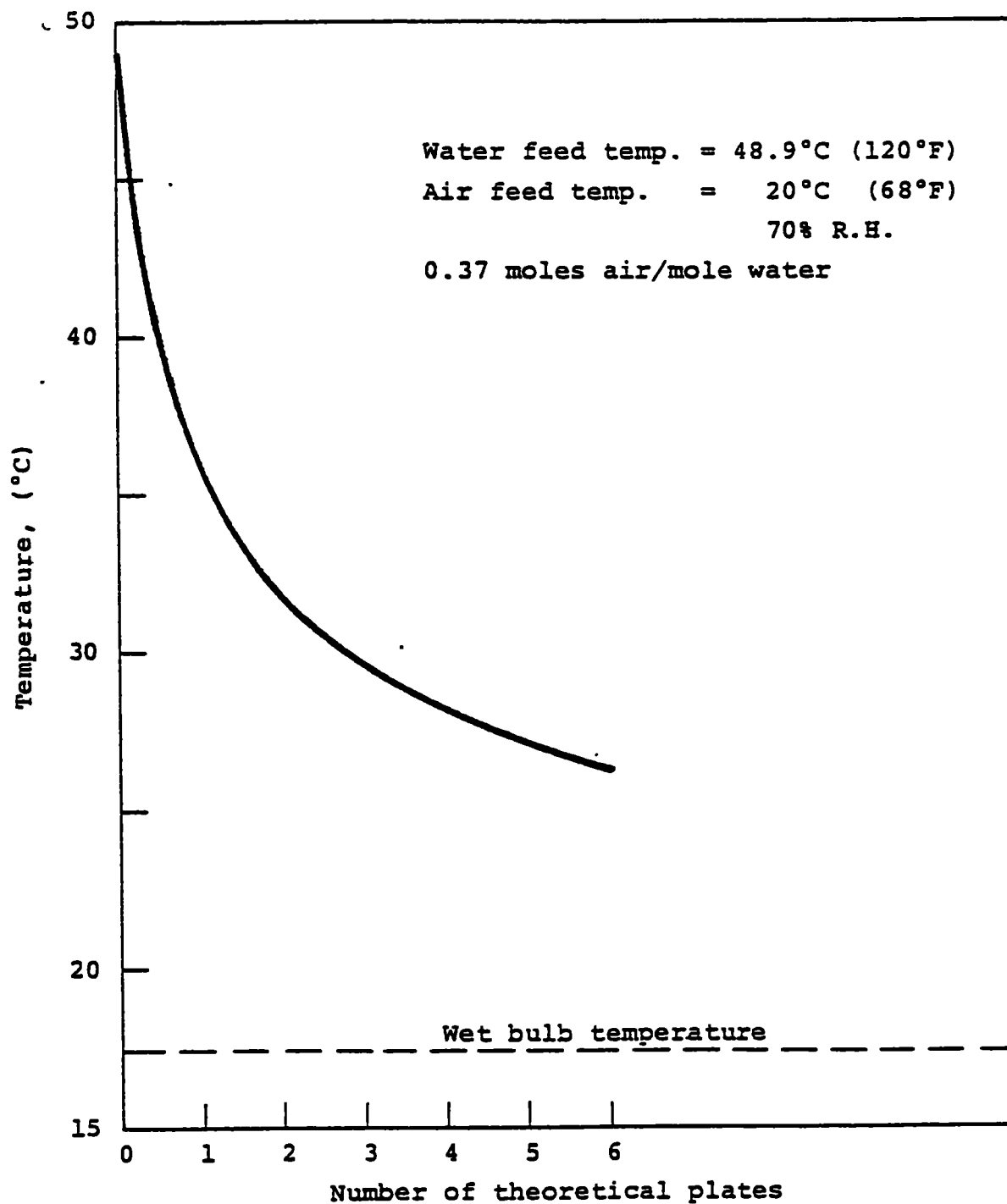


Figure 5-9. Water temperature when stripping warm water with air.

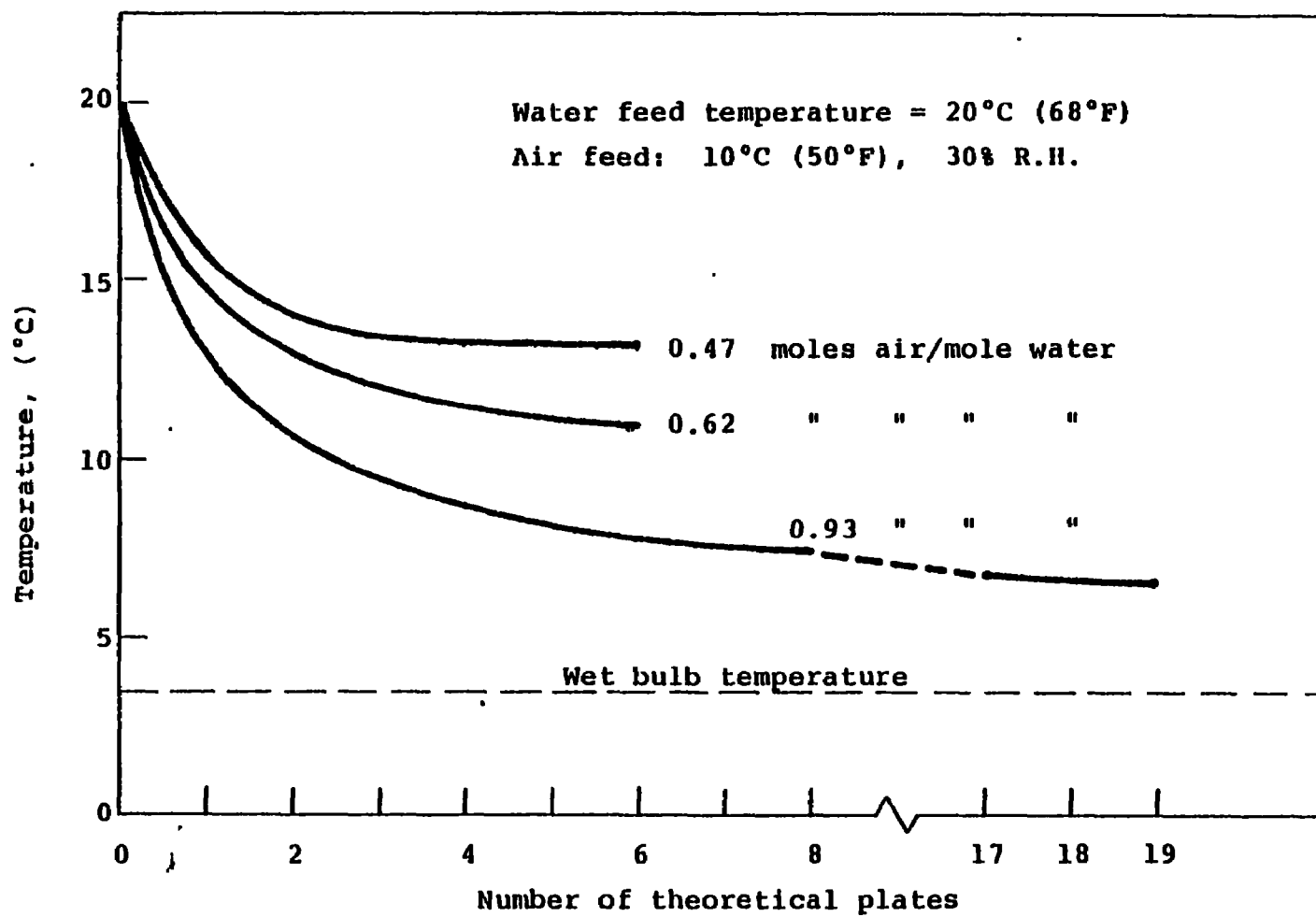


Figure 5-10. Water temperature when stripping cold water with air.

water temperature changes very little. The approach to the air wet bulb temperature is very slow. The vapor pressure of water falls off rapidly as the temperature falls and so, therefore, does the driving force for mass transfer. The fractional approach to the wet bulb temperature falls rapidly as the water temperature falls.

While it is not difficult to calculate the temperature on each plate with a computer, it is very tedious to do by hand. We have not made enough estimates to find any reliable simplification. The best we can suggest, and it is not accurate, is that isothermal stripping be assumed to occur at a temperature which is the arithmetic mean of the feed water temperature and the air wet bulb temperature.

When the air rate is about doubled from 0.47 moles/mole water to 0.93 moles/mole water, the steady temperature on all but about the top three plates is reduced from about 13.2°C to about 7.5°C. The stripping of an organic depends on the group  $VK/W = (\text{at one atmosphere}) VH/W$ . Returning to a previous example of nitrobenzene we find that

$$\begin{aligned} H(13.2^{\circ}\text{C}) &= 0.632 \\ \text{and} \quad H(7.5^{\circ}\text{C}) &= 0.454 \end{aligned}$$

This means that doubling the air rate multiplies the fraction stripped by  $(0.454 \times 2)/0.632 = 1.4$ . There is a positive advantage to increasing the air flow, but it is a much smaller advantage than might have been thought to occur if the effect of temperature had been neglected. Each case will have to be estimated but our preliminary conclusion is that varying the air rate is not an efficient way to control a stripping tower.

But some control is necessary. The temperature and humidity of the air vary from hour to hour, day to night and season to season. If the organic is very easily stripped, the variations in the air conditions will matter very little. A small overdesign will guarantee satisfactory stripping under all likely conditions. For example, Recon Systems, Inc., of Somerville, NJ, have designed and installed very reliable stripping columns for such extremely volatile contaminants as trichloroethane and trichloroethylene. There is, however, a lot of difficulty in designing a column for stripping a less volatile compound. Consider o-nitrotoluene as an example. Take 99% stripping at  $V/W = 1$ .



<u>Temp (°C)</u>	<u>Number of Theoretical Plates</u>
20	2.6
15	2.8
10	3.2
5	6.6

The column can be designed for 5°C water on the coldest winter days and the column will be twice as high as needed in summer time, or the column can contain about 3 plates and satisfactory stripping will not be obtained on the coldest days.

One alternative is to use steam stripping, which is not dependent on the weather, for difficult-to-strip compounds. The energy cost will not be higher, but the capital cost is usually higher than for air strippers because the influent and effluent water must be heat exchanged for reasonable energy efficiency.

A possible alternative, briefly explored below, is to mix steam and air.

#### 5.9 The Use of Air-Steam Mixtures

If, to air at 10°C, 30% RH, is added 0.0085 moles steam/mole air, which is the quantity of steam needed to saturate the air at 10°C, the dry bulk temperature rises to 10.9°C and the wet bulb temperature is raised from 3.4°C to 10°C.

Now suppose that a stripping column does a good job when the air and water enter at about 20°C, the air has a high humidity and the air to water rate is 0.93 moles air/mole water. As is shown on Figure 5-10, if the air temperature and humidity drop to 10°C, 30% RH, the mean water temperature approaches 7.5°C. However, adding a little steam (less than 1% of the air) raises the mean water temperature to about 11°C. In our example for o-nitrotoluene we have seen that an increase in temperature from 7.5 to 11°C can divide the plates necessary to do a given stripping job by about 1.7°.

The addition of a little steam when the air is dry seems to be a good way of controlling a stripping tower.

#### 5.10 The Effect of Recirculating the Water

Water can be recirculated to obtain more net stripping in a tower of lower height or less plates. The penalty is a bigger tower cross section and pumping costs. In a cooling tower, as pictured on Figure 5-11, recirculation of the water is the normal practice.

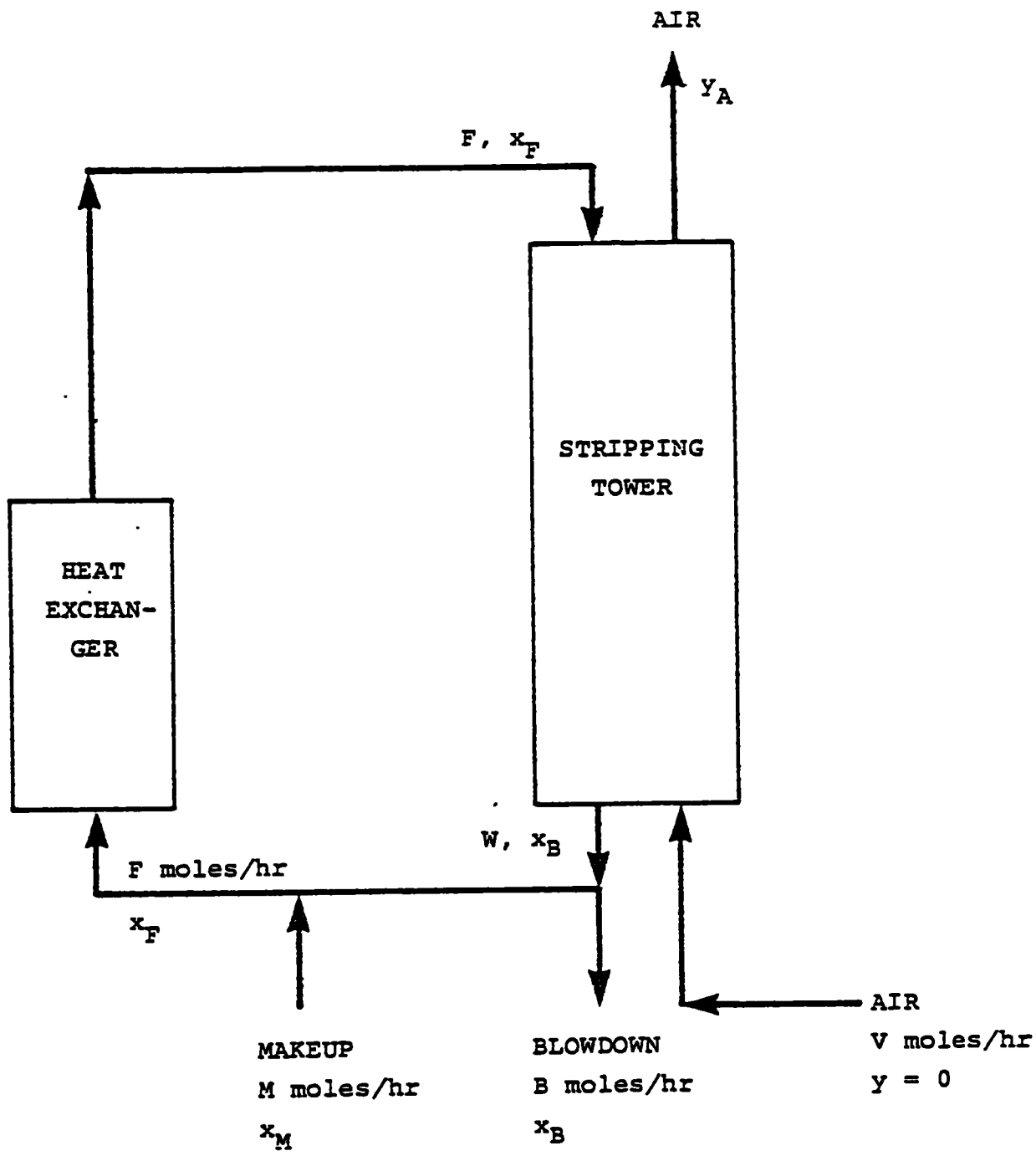


Figure 5-11. Stripping in a cooling tower with circulated water.

Suppose that in a single pass down the stripping tower the feed concentration at the top,  $x_F$ , is reduced to a bottoms concentration,  $x_B$ , and we write

$$\frac{x_B}{x_F} = r \quad (\text{the removal})$$

$r$  is a function of the water rate, air rate and Henry's Law constant, but does not depend on  $x_F$ . It is important to remember that if water is evaporated, as it usually is, the concentration of organic may increase in a pass through the tower if the organic is not volatile; that is  $r$  can be greater than 1.

Now let suffix,  $n$ , denote the conditions of the circulating water entering or leaving the tower for the  $n$ 'th time. Water leaving the tower from the  $n$ 'th pass is circulated and enters the tower for the  $(n+1)$ 'th pass.

$$Fx_{F, n+1} = Wx_{B, n} - Bx_{B, n} + Mx_M$$

so

$$Fx_{B, n+1}/r = (W - B) x_{B, n} + Mx_M$$

but,

$$F = W - B + M$$

or

$$W - B = F - M$$

so

$$Fx_{B, n+1}/r = (F - M) x_{B, n} + Mx_M$$

If, now, one puts

$$F/M = R \quad (\text{the recycle ratio})$$

$$x_{B, n+1} = \frac{(R-1)r}{R} \cdot x_{B, n} + \frac{r}{R} x_M$$

The average number of passes made by the water is, in fact, equal to the recycle ratio, that is

$$n = R$$

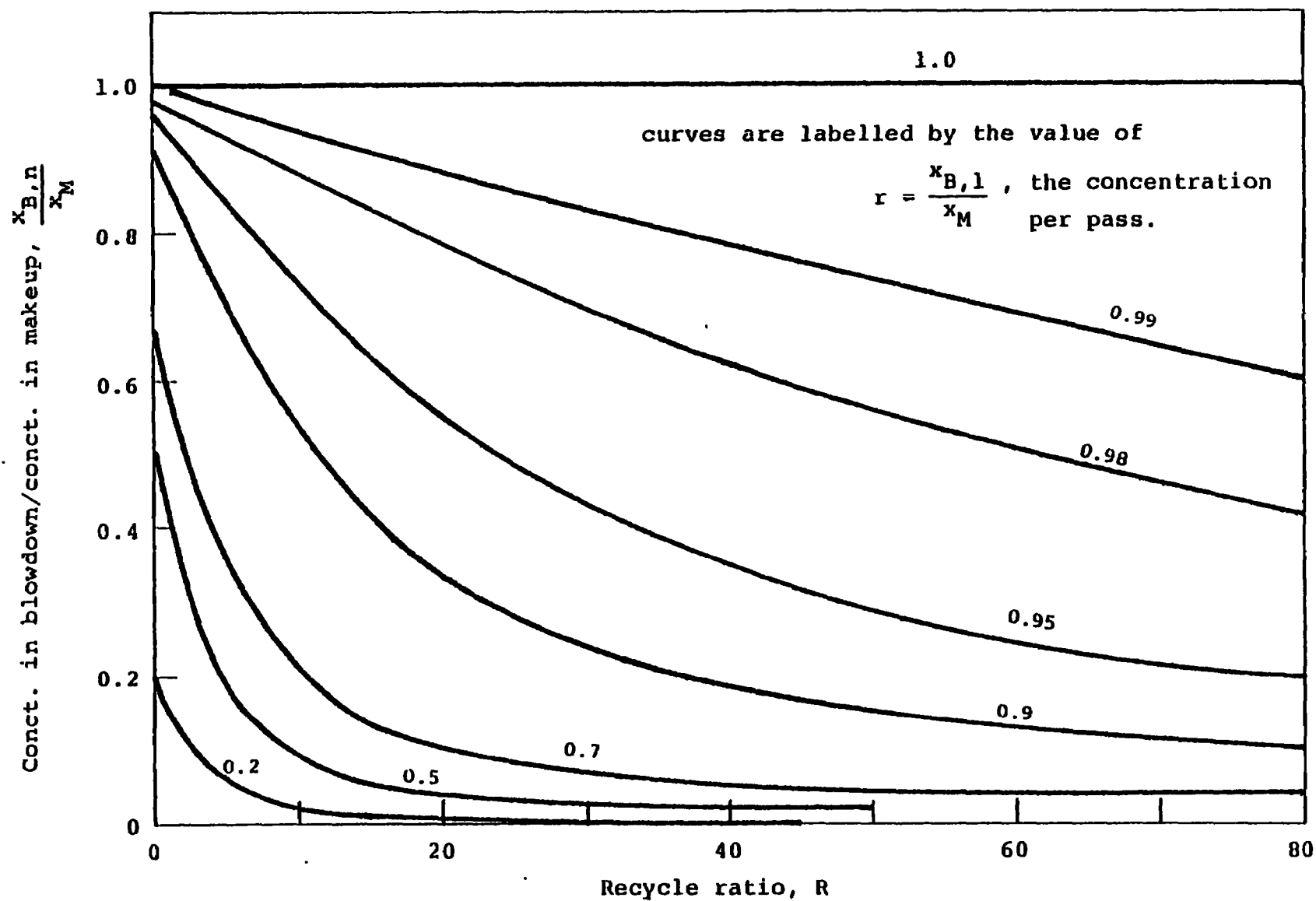


Figure 5-12. The effect of recycle when the organic is stripped.

When the system is first started up the concentration everywhere is the makeup concentration  $x_M$ ; that is

$$\begin{aligned}x_{F,1} &= x_M \\x_{B,1} &= r x_M\end{aligned}$$

It follows that

$$x_{B,2} = \frac{(R-1)r^2}{R} x_M + \frac{r}{R} x_M$$

$$x_{B,3} = \frac{(R-1)^2 r^3}{R^2} x_M + \frac{(R-1)r^2}{R^2} x_M + \frac{r}{R} x_M$$

$$x_{B,4} = \frac{(R-1)^3 r^4}{R^3} x_M + \frac{(R-1)^2 r^3}{R^3} x_M + \frac{(R-1)r^2}{R^2} x_M + \frac{r}{R} x_M$$

or

$$\frac{x_{B,n}}{x_M} = \frac{(R-1)^{n-1} r^n}{R^{n-1}} + \frac{(R-1)^{n-2} r^{n-1}}{R^{n-1}} + \frac{(R-1)^{n-3} r^{n-2}}{R^{n-2}} + \dots + \frac{r}{R}$$

Also

$$\begin{aligned}\frac{(R-1)r}{R} \frac{x_{B,n}}{x_M} &= \frac{(R-1)^n r^{n+1}}{R^n} + \frac{(R-1)^{n-1} r^n}{R^n} + \frac{(R-1)^{n-2} r^{n-1}}{R^{n-1}} \\&\quad + \dots + \frac{(R-1)r^2}{R^2}\end{aligned}$$

and

$$1 - \frac{(R-1)r}{R} \cdot \frac{x_{B,n}}{x_M} =$$

$$\frac{r}{R} + \frac{(R-1)^{n-1} r^n}{R^{n-1}} - \frac{(R-1)^{n-1} r^n}{R^n} - \frac{(R-1)^n r^{n+1}}{R^n}$$

Putting

$$n = R$$

and consolidating gives

$$\frac{x_{B,n}}{x_M} = \frac{r + \frac{(R-1)R^R}{R^{R-1}}(1-r)}{R(1-r) + r}$$

A numerical investigation of the above equation shows that for nearly any recycle ( $R \geq 2$ ) if an important amount of stripping occurs per pass so  $r$  is small ( $r \leq$  approx 0.2) it is sufficiently accurate to write

$$\frac{x_{B,R}}{x_M} = \frac{r}{R} = \frac{1}{R} \frac{x_{B,1}}{x_M}$$

for

$$\begin{aligned} R &\geq 2 \\ r &\leq 0.2 \end{aligned}$$

For larger values of  $r$  the equation is graphed on Figure 5-12. So long as  $r < 1$ , the concentration in the blowdown falls rapidly as the recycle ratio increases to 10 or 20 and then falls much less with additional recycling. (A cooling tower has a recycle ratio on the order of 50).

If  $r = 1$ , recycle has no effect. It must be remembered that when  $r = 1$ , the concentration of the organic caused by evaporation of water is exactly offset by the stripping of the organic.

When  $r > 1$ , Figure 5-13 shows that the concentration increases rapidly with the recycle ratio.

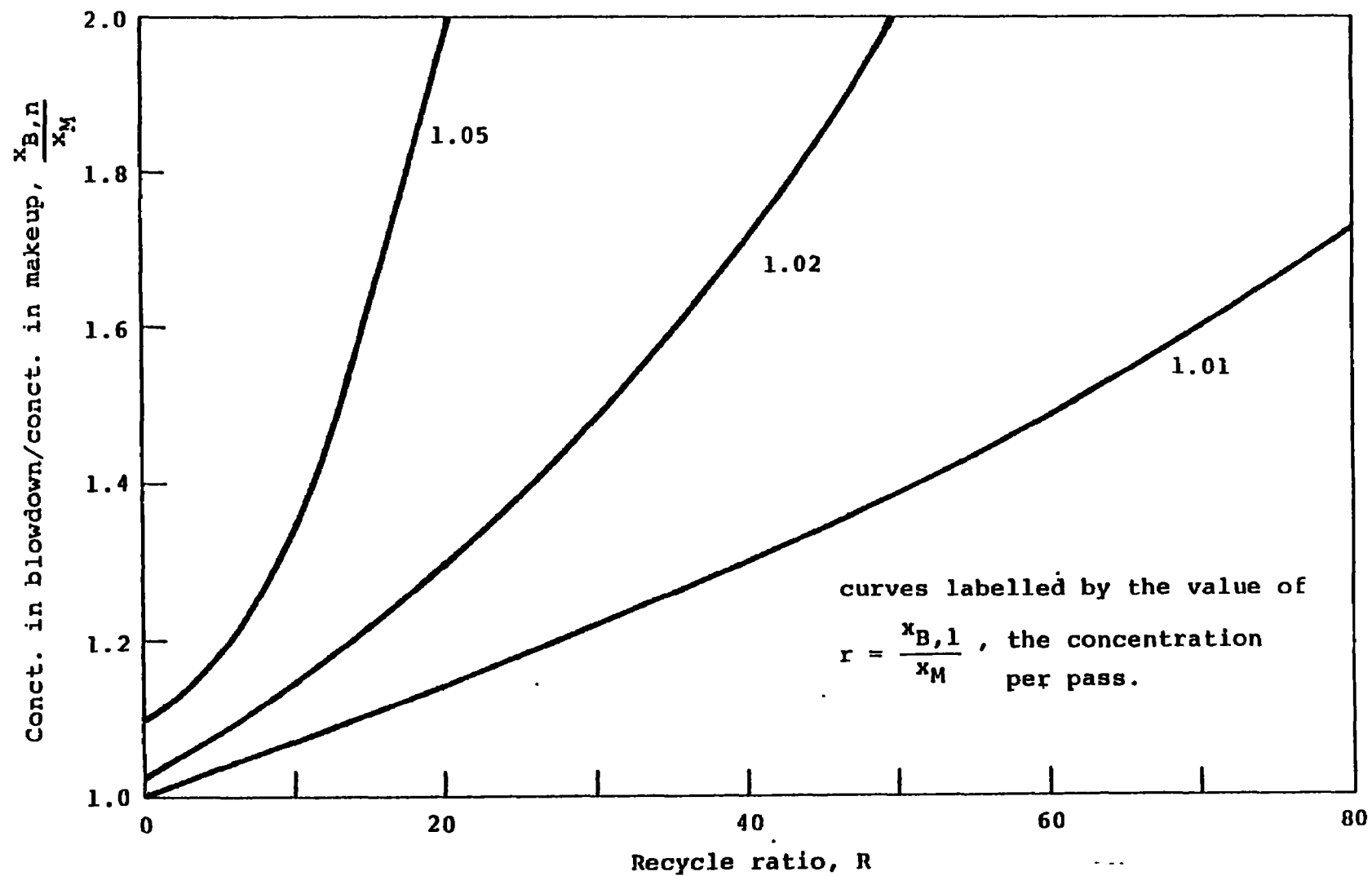


Figure 5-13. The effect of recycle when the organic is concentrated.

## 6. THE EFFICIENCY OF STRIPPING EQUIPMENT

### 6.1 Introduction and Summary

The development of the theory of stripping was based on the number of theoretical plates required to do a given job of stripping. The number of theoretical plates depends on the Henry's Law constant (and therefore on the temperature) and on the ratio of water to vapor rates. The number of real plates depends on their efficiency. We have found no data on the efficiency of distillation trays or of packed towers for stripping toxic pollutants, and very little data on stripping of any sort. All available data comes from distillation and absorption. The efficiency for distillative separation of miscible organic liquids is usually in the range 60% to 100%. But the efficiency for absorption of  $\text{CO}_2$  into water can be as low as 1%. Stripping of an insoluble organic is probably more related to adsorbing an insoluble gas than to a distillation, and we cannot assume a high efficiency.

A theoretical (equilibrium) stage can be obtained in practice. It is the usual method for measuring the Henry's Law constant experimentally. However, the liquid must be at least 60 cm deep, the vapor must be well distributed and in fine bubbles and the flow rates must be low. It is never economical to use multiple theoretical stages and cheaper, less efficient equipment is always used.

The factors which affect the efficiency of a bubble-cap tray and of a packed bed are listed in Sections 6.2 and 6.3. It is reported that efficiency decreases as the Henry's Law constant increases. This phenomenon is explained on the basis of the two film theory of mass transfer. For most stripping jobs of interest here the liquid film will be the controlling resistance. This is shown in Section 6.4. Finally a few reasons for choosing particular equipment are given in Section 6.5.

The design of any particular piece of equipment is not given here; in particular, the sizing of equipment to the correct capacity is not discussed, nor do we describe the determination of optimum liquid and vapor rates and of pressure drop. Designs are best made from manufacturers' design manuals after the type of equipment has been chosen.

### 6.2 Factors Affecting the Efficiency of a Bubble Cap Tray

Real trays do not reach equilibrium and a real tower requires more trays to perform a given degree of stripping than the calculated number of theoretical stages. One way to define tray efficiency is to use an overall efficiency,  $E^o$ , defined as



$$E^* = \frac{\text{Number of theoretical stages required}}{\text{Number of actual trays required}}$$

The overall efficiency has been found to depend on the following factors (as summarized by Gilliland<sup>2</sup> and the Chemical Engineers Handbook<sup>16</sup>).

Viscosity. Efficiency increases as the liquid viscosity decreases. Different authors have found different expressions for the dependence but the variation is approximately

$$E^* \text{ is proportional to } (\text{viscosity})^{-n}$$

where n is 0.7 to 0.9

so the effect is large. Since the viscosity of water decreases from 0.89 centipoise at 25°C to 0.28 at 100°C there will be an important increase in efficiency with temperature.

Liquid Depth. The efficiency increases as the depth of liquid on the tray is increased. The price is an increased pressure drop.

Vapor Rate. The efficiency is not much dependent on vapor rate up to the point where frothing and entrainment occur. Entrainment causes liquid to be mixed backwards up the tower and the efficiency to decrease.

Liquid Rate. Since liquid on a bubble-cap tray flows across the vapor (see Figure 6-2 below), it is possible for there to exist more than one equilibrium stage on a tray. Insofar as an increased liquid rate causes more back mixing in the liquid, the efficiency falls somewhat as the liquid rate increases. The effect is dependent on tray design.

Henry's Law Constant. The efficiency decreases as the Henry's Law constant increases. This is a most important consideration in the design of strippers because we are most often concerned with compounds having a high Henry's Law constant. The effect of Henry's Law constant cannot be understood in terms of intimacy of contact between vapor and liquid, as the preceding factors have been. The effect is caused by the controlling resistance to mass transfer being increasingly due to the rate of diffusion of the organic through the liquid as the Henry's Law constant increases. A preliminary understanding was given in Section 5-2 where evaporation from a lake was considered.

The overall efficiency is not a useful tool for understanding resistances to mass transfer and it is customary to use an efficiency called a Murphree efficiency,  $E_{MV}$  which is defined as

$$E_{MV} = \frac{y_i - y_o}{y_i - y_e^*}$$

where

$y_i$  = vapor composition entering the plate  
 $y_o$  = vapor composition leaving the plate  
 $y_e^*$  = vapor composition in equilibrium with the liquid leaving the plate

Since, on a theoretical plate,  $y_o = y_e^*$ , the Murphree efficiency is a measure of

$$\frac{\text{depth of liquid on the plate}}{\text{depth of liquid on a theoretical plate}}$$

that is, the Murphree efficiency compares the depth of liquid on the plate to the height of liquid equivalent to a theoretical plate.

The mathematical model for defining a Murphree efficiency is just the same as the model used in Section 5.5 where the height of packing equivalent to a theoretical plate was determined. We will, therefore, next list the factors affecting the efficiency of a packed bed and then describe the two film theory for rate of mass transfer and show how the HETP increases and tray efficiency decreases as the Henry's Law constant gets larger.

### 6.3 Factors Affecting the Efficiency of a Packed Bed.

A packed bed is more efficient the smaller is the height of an equivalent theoretical plate (HETP) or the height of a transfer unit (HTU). HETP and HTU are affected by the following factors:

<u>HETP and HTU</u>	<u>Factor</u>
Decrease	<u>Viscosity decreases</u>
	<u>Liquid flow rate decreases</u>
Little change	<u>Vapor flow rate</u> alters below the flooding rate
Increases	<u>Henry's Law constant</u> or relative volatility increases

The increase in HETP with relative volatility has been given by Coulson and Richardson (Ref. 30 page 649) who quote both Murch and Ellis to show that HETP is directly proportional to relative volatility. An understanding of this phenomenon comes from the two film theory for mass transfer.

#### 6.4 Two Film Theory of Mass Transfer.

We assume that for an organic molecule to be stripped it must diffuse through a liquid film to the liquid-vapor interface where it transfers to the vapor phase. Then the organic molecule must diffuse through the vapor film to the main body of the vapor where it is swept away. The rate of mass transfer can, therefore, be written

$$J \text{ (moles/hr) (ft}^3 \text{ of packing)} \\ = k_L a (x - x_i) = k_G a (y_i - y) = K_L a (x - x^*)$$

where

- $a$  = interfacial area,  $\text{ft}^2/\text{ft}^3$  of packing
- $k_L$  = transfer rate through the liquid film, moles/(hr)  
( $\text{ft}^2$  of interface)(mole fraction driving force)
- $k_G$  = transfer rate through the vapor film, moles/(hr)  
( $\text{ft}^2$  of interface)(mole fraction driving force)
- $K_L$  = overall mass transfer rate for a liquid concentration driving force

The mole fractions  $x$ ,  $x_i$ ,  $x^*$ ,  $y$ ,  $y_i$  are defined on Figure 6-1.  
at equilibrium

$$y = Kx^*$$

$$y_i = Kx_i$$

Algebraic manipulation gives

$$\frac{1}{k_L} \left[ \frac{y_i - y}{x - x_i} \right] = \frac{1}{k_G} = \frac{K}{k_L} \left[ \frac{x_i - x^*}{x - x_i} \right]$$

Also

$$\frac{1}{K_L} = \frac{1}{k_L} \left[ \frac{x - x^*}{x - x_i} \right] = \frac{1}{k_L} \left[ \frac{x - x_i}{x - x_i} \right] + \frac{1}{k_L} \left[ \frac{x_i - x^*}{x - x_i} \right] = \frac{1}{k_L} + \frac{1}{Kk_G}$$

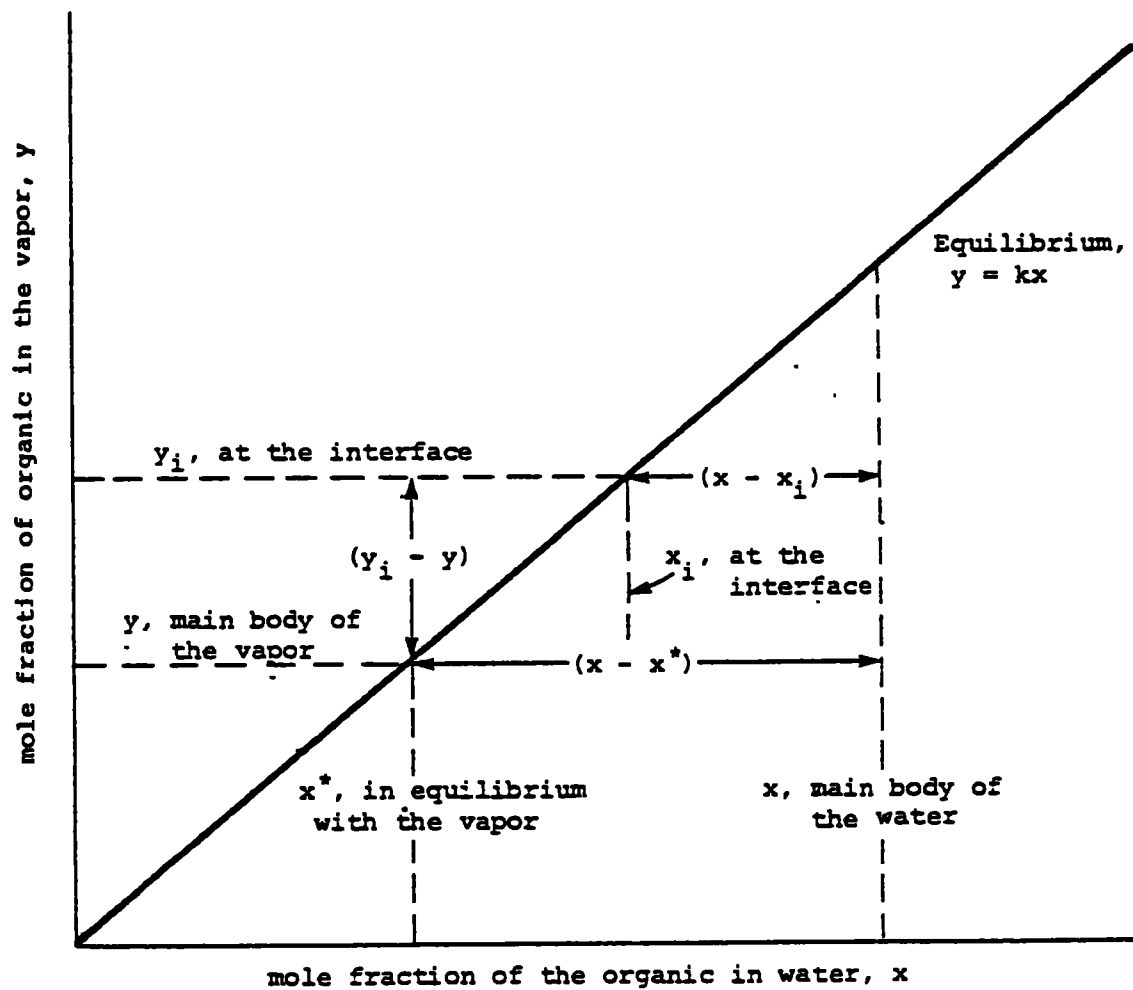


Figure 6-1. Two film theory of mass transfer.

or, at 1 atmosphere total pressure when

$K = H$  measured in atmospheres

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G}$$

In Section 5.5 it was shown that the height of a packed tower necessary to perform a desired job of stripping is given by

$$Z(\text{height}) = \text{NTU} \times \text{HTU}$$

In this equation NTU (the number of transfer units) is a function of

Inlet water concentration

Outlet water concentration

Henry's Law constant

NTU is a measure of the degree of stripping required. It does not depend on the tower packing or the flow rates. The higher the Henry's Law constant, the lower the NTU for the same reduction in water concentration.

HTU, the height of a transfer unit, is given by

$$\text{HTU} = \frac{W}{K_L a S}$$

where

$W/S$  is the moles of water flowing per hour per unit cross section of packing ( $\text{moles}/(\text{hr})(\text{ft}^2)$ ),

and

$K_L a$  is the overall mass transfer rate for a liquid concentration driving force defined above in the units  $\text{moles}/(\text{hr})(\text{ft}^3 \text{ of packing})$

HTU can be written

$$\text{HTU} = \frac{W}{Sa} \left( \frac{1}{k_L} + \frac{1}{Hk_G} \right)$$

and is seen to depend on the resistance to mass transfer in both the liquid and gas films.

The liquid film resistance is found by measuring the overall rate coefficient,  $K_L a$ , when absorbing a slightly soluble gas such as carbon dioxide or oxygen. The gas side resistance is small because pure gas is used and all the resistance is in the liquid film. It is found that

$k_L a$  is proportional to  $D^{0.5}$  and  $W^n$   
 where  $D$  is the molecular diffusivity (so transfer is more rapid with lower molecular weight molecules than with large molecules)  
 $W$  is the water rate  
 $n$  is 0.5 to 0.8

Although  $k_L a$  increases as the water rate increases,  $HTU = W/Sk_L a$  also increases as  $W$  increases; that is, more packing is needed to deal with the increased load even though transfer becomes faster.

The values of  $k_L a$  and  $HTU$  depend on the packing as well as on the properties of the gas being absorbed and on the flow rates, but the order of magnitude can be given. Water rates vary from a low of

5 gallons/(min) (ft<sup>2</sup> of cross section)

for very open slatted towers like cooling towers, to more than

60 gallons/(min) (ft<sup>2</sup>).

That is, water rates are in the range

2,500 lb/(hr) (ft<sup>2</sup>) to more than 30,000

or.

140 moles/(hr) (ft<sup>2</sup>) to more than 1,700

$HTU$  is in the range 1 to 5 ft with the larger values applying to higher flow rates<sup>16,34,35,36</sup>. The order of magnitude of  $k_L a$  is 100 to 400 moles/(hr) (ft<sup>3</sup>) (mole fraction).  $k_L a$  is sometimes expressed in dimensioned concentration units; since 1 ft<sup>3</sup> of water = 3.47 lb moles, 1 mole/(hr) (ft<sup>3</sup>) =  $\frac{1}{3.47}$  moles/(mole fraction) = (hr) (ft<sup>3</sup>) (moles/ft<sup>3</sup>).

Trulsson<sup>38</sup> has measured  $k_L a$  for adsorption and desorption of  $\text{CO}_2$  from air to deionized water in three plastic packings, Intalox saddles, Tellerettes and Plasdek (Munter's) Corp. He found  $k_L a$  to lie in the range 0.01 to 0.05  $\text{sec}^{-1}$  (125 to 625 moles/(hr)(ft<sup>3</sup>)(mole fraction)) with the value depending mainly on liquid load. The liquid load varied from 6 to 60 Kg/(m<sup>2</sup>)(sec) (10 to 100 gpm/ft<sup>2</sup>, 280 to 2,800 moles/(hr)(ft<sup>2</sup>)) and the higher loadings gave the higher values of  $k_L a$ .

The gas film resistance is found by evaporating water into an air stream or absorbing the very soluble gas, ammonia, from a dilute gas stream into water.  $k_G a$  varies with the gas rate to about the 0.8 power, and HTU is the same order of magnitude as for liquid film controlled systems. Thus  $k_G a$  will be the same order of magnitude as  $k_L a$  when the liquid and vapor rates are the same (as in air strippers) and  $k_G a$  may be as low as 0.1  $k_L a$  when the vapor rate is much lower than the liquid rate, as in a steam stripper. Since  $k_L a$  and  $k_G a$  are the same order of magnitude in air strippers, HTU for evaporating water is close to HTU for stripping which means that the difficulties in calculating adiabatic strippers mentioned in Section 5.8 may not be large.

It also follows that the overall rate of mass transfer,  $K_L a$ , is predominantly controlled by the liquid film resistance when the Henry's Law constant,  $H$ , is greater than about 10 atm for air stripping or greater than about 100 atm for steam stripping. All the compounds shown on Table 5-2 as "very easily stripped", and many of those shown as "easily stripped" will be liquid side controlled.

### 6.5 Choice of Equipment

The advantages and disadvantages of various water-vapor contacting devices are listed in many texts. We summarize here the suggestions given by King<sup>34</sup> and by Morris & Jackson<sup>35</sup>, and by other sources referred to below.

The simplest equipment is a simple spray tower. Small water drops should be helpful when the resistance is on the liquid side; however, spray towers are prone to entrainment which causes internal circulation of the liquid. Thus, true counter-current flow is not obtained and spray towers do not do more than one theoretical stage. A spray tower is only useful for easily stripped compounds when only one theoretical stage is needed.

Similarly, in an agitated vessel the liquid is mixed and only one stage is obtained. It is quite simple to obtain a full equilibrium plate at the price of a deep vessel and a larger pressure drop, but not more. Agitated vessels are used for batch stripping but not continuous stripping.

When more than one theoretical plate is required, packed towers or tray towers are used.

#### 6.6 Choice of Packing or Trays

The choice of a packed tower or a tray tower, and the choice of type of packing or type of tray, will be made on the basis of cost. A few rules can be given:

(1) For steam stripping with only a moderate number of theoretical plates (5 to 20) required, it is not certain whether packing or trays will be cheaper. When many stages are needed, trays are usually cheaper. With air stripping, when plastic packing can be used, packing is usually cheaper than trays.

(2) The pressure drop is less through packing than through trays and packing is the first choice for air stripping.

(3) The efficiency of a packed tower decreases steadily as the liquid flow rate is decreased below the design rate. This is because the liquid tends to channel and not wet all of the surface of the packing. If very variable liquid flows, or very low liquid flows are expected, bubble-cap trays should be considered. A bubble-cap tray is pictured in Figure 6.2. The liquid level on the tray is controlled by the overflow weir height. The liquid flows across the tray and the vapor-liquid contact area is independent of the flow rates. A valve tray is similar to a bubble-cap tray but sieve trays and perforated trays are not the same and cannot be used with variable liquid rate.

(4) Trays redistribute the liquid repeatedly and tall towers do not result in the channeling usually found in tall packed towers. Thus, when a close approach to equilibrium is required with many theoretical plates, a tray tower is preferred.

(5) Tray towers are easier to clean than packed towers and are used when suspended solids are present or precipitation may occur (such as when lime is added to release ammonia for stripping). Very open packings can also be used on turbid streams.



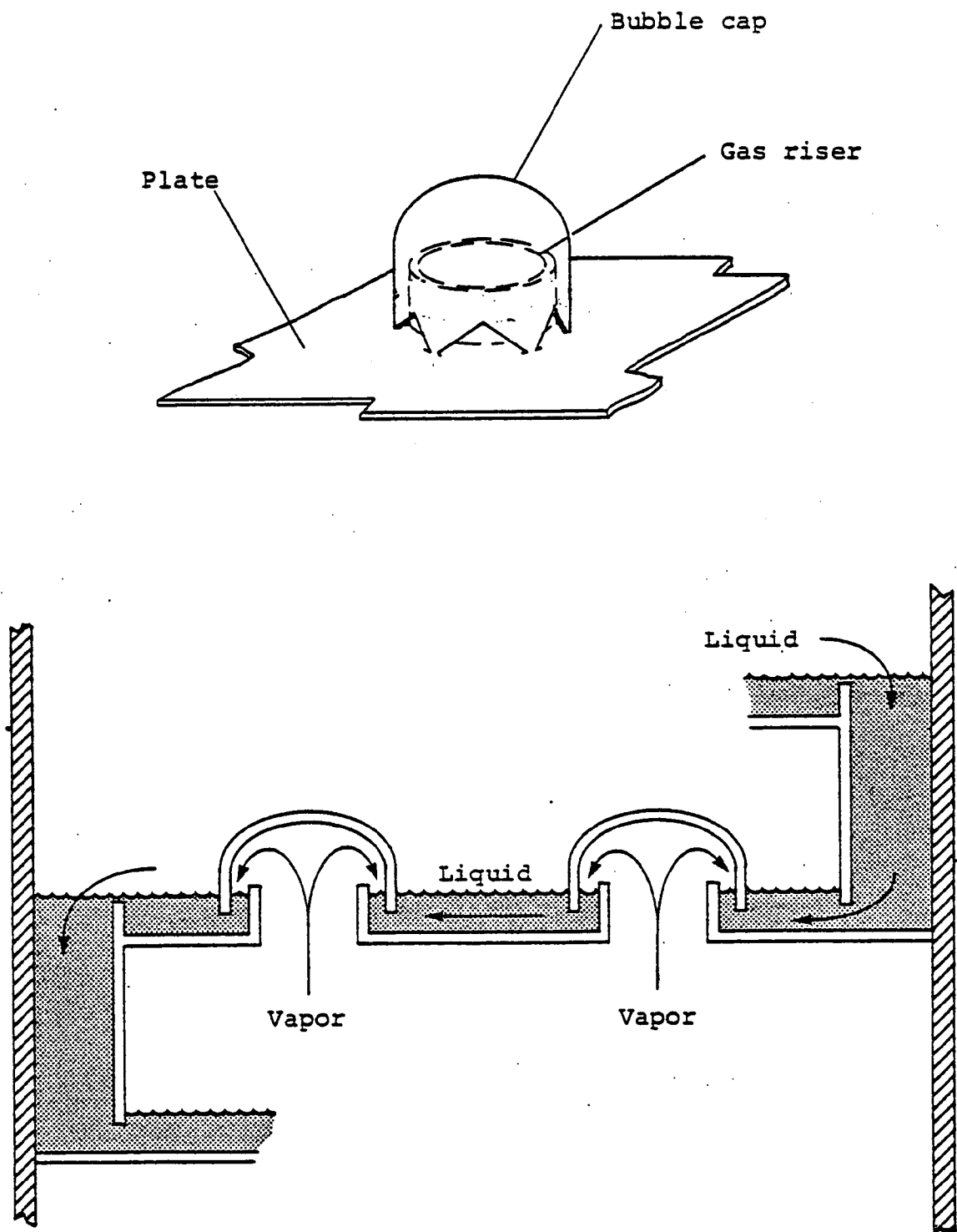


Figure 6-2. Bubble-cap tray.

### Efficiency

It appeared to us that packing, which distributes the liquid in a thin film, should be more efficient than trays when the liquid side is controlling. We had very brief consultation with makers of packings (Mass Transfer, Inc., Houston, Texas, and the Munters Corporation, Fort Myers, Florida) and with firms who make both packings and trays (Glitsch, Inc., Dallas, Texas and Koch Engineering Company, Ltd., Wichita, Kansas). The manufacturers gave the opinion that overall cost was the deciding factor and that trays need not be less efficient than packing.

For steam stripping both types of equipment are used. For air stripping it is so important to maintain a low pressure drop that plastic (cheap) packing is the first choice. All the manufacturers provide correlations and manuals for design. Pressure drops are usually in the range 0.2 to 1 inch water per foot of packing, but can be as low as 0.05 inch water/ft for very open grid packings. Open grid packings, such as used in small cooling towers, should be given first consideration.

## 7. COMPARISON OF PREDICTIVE CALCULATIONS TO STRIPPING DATA AT LOW CONCENTRATIONS

In this section the results obtained from strippers in operation are compared to those from theoretical predictive calculations. The applicability of theoretical models were assessed by:

- Developing a methodology of comparison
- Identifying limitations of the existing predictive calculation methods, if any, and
- Performing sensitivity calculations to determine the effect of identified parameters on tower sizing and effluent contaminant concentrations.

### 7.1 Methodology of Comparison.

Organic removal by air/steam stripping is a function of numerous interrelated parameters, as discussed in previous sections of this report. In light of the variety of toxic organic pollutants being considered in this study, it is not feasible to incorporate the effect of each design and operating parameter on the theoretical predictive calculations. Thus, a one-to-one correspondence between the theoretical and experimental data for all the organic pollutants is unlikely.

The simplified methodology of comparison, as developed and used in the analysis, is more of a qualitative nature and consists of the following steps:

1. The predictive calculations are based on sound engineering principles and the results should be compared only with reasonably accurate and precise experimental data. Thus, all data were first checked for consistency. This was especially necessary when the sampling data was gathered over a period of time and/or the analysis was performed by two or more laboratories.

2. If inconsistencies were found, original sources of the data were contacted to determine whether problems were encountered during sampling and analysis.

3. A comparative analysis is more meaningful and conclusive if enough data is available. Since the quantity of data available in the beginning of this study was judged inadequate, a limited review of current literature was made to obtain additional experimental stripping data at low concentrations.

4. The ease with which a particular compound is stripped depends on the volatility, and thus Henry's Law Constant is one of the most important parameters in determining the feasibility of organic removal by stripping. For a given set of experimental data, the relative degree of removal was, therefore, compared to the relative magnitude of Henry's Law Constant for all the components. Calculations were made using predictive methods whenever necessary production and equipment data, such as stripping agent, type of contact, and the configuration of the contacting device were available. The differences and disagreements were outlined.

5. Further investigation was made to identify design parameters or unreasonable assumptions in the theoretical models that could be responsible for the disagreements in the results.

6. A hypothetical system of compounds with different characteristics was utilized to demonstrate the degree of influence of the identified parameters on the strippability of a compound.

#### 7.2 Stripping Data at Low Concentration.

Table 7.1 provides a summary of sources and characteristics of stripping data that were analyzed in this study. This section provides additional information on the sources and the quality of data.

##### A. Commercial Scale Units

In the EPA organic data base, commercial wastewater strippers used in petrochemicals and plastics plants were selected for sampling of influent and effluent organic concentrations. The waste streams contained phenolic compounds and chlorinated hydrocarbons. Sampling was conducted for about thirty days period and part of the samples were analyzed by two laboratories.

Water Factory 21 is a  $0.66 \text{ m}^3/\text{s}$  plant that employs several of the wastewater treatment processes, including air stripping, to treat wastewater for trace organic contaminants. The data presented is for cooling towers that use polypropylene splash-bar packing with an air-to-water ratio of  $3000 \text{ m}^3/\text{m}^3$  at design capacity. The important information in these data is that the towers were originally designed for ammonia removal and the type of packing used has very low contact area per  $\text{m}^3$  of packing volume than most other packing materials.

TABLE 7-1. SUMMARY OF AVAILABLE STRIPPING DATA AT LOW CONCENTRATION

Source	Scale	Type of Stripper	Stripping Agent	Organic Compounds in Aqueous Waste Stream
1. EPA Organic Data Base Plant #1290-010	Commercial	Multistage Tray Tower with Total Reflux	Steam	Benzene, Nitrobenzene, 2-Nitrophenol, 4-Nitrophenol, 2,4 Dinitrophenol, phenol
2. EPA Organic Data Base Plant #2930-035	Commercial	Multistage Tray Tower  Information on refluxing Not Known	Not Known	Benzene, Carbon Tetrachloride, Chlorobenzene, 1,2 Dichloroethane, 1,1,1-Trichloroethane, 1,1-Dichloroethane, Chloroethane, 1,1,2-Trichloroethane, Chloroform, Ethylbenzene, 1,1-Dichloroethylene, Methylene Chloride, Toluene, Vinyl Chloride, Tetrachloroethylene, Trichloroethylene, Cis-1,2-Dichloroethylene
3. EPA Organic Data Base Plant #3390-005	Commercial	Packed Tower  Information on refluxing Not Known	Not Known	Chloroform, Methylene, Chloride, Toluene, Trichloroethylene, Vinyl Chloride
4. Water Factory Data	Commercial	Cooling Tower Polypropylene Splash-bar Packing	Air	Chloroform, Bromodichloromethane, Dibromochloromethane, Chlorobenzene, 1,2; 1,3; and 1,4-Dichlorobenzene, Tetrachloroethylene, 1,1,1-Trichloroethane
5. Robert S. Kerr Environmental Research Lab.	Laboratory	Packed Tower Berl Saddles No Reflux	Steam	Benzene, Chloroform, 1,1,2,2-Tetrachloroethane, Chlorobenzene, Ethyl Benzene, Tetrachloroethylene
6. Water General Corporation	Laboratory	Multistage Tray Tower No Reflux	Steam	Ammonia, Phenol
7. Treatability Manual	Laboratory	Packed Tower Polypropylene Pall Rings	Steam	Same as in 5 + 1,2-Dichloroethane, 1,2-Trans Dichloroethylene, 1,1,1 and 1,1,2 Trichloroethane, Trichlorofluoro Methane

In the EPA organic data base, information on the type of stripping agent and the mode of refluxing is not available for Plant Nos. 2930-035 and 3390-005. In all cases, the influent and effluent concentrations of each organic is available over a period of time.

#### B. Laboratory Scale Units

Nineteen bench-scale steam stripping runs were carried out in the study by the Robert S. Kerr Laboratories. Three of these runs involved acetone, methanol and 2-propanol to evaluate the performance of the equipment, and the rest involved some single and some mixtures of priority pollutants listed in the table. The experimental results were compared to those calculated using stripping factor design models. The draft report of the study concludes that the performance of the bench-scale stripper for priority pollutants was unexpectedly low and further states that the use of estimated K-values instead of the experimentally determined values may be the cause of poor performance. It recommends that before future evaluations of steam stripping are performed, the K-values be determined experimentally.

The data of WGC were obtained from a 20 tray continuous steam stripper of laboratory scale. These data are limited in terms of the number and type of compounds that are of interest in this study.

#### 7.3 Data Analysis and Results.

All stripping data were first checked for consistency. A simple and effective parameter that was used in this test is the removal efficiency defined as:

$$\eta (\%) = \left[ \frac{\text{concentration in} - \text{concentration out}}{\text{concentration in}} \right] \times 100$$

since it requires a minimum amount of information. However, for plants for which additional information was available, a suitable theoretical model for removal efficiency was used. For example, a continuous plate tower model with total reflux was used to analyze the results of plant No. 1290-010.

Inconsistencies were identified in the EPA organic data base, especially in the data obtained from Plant No. 1290-010. The samples obtained from the plant were analyzed by two laboratories and the results were found to vary significantly. The data sources were contacted and it was learnt that significant problems were encountered during sampling and

analysis. Table 7.2 tabulates all efficiency calculations for data collected over a two months period. Similar calculations were performed for plant No. 2930-035 which are tabulated in Table 7.3. Table 7.4 presents results of the Water Factory study. The ease with which a particular compound is stripped depends on the volatility, and thus Henry's Law Constant is one of the primary determinants of feasibility of organic removal by stripping. For a given set of experimental data, the removal efficiency was, therefore, compared to the magnitude of Henry's Law Constant for all compounds. As expected and supported by predictive calculations, most stripping data indicated significant removal of compounds with high Henry's Law Constant ( $H @ 100^{\circ}\text{C} > 20 \text{ atm}$ ).

Deviations from this behavior were observed for certain compounds. There was not necessarily a direct correlation between a compound's Henry's Law Constant and the removal efficiency. This means the removal efficiency of compound A with Henry's Law Constant higher than that of compound B, may not be higher than the removal efficiency of compound B. In addition, the removal efficiencies of some compounds with high Henry's Law Constant were not consistently high as would be expected. In many cases this may be due to analytical and sampling errors. Nevertheless, we spent some time searching for alternative explanations. High liquid-phase resistance would be one reason for low removal efficiencies over with high Henry's Law Constant. The problem was investigated from theoretical aspects using pure component properties. It was confirmed that liquid diffusivity does affect the degree of removal and consequently is important in the design and sizing of stripping equipment. This is discussed in further details with specific examples in the next section.

In case of packed towers stripping a waste stream consisting of compounds with Henry's Law Constant higher than 100 atm, the height of packing on the removal efficiency was found to be nearly independent of the magnitude of Henry's Constant. Liquid-phase resistance (diffusivity) was a factor affecting the performance. Again, experimental data on liquid-diffusivity is not abundant and empirical methods to estimate diffusivity may not provide reliable values for many organic compounds. Developing better contacting devices in terms of reducing liquid-phase resistance through more efficient packing and better liquid distribution in plate columns seems to be the probable solution to improving the performance of strippers.

TABLE 7-2. ORGANIC REMOVAL EFFICIENCY-CALCULATIONS FOR PLANT  
NO. 1290-010 OF THE EPA ORGANIC DATA BASE

Date of Sampling	$\eta^1$					
	Benzene (M = 1190) <sup>2</sup>	Nitrobenzene (M = 17)	2-Nitrophenol (M = 14.8)	4-Nitrophenol (M = 4x10 <sup>-3</sup> )	2,4-Nitrophenol (M < 1.5)	Phenol (M = 2)
1979						
10/2	> 99.7	99.9	89.9	> 99.2	78.4	96.3
10/3	> 99.8	99.9	91.4	9.2	90.7	60.8
10/5	> 99.8	99.9	87.5	43	99.3	99.9
10/9	> 99.5 (99.9) <sup>3</sup>	85.0 (99.9)	80.0 (35.5)	86.4	58.3 (99.9)	94.5 (91.8)
10/10	> 99.7	98.8	- 86.5	> - 31.5	- 48.9	73.2
10/11	87.6 (97.2)	99.9 (99.7)	69.9 (15.8)	70 (-139.3)	89 (90.9)	> 99.9 (>99.8)
10/13	> 99.8	99.8	- 15.9	- 4.2	- 34.6	57.1
10/16	> 98.9 (>99.7)	99.9 (99.8)	21.7 (- 6.4)	28.1 (-101.1)	64.3 (-40.8)	- 40.7 (41.0)
10/17	> 99.2	99.9	44.1	50.8	14.8	- 145.4
10/18	> 99.5 (99.9)	66.7 (99.9)	44.6 (10.4)	68.9 (78.2)	30.0 (38.7)	85.5 (-46.3)
10/19	> 99.7	99.9	82.1	49.5	45.9	84.7
10/23	> 99.7	99.0	89.4	62.7	17.9	84.1
10/24	> 99.8	99.9	87.2	45.2	7.1	80.4
10/25	> 99.5	99.9	22.2	8.2	33.0	68.1
10/26	> 99.7 (>99.6)	99.9 (99.6)	7.1 (-86.6)	48 (46.9)	92.4 (79.0)	51.1 (-12.9)
10/30	> 99.4	99.9	70.3	30.9	16.0	69.3
10/31	> 98.7 (99.9)	98.8 (99.9)	90.8 (-72.8)	2.7 (-56.1)	- 8.7 (-38.3)	89.7 (-595.4)
11/1	48.6	85.6	34.8	- 40.7	15.0	68.9
11/2	> 99.3 (M)	90.7 (99.9)	77.7 (-42.9)	81.0 (63.3)	60.9 (29.6)	66.0 (-292.3)
11/6	> 99.4	99.7	98.6	17.0	43.7	> 9.1
11/7	> 99.0 (>98.5)	99.8 (99.4)	66.1 (-402.6)	38.7 (M)	42.8 (89.0)	> 30 (>99.5)
11/8	> 99.6	99.9	44.9	81.3	43.9	> 98.8
11/9	> 99.2	99.9	87.0	44.7	89.9	21.2
11/13	> 99.1	99.9	54.5	27.6	20.5	9.1
11/15	> 98.3	99.9	99.8	81.0	4.3	18.8
11/16	> 97.5 (>99.0)	99.9 (99.9)	67.7 (-120.8)	91.5 (-250.0)	84.1 (50.6)	> 99.7 (>99.6)
11/20	> 99.0	99.9	10.2	57.1	22.2	99.9
11/21	- (>24.4)	99.9 (99.9)	82.0 (48.8)	63.5 (69.1)	48.4 (99.0)	> 99.9 (95.4)
11/22	> 99	-	-	-	-	-
11/23	> 99.5 (>98.5)	99.9 (99.9)	85.7 (92.8)	52.3 (-55.2)	90.3 (-4647)	> 99.6 (>74.2)
11/27	- ( - )	99.9 (99.7)	59.8 (38.1)	89.7 (-146.7)	29.1 (-533.0)	98.8 (79.8)
11/29	> 98.8	99.4	47.3	89.7	55.8	99.8
11/30	> 99.3	52.4	79.1	33.6	67.3	99.9

Notes:

$$1. \text{ Efficiency } \eta\% = \left[ \frac{\text{Conc (in)} - \text{Conc (out)}}{\text{Conc (in)}} \right] \times 100$$

2. Henry Law Constant M @ 100°C.

3. Values in brackets represent analysis of the same samples by another laboratory

4. Negative values indicate outflow conc. greater than inflow conc.

5. High steam/feed ratio (25 or greater).



TABLE 7-3: ORGANIC REMOVAL EFFICIENCY CALCULATIONS FOR PLANT NO. 2930-035  
OF THE EPA ORGANIC DATA BASE

Date of Sampling 1979	n %							
	March 4		March 10		March 11		March 12	
Unit	1	2	1	2	1	2	1	2
Compound								
A	-134	99.9	60.5	99.3	-25.7	99.8	72.6	99.7
B	88.2	99.3	99.2	99.5	NL	100	NL0	100
C	NL0	100	NL0	100	100	100	NL0	100
D	80	99.2	83.4	92.4	76.8	93.2	NL	-158
E	NL	100	NL	99.1	NL	99.2	NL	100
F	97.9	> 99.6	99.1	> 99.6	100	100	100	100
G	78.8	97.6	94.8	98.9	95.7	99.8	96.6	95
H	98.9	100	97.6	100	100	100	99.9	100
I	31.2	65.8	NL	66.9	93.2	64.2	99.9	88.3
J	80.1	100	94.6	99.5	96	99.7	91.7	99.3
K	NL0	NL0	NL0	NL0	NL0	NL0	NL0	NL0
L	96.4	100	99.6	100	100	100	99.9	100
M	-653	100	-1196	87.5	-1722	97.8	NL	91.9
N	< 83	98.2	100	NL	NL0	-	NL0	99.8
O	-52.4	99.3	97.5	96	75.6	98.6	NL	97.2
P	99.4	100	99	100	100	100	96.6	100
Q	NL0	100	99	100	98.9	100	100	NL0

Notes:

- Efficiency  $n \% = \left[ \frac{\text{Conc (in)} - \text{Conc (out)}}{\text{Conc (in)}} \right] \times 100$
- Unit 1 = OMC Stripper (pH range 1-2)  
Unit 2 = WTU Stripper (pH range 10-12)
- NL = Not detected in influent but detected in effluent  
NL0 = Not detected in influent and effluent
- Negative values indicate higher concentration in effluent than in influent
- Name of the compounds: ( $@ 100^{\circ}\text{C}$ ) Henry's Law Constant
 

A = Benzene	1190
B = Carbon Tetrachloride	3167
C = Chlorobenzene	758
D = 1,2-Dichloroethane	265
E = 1,1,1-Trichloroethane	801
F = 1,1-Dichloroethane	862
G = 1,1,2-Trichloroethane	250
H = Chloroethane	1257
I = Chloroform	3244
J = 1,1-Dichloroethylene	-
K = Ethyl Benzene	901
L = Methylene Chloride	1812
M = Tetrachloroethylene	3596
N = Toluene	1118
O = Trichloroethylene	1600
P = Vinyl Chloride	> 2000
Q = Cis-1,2-Dichloroethylene	-

continued.....

Date of Sampling 1979	May 5		May 12	
Unit	1	2	1	2
Compound				
B	N1	N1	N1	N1
D	N1	63.6	N1	66
E	N1	99.8	N1	99.3
F	99.8	100	> 99.7	100
G	N10	92.2	N10	99.6
H	99.8	99.9	> 98.9	100
I	N1	85.1	N1	N1
J	98.5	99.9	> 99.6	100
L	100	100	> 99.9	100
M	-1.27	99.7	> -1.9	98.2
N	-	-	> 98.9	99.6
O	97.6	99.9	> 78.6	99.9
P	98.6	100	98.9	99.9
Q	99.9	99.9	-	-

Date of Sampling 1979	March 17		March 24		April 2		April 8	
Unit	1	2	1	2	1	2	1	2
Compound								
B	N1	100	N1	N1	N10	N10	N10	100
D	78.8	91.0	N1	N1	N1	N1	> 99.7	99.4
E	99.9	100	N1	100	N1	100	N1	100
F	99.9	99.9	99	100	99.5	100	100	100
G	100	84.2	-	N1	N1	98.9	N1	99.8
H	99.9	99.9	99.4	N1	99	100	> 99.9	100
I	65.5	99.2	N1	N1	N1	N1	> 99.9	99.4
J	97.3	99.9	96.7	99.9	99.6	100	100	100
L	99.9	99.9	99.9	99.9	99.2	99.9	100	100
M	N1	97.4	1.68	99	N1	99.9	N1	99.9
O	N1	99.9	88.8	99.8	99.3	99.9	99.7	99.9
P	99.9	99.6	98.3	100	91	100	100	100
Q	-	100	99.9	N10	100	100	100	100

Notes:

- Efficiency  $\eta$  % =  $\left[ \frac{\text{Conc (in)} - \text{Conc (out)}}{\text{Conc (in)}} \right] \times 100$
- Unit 1 = GAC Stripper (pH range 1-2)  
Unit 2 = WTU Stripper (pH range 10-12)
- N1 = Not detected in influent but detected in effluent  
N10 = Not detected in influent and effluent
- Negative values indicate higher concentration in effluent than in influent
- Name of the compounds: (@ 100°C) Henry's Law Constant
  - A = Benzene 1190
  - B = Carbon Tetrachloride 3167
  - C = Chlorobenzene 758
  - D = 1,2-Dichloroethane 263
  - E = 1,1,1-Trichloroethane 801
  - F = 1,1-Dichloroethane 862
  - G = 1,1,2-Trichloroethane 250
  - H = Chloroethane 1257
  - I = Chloroform 3244
  - J = 1,1-Dichloroethylene -
  - K = Ethyl Benzene 901
  - L = Methylene Chloride 1812
  - M = Tetrachloroethylene 3596
  - N = Toluene 1118
  - O = Trichloroethylene 1600
  - P = Vinyl Chloride > 2000
  - Q = Cis-1,2-Dichloroethylene -

TABLE 7-4. ORGANIC REMOVAL EFFICIENCY RESULTS OF THE WATER FACTORY DATA

<u>Compound</u>	<u>% Range</u>
Chloroform	79-83
Dichlorobromomethane	-
Chlorodibromomethane	82
Chlorobenzene	96
1-2 Dichlorobenzene	88
1-3 Dichlorobenzene	83
1-4 Dichlorobenzene	92-97
1-1-1 Trichloroethane	91
Tetrachlorethylene	95

#### 7.4 Development of a Correlation for the Effect of Liquid-diffusivity on Tower Sizing and Organic Removal Efficiency.

The effect of diffusivity was demonstrated by considering the example of a continuous packed bed tower stripping organics from aqueous waste stream.

The height of a packed bed (Z) can be determined from the knowledge of two factors: the height of a transfer unit (HTU) and the number of transfer units (NTU)

$$Z = \text{HTU} \times \text{NTU} \quad (1)$$

The NTU is defined in terms of an integral of influent and effluent concentrations and this integral equation can be solved analytically for dilute solutions and solutes obeying Henry's Law to give the following expression

$$\text{NTU} = \frac{1}{(1 - \frac{1}{S})} \ln \left[ \frac{X_i}{X_o} \left(1 - \frac{1}{S}\right) + \frac{1}{S} \right] \quad (2)$$

where

S = stripping factor

=  $H a G/P_t L$

$X_i$  = mole fraction in influent

$X_o$  = mole fraction in effluent

We have plotted the NTU as a function of stripping factor for various removal efficiencies ranging from 60 percent to 99.99 percent. The results are illustrated in Figure 7.1. An important observation made from this figure is that for compounds with high Henry's Law Constant and consequently high stripping factor ( $> 50$ ), the number of transfer units is nearly independent of the magnitude of Henry's Law Constant for any given removal efficiency. Thus, it can be stated that for compounds with high Henry's Law Constant,

$$\text{NTU} \approx (\text{removal efficiency alone}) \quad (3)$$

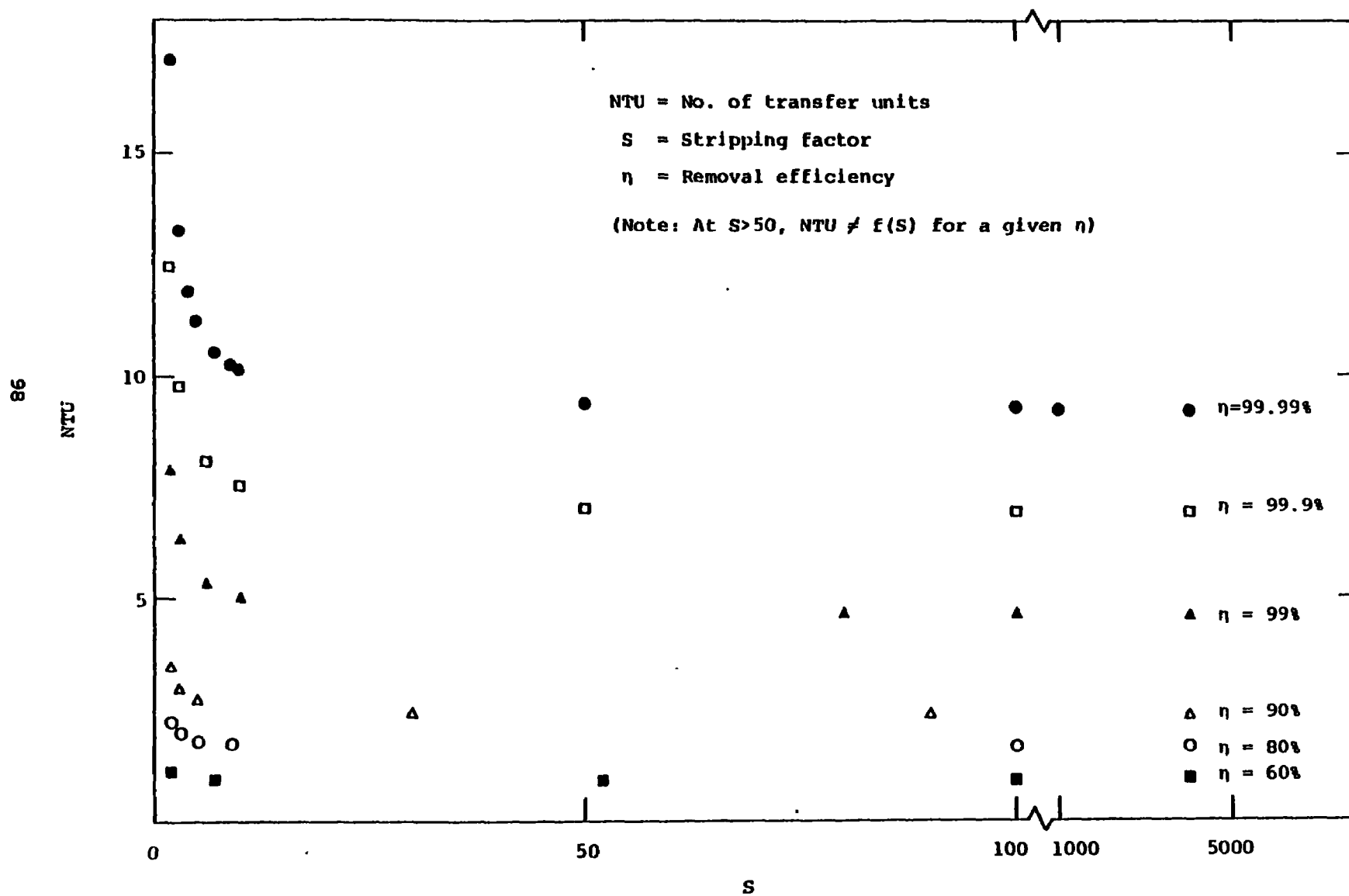


Figure 7-1. Dependency of NTU on stripping factor and removal efficiency.

and therefore, for a given removal efficiency

$$Z \propto \text{HTU} \quad (4)$$

The height of a transfer unit is defined as

$$\text{HTU} = L/K_L a C_0 \quad (5)$$

When a solute has a large Henry's Law Constant, as do slightly soluble gases or volatile liquids, the overall transfer coefficient  $K_L$  depends primarily on the local transfer coefficient ( $k_L$ ), and therefore

$$\text{HTU} = L/k_L a C_0$$

For a given packing and loading rate  $L$ ,  $a$  and  $C_0$  are the same for any compound in the mixture, and therefore

$$\text{HTU} \propto 1/k_L \quad (6)$$

A typical empirical correlation used for liquid-phase mass transfer coefficients in towers containing randomly packed materials is given by

Perry:

$$\frac{k_L a}{D_A} = \alpha \left( \frac{L}{\mu_L} \right)^{1-n} \left( \frac{\mu_L}{\rho_L D_A} \right)^{0.5}$$

All the factors in this expression, except the diffusivity  $D_A$ , are the same for any organic in the mixture which means that

$$k_L \propto \sqrt{D_A} \quad (7)$$

Combining Equations 4, 6 and 7 we arrive at the final correlation:

$$Z \propto 1/\sqrt{D_A}$$

In other words, for a given removal efficiency and for compounds with high Henry's Law Constant, the height of a packed bed is inversely proportional

to the square root of the component's liquid diffusivity in dilute aqueous solutions.

For example, if there are two compounds in a solution with diffusivities  $D_1$  and  $D_2$ , and the height of packed bed required is  $Z_1$ , and  $Z_2$  respectively, then the relationship between the ratios  $D_1/D_2$  and  $Z_2/Z_1$  will be as shown in Figure 7.2.

$DR(1:2)$  = Ratio of Diffusivities (Compound 1/Compound 2)

$ZR(2:1)$  = Ratio of Heights for any removal efficiency and stripping factor greater than 50  
(Compound 2/Compound 1)

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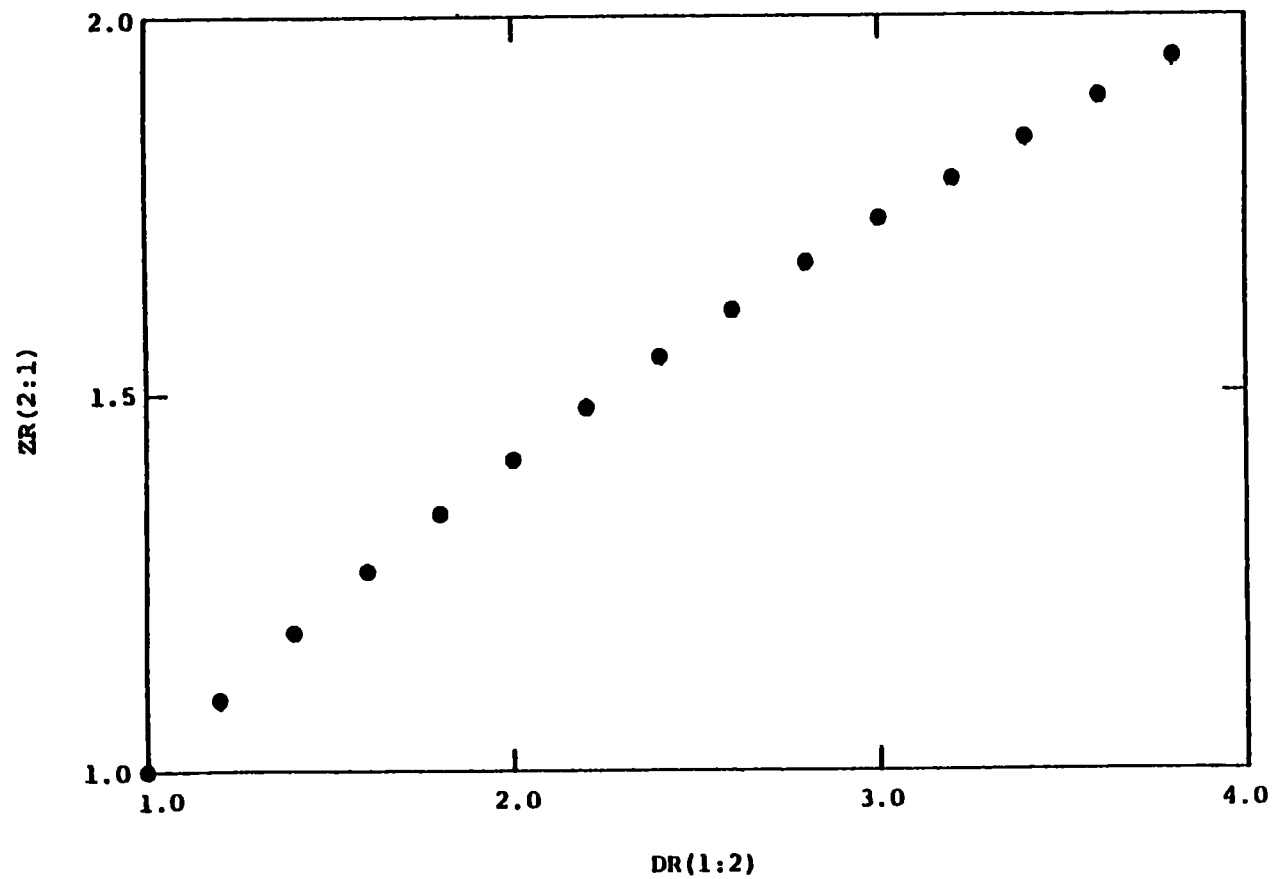


Figure 7-2. The effect of liquid diffusivity on the height of a packed bed.



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