DETERMINATION OF HENRY'S LAW CONSTANTS OF
SELECTED PRIORITY POLLUTANTS

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SECTION 1

INTRODUCTION

Millions of people living in this nation are concerned with the effect their environment has on them. The weight of this concern has produced legislation which will, it is hoped, protect them from the hazards of their environment. One result of this concern was the issuance of the Consent Decree in 1976 which designates specific compounds considered to be potentially toxic to various life forms. This decree and other legislation require that the U.S. Environmental Protection Agency (USEPA) act to answer questions concerning the ultimate fate and effect of these materials on those life forms and to reduce, through effective regulation, the consequences of unregulated dissemination of those compounds which are found to be toxic.

The responsibility given to the USEPA provokes many questions.

- Of these compounds, are any present in concentrations sufficient to be toxic?

- If so, what are their origins?

- By what mechanism do they enter the environment?

- What are their health related effects on various life forms?

- How can they be controlled?

- Where should they be controlled?

A very complex multi-disciplinary effort is required to answer these questions.

The USEPA through its Municipal Environmental Research Laboratory (MERL) in Cincinnati, Ohio, is addressing some of these questions by characterizing the ability of municipal wastewater treatment systems to remove pollutants of health concern and by providing information relating to the fate of these pollutants as they pass through these systems.

Part of this effort involves the determination of Henry's Law constant (H) for as many of the volatile priority organics as possible. These values for H will enhance the ability to predict the fate of volatile organics in wastewater treatment systems.

SECTION 2

EXPERIMENTAL PROCEDURES

The apparatus used in this study is that described by Mackay, et al., (1) with some modifications. The major modification was an increase in the liquid depth in the stripping vessel to assure system equilibrium for all compounds studied. Figure 1 is a diagram of the apparatus. Nitrogen from a high pressure cylinder was passed through a two-stage pressure regulator and rotameter, and then bubbled through water to saturate it and prevent water evaporation from the stripping vessel. The nitrogen was then introduced into the bottom of the stripping vessel through a sintered glass disc. The liquid depth in the stripping vessel was 60 cm with a liquid volume of 1 liter. The vessel was water-jacketed and maintained at $25^\circ \pm 0.05^\circ C$. The exit gas was vented to a hood for safety and the flow rate was measured by a soap bubble flow meter.

The general procedure was to prepare a saturated solution of the test compound by adding a quantity of the compound, sufficient to exceed its solubility, to distilled deionized water and mixing overnight. A portion of this solution, the quantity of which was dictated by analytical procedure, was mixed with the temperature-stabilized deionized water from the stripping vessel, the volume was adjusted to 1 liter, and the solution was returned to the vessel for stripping. The resulting test solution varied from 10 ug/l to 10 mg/l of solute, depending on compound solubility and analytical sensitivity.

Distilled deionized water was used in all experiments. Hydrocarbons used were of the purest quality available and were used without further purification. In most cases, the purity was stated as > 99%.

Several of the compounds with stated purities of >99% were significantly less pure than indicated and some contained impurities of up to 50%. These impurities complicated the sample analysis, and in a few instances, required the application of GC/MS analysis for identification of the test compound.

As suggested by Mackay, et al., (1), the system equilibrium should not be significantly dependent upon gas-flow rates and thus varying the rate should not significantly affect the experimentally-determined value for H. Confirmation of this can be seen in Figure 2. Varying the stripping gas flow rate from 50 to 250 cc/min with benzene as the solute produced an average value for H of 5.6×10^{-3} m^3 atm/mol and a standard deviation of $\pm 7.28\%$. The average experimental value compared favorably with the calculated value of 5.5×10^{-3} m^3 atm/mol. A "standard" flow rate of 100 cc/min was selected for the remainder of this study. This rate was chosen because it produced a good bubble pattern in the stripping vessel, and it allowed adequate time for sampling. Flow rates were checked before, during and after completion of each run as dictated by elapsed time to assure constancy of flow.
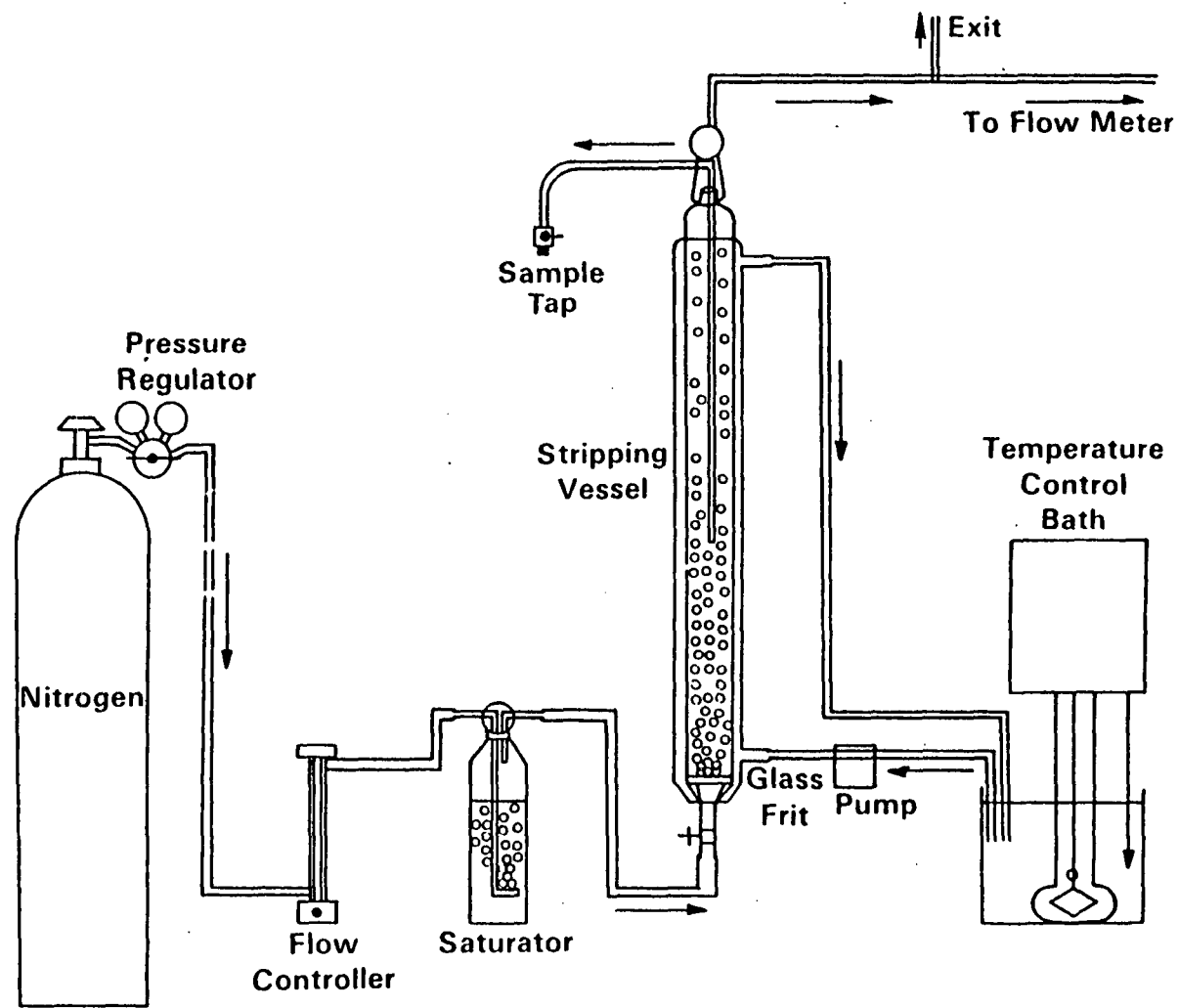
Figure 1. Stripping apparatus diagram

H, m³ at m/mol × 10^{-3}

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6

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4 − Cálculated
   • Experimental

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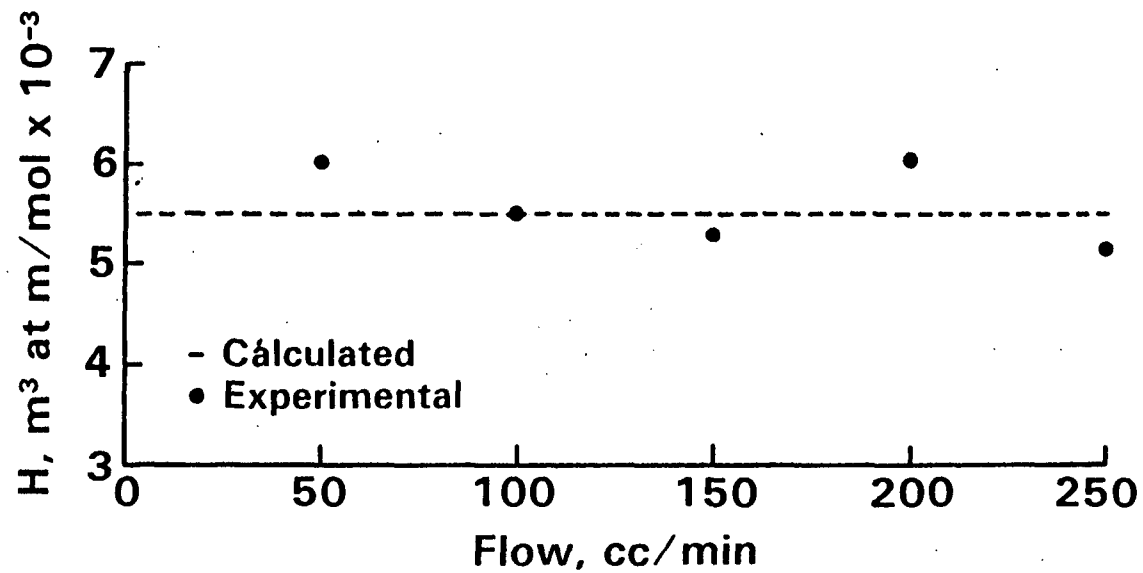0   50   100   150   200   250

Flow, cc/min

-4-

Figure 2. Flow rate vs Henry's law constant for volatilization of benzene

To evaluate the reproducibility of this system at the selected gas flow rate of 100 cc/min, repetitive runs were made using benzene as the solute. As can be seen in Table 1, no experimentally significant variation in the value for H was produced.

TABLE 1. REPRODUCIBILITY OF EXPERIMENTAL PROCEDURE

Run	H, m^3 atm/mol x 10^{-3}	Correlation Coefficient
1	5.41	0.999
2	5.76	0.999
3	5.34	0.998
4	5.49	0.998
5	5.62	0.999

These results give a mean value for H of 5.52 x 10^{-3} m^3 atm/mol and a standard deviation of $\pm$ 3%.

In order to assure that equilibrium within the stripping vessel was being attained, one of the more volatile compounds, benzene, was run repetitively at varying liquid depths. The results in Table 2, show no significant change in the experimental value for H was produced with reductions in liquid depth of up to 50%.

TABLE 2. EFFECT OF LIQUID DEPTH ON H

Liquid Depth, cm	H, m^3 atm/mol x 10^{-3}
60	5.50
50	5.73
40	5.69
30	5.85

Since system equilibrium was achieved with benzene at these depths, it was assumed that equilibrium would be achieved in systems with less volatile compounds.

Samples for analysis were taken from the stripping vessel with a glass syringe through a sample tap positioned at a depth of approximately 20 cm from the liquid surface. The sampling frequency varied from minutes to hours, depending upon the volatilization rate of the specific compound. Varying the sampling depth during stripping did not result in variation in concentration which confirmed that adequate mixing was accomplished by the bubbles in the stripping vessel. U-V spectroscopy and two gas chromatography techniques; purge and trap, and solvent extraction, were employed for analysis of the samples.

A few of the compounds in this study were light-sensitive and the stripping vessel was covered during the test. Some of the compounds were readily adsorbed on the glass surface of the stripping vessel. To minimize this effect, the stripping vessel surface was saturated with the compound, i.e., the adsorption sites were saturated by exposing them to the test compound repeatedly prior to each run.

SECTION 3

DISCUSSION AND RESULTS

Even a casual inspection of the organics on the list of priority pollutants will show that many of the low molecular weight chlorinated hydrocarbons are volatile compounds. It follows from this that loss of these compounds from solution can be an important route of removal from the aqueous flow, but this also indicates that the potential exists for contamination of the air around a wastewater treatment plant. Treatment plants offer ample opportunity for volatilization from processes such as the flows in the collection system, aerated grit chambers, settlers and most especially from aeration basins where the driving force for desorption from solution is provided by the air or oxygen aeration. Thus, it is not surprising that volatilization from water bodies to the atmosphere is generally recognized as a significant pathway for transfer of organics from one environmental medium to another.

The volatilization process from an aqueous solution is generally accepted as consisting of diffusion of the solute from the bulk of the water to the interface, followed by transfer across the interface and finally diffusion from the interface to the bulk of the air phase.

There have been many attempts in the literature to develop mathematical models which would predict the rate of volatilization of a compound from aqueous solution. Most models incorporate parameters such as Henry's Law constant, gas and liquid phase mass transfer coefficients and, more recently, models have incorporated coefficients which account for other parameters that affect the volatilization rate such as adsorption on solids and rate of biodegradation.

An important coefficient in virtually all of the models is Henry's Law constant (H). This constant is an expression of the distribution of a volatile solute at equilibrium between the liquid and vapor phases. Unfortunately for many of the comompounds of environmental interest, the value for H is not available. When the necessary information on aqueous solubility and vapor pressure is available, H can be calculated. However, published vapor pressure and solubility data are, in many cases, questionable, and in some cases, either erroneous or non-existent. Another method for obtaining H was required to overcome this inability to obtain or calculate a value for H from the literature.

Mackay, et al., (1) described an apparatus for the determination of Henry's Law constants for hydrophobic compounds with an accuracy of about 5%. This device was employed in this study to provide values of H for as many of the volatile priority pollutants as possible. The method involves measurement of the compound concentration in only the liquid phase while being stripped isothermally from solution at a known gas flow rate. H can readily be calculated from a plot of the natural log of the concentration vs. time which should be linear with a slope of $-(HG/VRT)$. Thus

$$H = -\frac{slope \times VRT}{G}$$

where

H   =   Henry's Law constant, m^3 atm/mol

V   =   Volume of test solution, m^3

R   =   Gas constant, m^3 atm/mol $^{\circ}K$

T   =   Temperature, $^{\circ}K$

G   =   Gas flow rate, m^3/min

Henry's law constant was determined for 41 compounds. The results of these tests are presented in Table 3. All experimental values for H reported in the table are averages of 2 or more replicates. Calculated values for H were based on data from many published sources (1-11), and can be calculated by

$$H = \frac{VP \times MW}{S}$$

where

H   =   Henry's law constant, m^3 atm/mol

VP   =   Vapor pressure of solute, atm

MW   =   Molecular weight of solute, g/mol

S   =   Solubility of solute, g/m^3

In all cases, except during the first few minutes when it is believed that high solute concentrations overloaded the analytical detectors, resultant curves were linear, with correlation coefficients (r) normally greater than 0.980; see Figures 3 and 4. In all but two of the compounds studied a precision corresponding to a standard deviation of approximately 6% was achieved.

As can be seen in Table 3, many of the calculated results correspond closely to the experimental values, however, several deviate significantly from these values and for some of the compounds, no values could be calculated due to insufficient data. Some deviation between experimental and calculated values for H can be attributed to the use of the only available data at temperatures different from the selected system temperature. Other deviations are due to incorrect solubility and vapor pressure information. Literature values can vary over three orders of magnitude for some compounds. Some of the deviation can be attributed to experimental error, however, questionable published data and confidence in the experimental method dictates that H values determined experimentally are preferred over calculated values.
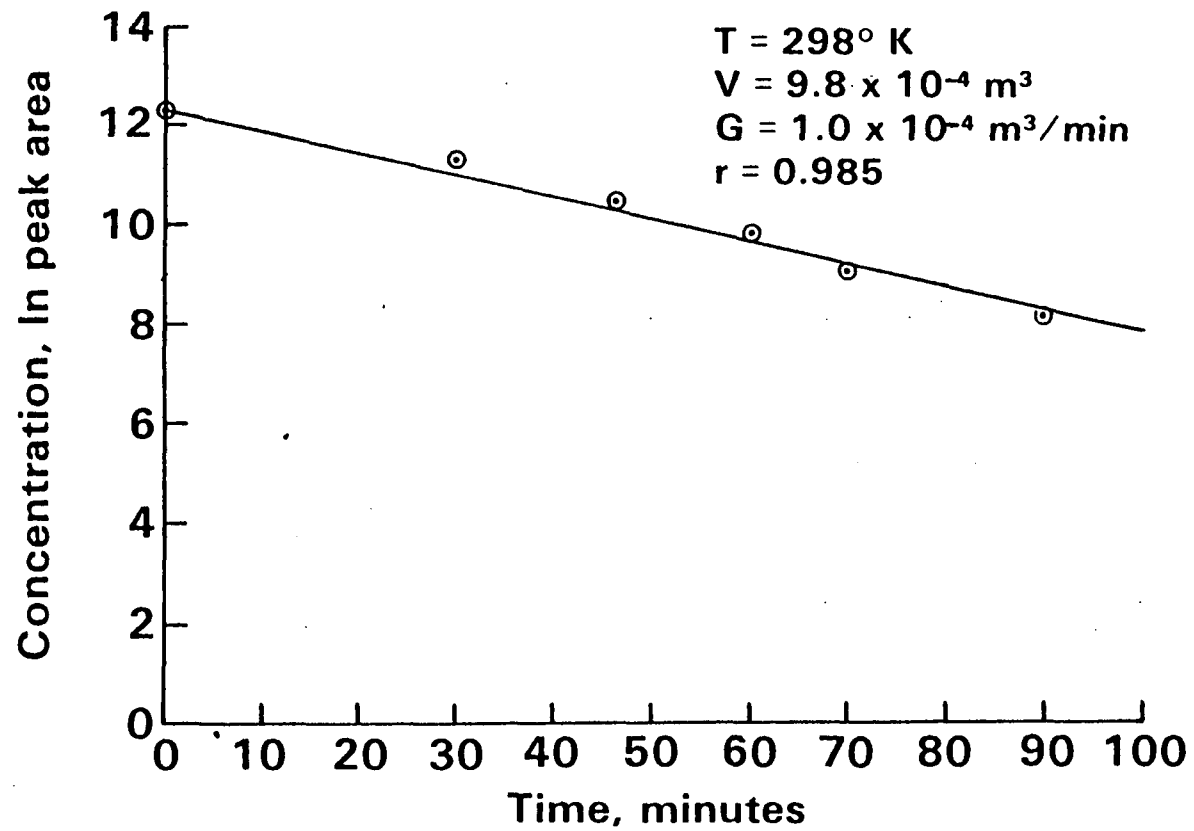
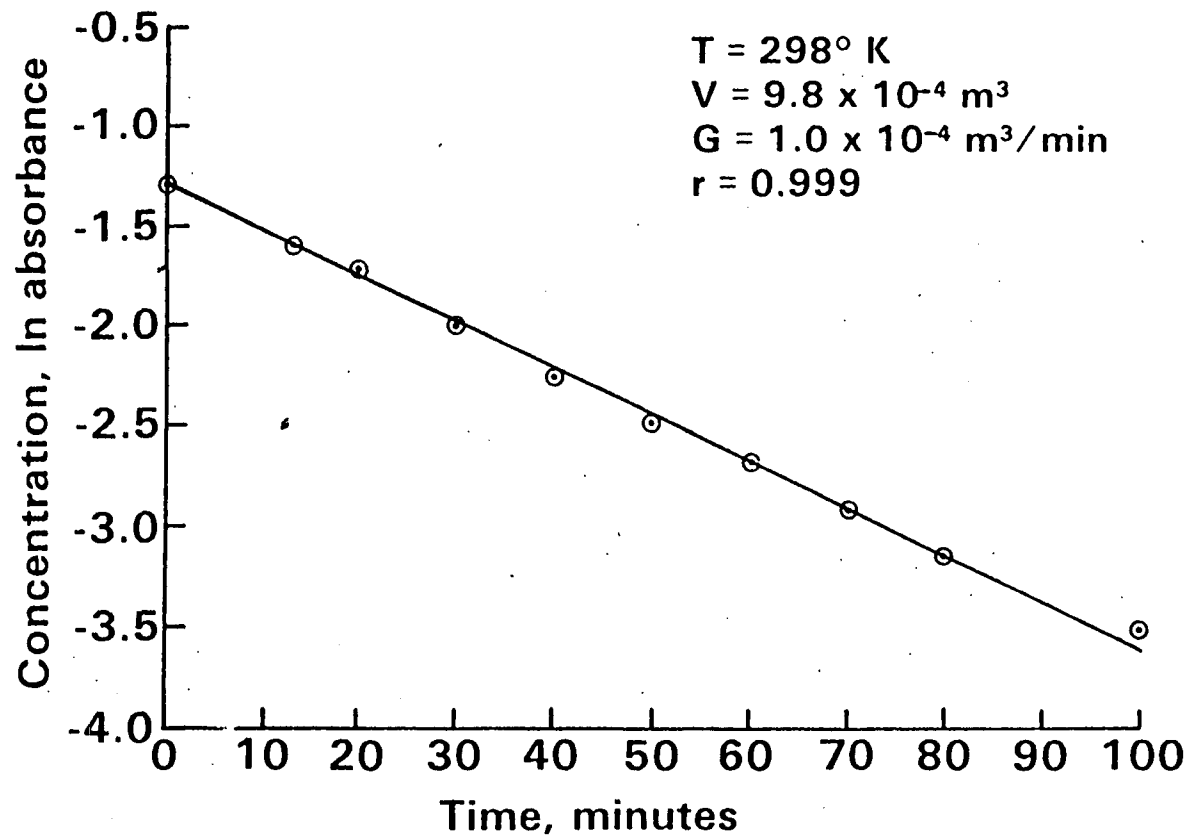Figure 3. Typical plot for volatilization of trichloroethylene

Figure 4. Typical plot for volatilization of benzene

TABLE 3. SUMMATION OF DATA FOR HENRY'S LAW CONSTANT

Compound	Vapor Pressure atm.x 10^{-3}	Temp. °K	Solubility g/m^3	Temp. °K	Molecular Weight g/mol	H, m^3 atm/mol x 10^{-3} Calculated	Experimental
Acenaphthene	--	-	3.93(1)	298	154.2	--	0.241
Benzene	125(3)	298	1780(10)	298	78.1	5.48	5.55
Carbon tetrachloride	149(4)	298	800(2)	298	153.8	28.6	30.2
Chlorobenzene	15.5(4)	298	472(1)	298	112.6	3.70	3.93
1,2,4-Trichlorobenzene	0.383(6)	298	30(7)	-	181.5	2.32	1.42
Hexachlorobenzene	--	-	0.006(6)	298	284.8	--	1.70
1,2-Dichloroethane	113*(4)	298	8300(6)	298	99.0	1.35	1.10
1,1,1-Trichloroethane	168*(4)	298	5497*(4)	298	133.4	4.08	4.92
Hexachloroethane	--	-	50(5)	295	236.7	--	9.85
1,1-Dichloroethane	308(4)	298	5500(4)	293	99.0	5.54	5.45
Chloroform	260(6)	298	9600(4)	298	119.2	3.23	3.39
1,2-Dichlorobenzene	1.97(4)	298	145(4)	298	147.0	2.00	1.94
1,3-Dichlorobenzene	2.48(6)	298	123(4)	298	147.0	2.96	2.63
1,4-Dichlorobenzene	--	-	79(4)	298	147.0	--	2.72
1,1-Dichloroethylene	778(4)	298	5000(6)	293	97.0	15.1	15.0
1,2-trans-Dichloroethylene	263(4)	287	6300(2)	293	96.9	4.05	5.32
1,2-Dichloropropane	65.8(4)	298	2700(4)	293	113.0	2.75	2.82
1,3-Dichloropropylene	32.9(5)	293	2700(5)	298	111.0	1.35	3.55
Ethylbenzene	12.5(3)	298	206(11)	298	106.2	6.44	6.44
Methylene chloride	599*(4)	298	16700(4)	298	84.9	3.04	3.19
Bromoform	7.37(4)	298	3130*(5)	298	252.8	0.595	0.532

TABLE 3. (cont'd) SUMMATION OF DATA FOR HENRY'S LAW CONSTANT

Compound	Vapor Pressure atm.x 10^{-3}	Temp. ^{o}K	Solubility g/m^3	Temp. ^{o}K	Molecular Weight g/mol	H, m^3 atm/mol x 10^{-3} Calculated	H, m^3 atm/mol x 10^{-3} Experimental
Bromodichloromethane	- -	-	- -	-	163.8	- -	2.12
Trichlorofluoromethane	833*(4)	298	1100(4)	298	137.4	104	58.3
Dibromochloromethane	65.8(5)	293	- -	-	168.8	- -	0.783
Hexachlorobutadiene	0.197(5)	293	2(5)	293	260.8	25.7	10.3
Hexachlorocyclopentadiene	0.107(4)	298	0.805(5)	298	272.7	36.2	16.4
Nitrobenzene	0.374(6)	298	2000(6)	298	123.1	0.023	0.024
4,6-Dinitro-o-cresol	- -	-	- -	-	198.1	- -	0.0014
Phenol	- -	-	67000(6)	298	94.1	- -	0.0013
Acenaphthylene	- -	-	3.93(5)	298	152.2	- -	0.114
Fluorene	- -	-	1.98(5)	298	116.2	- -	0.117
Tetrachloroethylene	25.8*(4)	298	150(4)	298	165.8	28.5	28.7
Toluene	37.4(6)	298	535(9)	298	92.1	6.44	5.93
Trichloroethylene	97.8(6)	298	1100(4)	298	131.5	11.7	11.7
Aldrin	- -	-	0.2(6)	293	364.9	- -	0.496
Dieldrin	- -	-	0.186(6)	298	380.9	- -	0.058
Chlordane	- -	-	1.85(8)	298	409.8	- -	0.048
Heptachlor	- -	-	0.056(6)	298	373.4	- -	1.48
Heptachlor epoxide	- -	-	0.275(6)	298	389.3	- -	0.032
Arochlor 1254	- -	-	0.012(5)	298	328.4	- -	8.37
Toxaphene	- -	-	1.75(8)	298	413.9	- -	4.89

( ) Reference designation. * Data interpolated between two data points. - Data unavailable.

REFERENCES

1. Mackay, D., Shiu,W. Y. and Sutherland, R. P.,
    "Determination of Air-Water Henry's Law Constant for Hydrophobic
    Pollutants." Environ. Sci. & Tech., 13, 333 (March 1979).

2. Dilling, W. L., "Interphase Transfer Processes. II. Evaporation
    Rates of Chloro Methanes, Ethanes, Ethylenes, Propanes, and
    Propylenes from Dilute Aqueous Solutions. Comparison with
    Theoretical Predictions." Environ. Sci. & Tech., 11, 405 (April 1977).

3. Zwolinski, B. J., and Wilhoit, R. C., "Handbook of Vapor Pressures
    and Heats of Vaporization of Hydrocarbons and Related Compounds,"
    API, 44-TRC Publications in Science and Engineering, 1971.

4. Verschueren, K., "Handbook of Environmental Data on Organic Chemicals,"
    Van Nostrand Reinhold Company, 1977.

5. Water-Related Environmental Fate of 129 Priority Pollutants. A
    Literature Search by Versar, Inc., for USEPA Office of Water Planning
    and Standards. Contract No. 68-01-3852. January-February 1979.
    Draft copies.

6. ISHOW Data Base, University of Minnesota, Duluth. April 1979.

7. Spencer, W. F., and Farmer, W. J., "Assessment of the Vapor Behavior
    of Toxic Organic Chemicals," Contribution of Federal Research, SEA,
    USDA and the University of California, Riverside, California.

8. Weil, L., Dure, G., and Quentin, K. E.,
    Z. Wasser - Abwasser Forsch, 7(6), 169-185 (1974).

9. Strier, M., "Treatability of Organic Priority Pollutants," Part C.
    USEPA Office of Quality Review, June 1978. Unpublished Manuscript.

10. McAuliffe, C., Jour. Phys. Chem., 70, 1267 (1966).

11. Identification of Organic Compounds in Effluents from Industrial
    Sources. USEPA Report, PB-241 641/OBA.

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