

The Vapor Pressure of Environmentally Significant Organic Chemicals: A Review of Methods and Data at Ambient Temperature

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The experimental techniques and the prediction procedures for the determination or evaluation of the vapor pressure of environmentally relevant organic compounds are described; with 259 references examined. For each of them the characteristics of precision and accuracy are given, when available from the literature. The experimental methods are classified as "direct" and "indirect." The first class includes all those which can measure directly the vapor pressure, while the second concerns those which need "known" vapor pressures of reference compounds for the calibration. Prediction methods are based on the application of the Clapeyron–Clausius equation or on the quantitative structure-property relationships. Also correlation methods require a suitable calibration. The vapor pressures at ambient temperature for several polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and furans, selected pesticides, and some reference compounds are tabulated together with the vapor pressure equations and the enthalpy values in the temperature range of measurement. A critical comparison, based on a statistical analysis of the data obtained with different methods and derived from 152 references, is also carried out. © 1996 American Institute of Physics and American Chemical Society. [S0047-2689(96)00206-1]

Key words: chlorinated biphenyls; chlorinated dioxins; critically reviewed data; critically reviewed methods; pesticides; polynuclear aromatics; vapor pressure.

Contents

1. Introduction.....	157	4. Vapor pressure at 25 °C and enthalpy of sublimation of selected PCDDs and PCDFs.....	177
2. Experimental methods.....	158	5. Vapor pressure at 25 °C and enthalpy of vaporization of some reference compounds in GC.....	179
2.1. Direct experimental methods.....	158	6. Analysis of the vapor pressure data obtained with direct experimental methods.....	187
2.1.1. Manometric methods.....	158	7. Analysis of the vapor pressure data obtained by GC for selected PCB congeners.....	188
2.1.2. Boiling point at reduced pressures.....	159	8. Accuracy of the vapor pressure data obtained with indirect and prediction methods.....	189
2.1.3. Effusion.....	160	9. Vapor pressure ranges of measurement of the most important experimental methods employed with environmental contaminants.....	189
2.1.4. Gas saturation.....	161		
2.1.5. Partition coefficient.....	165		
2.1.6. Other methods.....	176		
2.2. Indirect experimental methods.....	178		
2.2.1. Relative volatilization rate.....	178		
2.2.2. Chromatographic methods.....	180		
3. Prediction methods.....	183		
3.1. Clausius–Clapeyron equation.....	183		
3.2. Estimation of vapor pressure using indices of molecular structure.....	184		
4. Analysis of the data and comments.....	186		
5. Acknowledgment.....	189		
6. List of symbols.....	189		
7. References.....	190		

List of Tables

1. Vapor pressure at 25 °C and enthalpy of sublimation of selected PAHs.....	162
2. Vapor pressure at 25 °C and enthalpy of sublimation of selected PCB congeners.....	166
3. Vapor pressure at ambient temperatures and enthalpy of sublimation of selected pesticides....	173

1. Introduction

The assessment of the transport, distribution and fate of chemicals is one of the most important tasks for environmental scientists. To simulate the behavior of chemicals in the environment, much effort is being directed towards developing models based on their physical and chemical properties, the biotic and abiotic degradation processes and the characteristics of the environmental compartments. As a matter of fact, the distribution of a chemical between air, water, sediment/soil is largely dependent on some key equilibrium parameters which include vapor pressure (P), water solubility (S), distribution coefficients for adsorption or desorption on soil/sediment (K_p or K_d), partition coefficients (octanol/

[water] (K_{ow}), and Henry's law constant (HLC or H).¹⁻⁶ Vapor pressure and water solubility are the fundamental parameters, because all others can be derived from them using suitable correlation equations⁷⁻¹⁰ and both can be combined to calculate $H(H = P/S)$.

The vapor pressure, P (Pa), of a substance in equilibrium with its liquid or solid phase at a given temperature can be regarded as a measurement of the maximum achievable amount or solubility of the substance in the vapor or air phase, the corresponding concentration being obtained from the gas law as P/RT (mol m^{-3}), where R is the gas constant ($8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K).¹¹

Vapor pressure influences the volatility of a chemical from various substrates¹²⁻¹⁶ and, therefore, will determine the evaporation from workplaces and disposal sites. It governs, through the Henry's law constant, the exchange rate of a chemical across an air-water interface¹⁷⁻²² and the volatilization from aquatic systems,²³⁻²⁸ from soils,²⁹⁻³⁷ and from plants³⁸⁻⁴⁰ and the transport of trace organics throughout the global environment.⁴¹ It also controls the adsorption of organics to airborne particulate matter (less volatile compounds are preferentially adsorbed),⁴²⁻⁴⁵ the removal of this matter from the atmosphere by rainfall and dry deposition, and the atmospheric residential times.⁴⁶⁻⁴⁹

As far as the volatility of chemicals from water systems is concerned, it has been pointed out that also compounds of high molecular weight and low vapor pressure (polychlorinated biphenyls—PCBs, DDT) can volatilize at an appreciable rate because they have remarkably high activity coefficients in water, which cause unexpectedly high equilibrium vapor pressure.⁴¹

Many experimental techniques for the determination of the vapor pressure are described in the literature, but no single method is applicable for the entire vapor pressure range of environmentally significant compounds ($\sim 10^5$ to 10^{-6} Pa).⁵⁰ Also it has been observed^{51,52} that sometimes wide variations exist in the data reported by different authors for the same low vapor pressure compound. This suggests the need for determining vapor pressure by standard procedures.

In this paper the experimental and prediction procedures for the determination or evaluation of the vapor pressure of several organic compounds are reviewed. The vapor pressure data at ambient temperature are collected and compared with the aim of evaluating the performances of the various methods. They are only those reported in the original sources. Also the entropy of sublimation or vaporization in the range of measurement is given, when available from the literature.

The selected compounds are restricted to those belonging to few classes: PCBs, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and furans (PCDDs, PCDFs), and pesticides. Furthermore, among these classes, only the compounds of low-vapor-pressure are selected, for which a number of data sufficient to allow a reasonable comparison and some details concerning the method of determination are available. Due to these limitations the number of compounds taken into consideration for each class

is much lower than that existing in the technical manuals or in the specific literature, which can be consulted by the reader interested in their use.⁵³⁻⁵⁸

2. Experimental Methods

The experimental methods are sometimes classified a "static" or "dynamic."⁵⁹⁻⁶¹ The static methods measure directly the pressure exerted by the vapor in equilibrium with the liquid or the solid under examination, while with the dynamic methods a sample of saturated vapor is removed and the vapor concentration is determined.⁵⁹ However these terms are often confusing or used incorrectly;⁶¹ thus it has been preferred here to classify the methods used for environmental contaminants simply into "direct experimental," "indirect experimental," and "prediction" methods.

The first class includes all the methods which are used to measure directly the vapor pressure or another parameter related to it, while the second and the third class methods need a series of known vapor pressures for the calibration.

2.1. Direct Experimental Methods

"Gas saturation" and "effusion" are generally considered the most accurate direct experimental methods for vapor pressures lower than ~ 1 Pa.⁶² Both are recommended by the Organization for Economic Cooperation and Development (OECD)⁶³ but only the first by the Environmental Protection Agency (EPA).⁶⁴

2.1.1. Manometric Methods

These methods measure directly the pressure exerted by the vapor in equilibrium with the test compound in the liquid or solid phase.^{60,61} They are sensitive to the presence of impurities in the sample.

In the simplest devices the substance is placed in a thermostated cell under vacuum and the pressure is measured with a suitable device (mercury manometer, or Pirani gauge, Bourdon gauge, McLeod gauge, "Alphatron," thermocouple gauge, etc.). Zabel⁶⁵ measured the vapor pressure of di-n-butyl phthalate at 25 °C with an ionization gauge.

Some of these gauges are equipped with pressure sensors which work as null-detectors, where the vapor pressure is balanced with a pressure of air. The vapor pressure of naphthalene between 40 and 180 °C has been measured with a high precision mercury manometer and a quartz helix gauge.⁶⁶ The samples were contained in a bulb connected to the quartz helix of a sensitivity of about 50 Torr for 100 degrees rotation. A mirror, lamp, and split photocell assembly on the helix enabled it to be used as a null-detector of better than 0.02 Torr (2.67 Pa) long-term sensitivity and stability. The precision of the measurement has been found better than 0.03 Torr (4.0 Pa) below 100 Torr (1.33×10^4 Pa) and 0.1 Torr (13.3 Pa) between 100 and 300 Torr (3.99×10^4 Pa).

Other manometric systems can measure differential pressures using diaphragm sensors with a constant reference pressure of 10^{-4} Pa in one side, obtained by permanent pumping.

De Kruif *et al.*^{67,68} measured the vapor pressure of naphthalene between 273 and 385 K with a MKS Baratron capacitance manometer fitted with two sensor heads, which were designed for measurements up to 133 Pa and 133 kPa respectively. The measuring system was contained in an air thermostat. Temperature differences on essential parts were less than 0.01 K. The root-mean square deviation of the pressure was 0.4%.

Ambrose *et al.*⁶⁹ used the same apparatus fitted with a 10 Torr (1.33×10^3 Pa) bakeable head. The pressure was read directly on a digital voltmeter recalibrated against an accurate mercury manometer. The sample was contained in a glass flask immersed in a water bath, the temperature of which was controlled within ± 0.03 K. The temperature of the gauge head was maintained within ± 0.01 K at approximately 373 K. Measurements on naphthalene were made between 264 and 343 K. The estimated ranges of error were of $\pm 2\%$ for $T > 280$ K and $\pm 5\%$ for $T < 280$ K as root-mean-square deviation.

The vapor pressures of some polyaromatic hydrocarbons (PAH)^{70,71} were obtained with a Datametrix Barocel electronic manometer equipped with a wide range pressure sensor. The system was capable of measuring differential pressures ranging from 10^{-3} Torr (0.133 Pa) to 10 Torr (1.33×10^3 Pa). The gauge output was connected to a digital voltmeter. The device resolution was 10^{-5} Torr (1.33×10^{-3} Pa). The uncertainty on the equilibrium temperature was ± 0.02 °C and on the pressure was estimated better than 2%.

Other authors^{72,73} measured vapor pressures of PAHs with a free inclined piston. This system consists of balancing the vapor pressure of the sample with the known weight of a free piston declined from the horizontal by a measured angle. The vapor pressure can be calculated from the area and weight of the piston, the angle of declination and the acceleration of gravity.

The isoteniscope can be included in the class of null-detectors and is used especially with liquid substances. The experimental device is shown in the literature.^{74,75} The vapor pressure of the substance contained into a side bulb is balanced with a pressure of air pumped in a second bulb, suitably joined with the first, containing another fraction of the same substance. This second bulb is connected to a manometer and to a reservoir which allows changing of air pressure. The vapor pressure is measured when the levels of substance into the two bulbs are the same. Method errors of the order of ± 0.2 mm Hg (26.6 Pa) have been found.

2.1.2 Boiling Point at Reduced Pressures

These methods are based on the reading of the temperature at which the liquid substance boils at a definite pressure.

The boiling apparatus may consist of a glass boiler connected to a vapor column in which three thermocouples are

located at different heights to give some indication of the purity of the sample, the readings of the three thermocouples being identical for a pure substance.^{76,77} The boiler is connected to a vacuum pump and to a system which allows admission of air or nitrogen at known pressure into the apparatus. The pressure is measured with a McLeod gauge⁷⁷ or with an oil manometer.⁷⁶ Initially, the sample is degassed and the temperature of the boiler is increased until vapors rise in the boiling-point tube; the presence of vapors causes the thermocouple system to indicate increases of temperature. Then air or nitrogen is admitted until pressure has reached a selected value. The pressure is held at this value until the temperature reaches a steady state; this temperature is regarded as the boiling point of the liquid at the selected pressure. This process can be repeated after increasing the air pressure. It is also possible to begin the process from high values of pressure decreasing it step by step with a vacuum pump.

The McLeod gauge may be constructed⁷⁷ to measure pressures between 0.001 and 4.840 mm Hg (0.133 and 6.45×10^2 Pa) with an accuracy of ± 0.001 mm of Hg (0.133 Pa). The precision of temperature reading was ± 0.2 °C.

A similar apparatus was built⁷⁸ to obtain vapor pressure data for high boiling hydrocarbons; it could measure boiling points at absolute pressures ranging from about 0.1 mm Hg (13.3 Pa) to atmospheric pressure.

The vapor pressure of butyl phthalate and other commercial high boiling solvents has been determined in the region 20 °C to 150 °C⁷⁹ by the Ramsay and Young's method⁶¹ which uses a very simple boiler with a mercury manometer.

In comparative ebulliometry, the condensing temperature of the substance under study and of a reference material are measured when the two liquids are boiling at the same pressure under a common helium atmosphere. Boiling-point equipment, based on comparative ebulliometry has been used for the determination of the vapor pressure of naphthalene at values above 10 kPa⁸⁰ and 4 kPa.⁸¹

The tensimeters are employed for the determination of very low vapor pressures of gasolines and heavy lubricating oils.^{82,83}

The tensimeter-hypsometer is a well-insulated, short, wide boiler connected with a water-jacketed condenser and equipped with a mercury manometer;⁶¹ it can measure pressure ranging from 0.03 to 4 mm of Hg (4.0 to 5.33×10^2 Pa) with an oil manometer.⁸⁴ In operation, the liquid under study is boiled with various pressures of residual air or inert gas.

The pendulum tensimeter consists in a boiler having an orifice, which can be closed with a duralumin disk suspended by a duralumin wire.⁶¹ The entire apparatus is submerged in a heating bath and is connected to a vacuum system capable of maintaining a pressure of $0.1 \mu\text{m}$ (1.33×10^{-2} Pa), as measured by a Pirani or similar vacuum gauge. Initially the apparatus is rotated until the disk just closes the orifice. When the thermic equilibrium is reached, the vapor blows the disk away from the orifice. The apparatus is then rotated until the orifice is again closed. The vapor pressure can be calculated from the weight of the pendulum, the diameter of

the hole and the rotation angle of the pendulum. This system was used for the determination of the vapor pressure of dibutyl phthalate and other non-volatile compounds.⁸⁴⁻⁸⁶

A method based on kinetic theory principles has been developed, whereby the slope of the vapor pressure-temperature curve of a liquid can be obtained at 25 °C when the vapor pressure is of the order of 10^{-7} mm of Hg (1.33×10^{-5} Pa) at this temperature.⁸⁷ A simple apparatus consisting of a boiler, slit system, and target is used to determine the dew point of the material under high vacuum. About 5 cm³ of degassed oil (butyl phthalate and others) is placed in the boiler and the whole apparatus placed in a vacuum chamber in such a way that the target can be readily seen. When the vacuum is somewhat below 10^{-4} mm Hg (1.33×10^{-2} Pa), the boiler temperature is slowly raised until a spot is seen on the target. By proper adjustment of the boiler temperature, a balance point is reached such that the spot formed by the dew remains constant in intensity and distribution. From the temperature of this dew point the slope can be calculated directly. If, in addition, a single value is known by other methods for the vapor pressure in the region of 10^{-3} mm Hg (0.133 Pa), then the value at 25 °C is easily found. The results are believed to be accurate to 30%.

This method in a different version was used to extend measurements of vapor pressure to temperatures above room temperature.⁸³ However, it was found that vapor pressures above approximately 200 μ m (26.7 Pa) could not be determined with this instrument. Hence, it was still necessary to employ a tensimeter for determination of higher vapor pressures.

The boiling point of liquids with moderately high vapor pressures (>1 mm Hg or 133.3 Pa) at different pressures may be measured by differential thermal analysis.⁵⁹ This method requires a small amount of sample (10 μ liters) and the measurement is rapid. The apparatus consists of a heating block with two wells into which thermocouples, and associated instrumentation for sensitive determination of temperature difference between the two thermocouples are inserted. A bell jar over the block controls the pressure in the system. Thin-walled glass tubes are loaded with microglass beads and placed in the block. The liquid under examination is injected into one tube and the thermocouples are inserted. After the pressure in the system is stabilized, the heating cycle is begun, and when the boiling point of the liquid is reached, vaporization prevents any further temperature rise in one tube; hence, the difference in temperature which develops is recorded on the graph by the machine. By raising the pressure in the bell jar the boiling is quenched, thus permitting several boiling point temperature measurements to be made on a single sample. The accuracy is better than 10 or 20% in most cases. Boiling point determinations are very inaccurate at lower vapor pressures and provide inaccurate estimates of the vapor pressure at ambient temperatures if a change of state or a transition temperature occurs between the boiling temperature and ambient temperature.⁶²

2.1.3. Effusion

The effusion methods, in their original versions, determine the vapor pressure at constant temperature of a single compound, from the measurement of the weight loss through a small orifice into a vacuum (typically 10^{-4} Pa).

The Knudsen effusion cell consists, essentially, of a cell having a small orifice of known diameter and immersed in a container connected to a high-vacuum system. The cell is weighed at the beginning of the experiment and at time intervals with a balance, which can be external or internal (see the references in Tables 1,2,5) to the apparatus. Alternatively, the vapor can be condensed on a liquid nitrogen cooled cold finger^{88,89} or on a surface cooled by dry ice-acetone or liquid nitrogen placed above the orifice,^{59,86} removed, and analyzed. The vapor pressure can be calculated from the equation

$$P = (W/AKt) \sqrt{2\pi RT/M},$$

where P is the vapor pressure, W the weight loss over a corresponding time t , A the area of the orifice, R the gas constant, T the absolute temperature, M the molecular weight of the effusing species, and K the Clausing factor, depending on the orifice diameter, which represents the probability of effusion through the orifice for a given molecule.

In the torsion-effusion method, the cell consists of two spheres having one hole each in opposite positions and suspended from a thin long quartz,⁹⁰ phosphor-bronze^{91,92} or tungsten⁹³⁻⁹⁵ wire. The effusion of the vapor through the two orifices exerts a torque which is directly proportional to the vapor pressure.⁹⁰⁻⁹³ A trap cooled with liquid nitrogen or CO₂-acetone mixture may ensure rapid passage of vapors away from the holes and protects the vacuum from vapors.⁹⁰ The sensitivity depends on the size and position of the holes and the stiffness of the suspension. At each temperature the pressure in the effusion cell can be determined by its torsion angle, α , from the relation

$$P = 2Ka/(a_1l_1f_1 + a_2l_2f_2),$$

where K is the torsion constant; a_1 , a_2 , l_1 , and l_2 are the areas of the effusion orifices and their distances from the rotation axis, respectively; and f_1 and f_2 are the corresponding geometrical factors.

Some authors^{91,92} used an apparatus in which torsion and weighing were combined.

In these methods it is assumed that the number of molecules exiting from the small hole under vacuum depends only on the size of the orifice and on the saturation vapor pressure.^{88,95,96} They can be affected by systematic errors, which depend on the orifice area, temperature, or impurities.^{59,97} However, when the vapors are condensed and collected for analysis, impurities can be "ignored" by appropriate choice of analytical method.⁵⁹

Effusion methods allow measurement of vapor pressures down to 10^{-3} Pa without great difficulty,⁹⁸ but are considered accurate for vapor pressures in the range between 10^{-1} and 10^{-5} Pa,^{59,99} with a minimum measurable value of 7×10^{-4} Pa⁹⁰ or a resolution of 10^{-4} Pa.⁹² The repro-

ducibility was $\pm 10\%$ at 2×10^{-3} Pa, $\pm 2\%$ between 2×10^{-2} and 1 Pa,⁹⁷ $\pm 1\%$ between 2 and 24 Pa.¹⁰⁰

2.1.4 Gas Saturation

The gas saturation (GS) method, also termed the "transpiration method," is generally used in the ambient temperature range. It was proposed by Regnault in 1845⁶¹ and then by Spencer and Cliath.¹⁰¹ Analogous techniques were proposed to measure water solubilities and octanol/water partition coefficients of chemicals.¹⁰²

It is based on the production of a saturated vapor phase by passing an inert gas, air, nitrogen, or oxygen (when a combustion procedure of analysis has to be used) through a thermostated column packed with the powdered compound^{103,104} or with an analyte-coated inert support. The saturation pressure of the substance is represented by its partial vapor pressure. Usually, the vapor is collected on liquid or solid traps and the substance is determined by suitable means. For pressures on the order of 10^{-4} to 10^{-5} mm Hg (1.33×10^{-2} to 1.33×10^{-3} Pa), the amount of substance transferred, assuming an average molecular weight of 250, is in the order of 10^{-6} g/l carrier gas.¹⁰⁵

The support may be quartz sand,^{38,62,106-108} various size glass beads,^{50,99,109-114} celite,¹⁰⁵ or a glass wool plug moistened with the liquid sample.¹¹⁵

The treated support is prepared by adding an amount of 0.4-3% in weight of the compound of interest dissolved in a volatile solvent. The solvent is slowly stripped off on a rotary evaporator using a heating bath.

Flow rates of the inert gas through the column must be such to ensure saturation with the compound of interest. Values up to 50 ml/min or higher^{104,105,116} have been employed. Sonnefeld *et al.*⁵⁰ pointed out that the flow rate will be dependent upon the generator column dimensions, the surface area of the analyte coated support, and the kinetic parameters of sublimation for the individual compounds of interest. Therefore residence times of the inert gas in the saturator may be of the order of 30-40 min^{62,114} or much less. It has been found that only a 30-s residence time is necessary for anthracene at 25°C.⁵⁰

Normally, the vapor transported by the inert gas is trapped on a solid adsorbent, such as Florisil,^{30,109,114,117} Chromosorb-102,¹¹⁸ active carbon,^{108,119} polyurethane foam,^{38,48,51,113,120} Tenax,^{110,121} porous octadecylsilane,^{50,102} Amberlite XAD-2 or Chromosorb-101.¹¹² Sometimes liquid traps, such as hexane,¹⁰⁶ ethylene glycol,^{101,107} ethyl alcohol,¹¹⁵ or cold traps^{50,99,102,116} are used.

The volume of the inert gas passed through the saturator is measured by a suitable flow meter, after leaving the condensation trap, and corrected for any temperature and pressure differences between the saturator and the flow meter and, if liquid traps are used, for the net volume of trapping solvent added to the inert gas.¹⁰¹

The final determination of the analyte can be obtained by:

- loss in weight of the saturation tube;¹⁰³
- increase of weight of the condensation trap;¹²²

- weighing the compound condensed on a cold trap;¹¹⁶
- UV spectrophotometric measurement of the compound in a liquid trap;^{106,115}
- combustion of the analyte and determination of the CO₂ produced by an IR analyzer;^{104,123,124}
- combustion of the analyte, adsorption on P₂O₅ and CaCl₂ of the produced CO₂ and water, and their determination by weight;¹²⁵
- decomposition of chlorinated compounds in alkali and determination of the produced HCl by potentiometric titration;¹²⁶
- collection of the ¹⁴C-labeled compound on a solid trap, elution and determination by liquid scintillation counting;¹¹³
- collection of the ¹⁴C-labeled compound on charcoal tubes, combustion of the tubes, and determination of the produced ¹⁴CO₂ by liquid scintillation counting;¹⁰⁸
- collection of the ¹⁴C-labeled compound on a solid trap, elution, combustion, and determination of the produced CO₂ by liquid scintillation counting;¹¹⁹
- collection of the analyte on liquid or solid traps, liquid-liquid extraction or elution, and determination by GC or HPLC (see the references in Tables 1-5).

The advantages of the chromatographic techniques over the others consist in eliminating any effect of impurities and allowing simultaneous measurements on many test compounds.

Some authors used an apparatus in which the two stages of saturation and analysis are combined. The chromatographic column acts as a trap at ambient temperature^{127,128} or is cooled with solid carbon dioxide above the level of connection with the apparatus;¹⁰⁵ then, when the collection is complete, the column is isolated from the gas saturation apparatus and heated to a temperature appropriate for the GC analysis¹²⁷ or disconnected and transferred to the gas chromatograph for the same purpose.^{105,128} A "continuous" method has also been proposed;^{127,129} an empty tube at elevated temperature replaces the packed column, the detector output corresponds to the total vapor content of the gas stream.

Bhagat¹³⁰ has recently described a simple technique to estimate the vapor pressure of phosphate esters, in which saturation and gas chromatography seem to be combined in the same column. This technique has been used for the determination of the enthalpy of vaporization, by depositing the compound on a chromatographic support and measuring the temperature dependence of the bleeding of the material at a fixed flow rate of the carrier gas with a flame ionization detector. Using these enthalpy of vaporization data and those of standard compounds, the vapor pressure can be determined on the basis of the Clausius-Clapeyron equation.

The vapor pressure, P , in GS methods can be calculated from vapor density with the following equation

$$P = d(RT/M),$$

TABLE 1. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PAHs

P_s	P_1	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
Naphthalene: $MW=128.18$; $MP=80.2$ °C						
9.64		E (Kn), VG	237–276	$\log P_s = -(4000/T) + 14.400$	76.59	144
10.8		E (Kn,i)	280–294	$\log P_s = -(3783/T) + 13.722$	72.4	88
11.4		E(Kn)	271–285	$\log P_s = -(3861.8/T) + 14.01$	73.93	216
					72.8	
					(298.15)	
11.3		E (T-W)	253–273	Clarke and Glew (Ref. 217)	74.4	91
					72.6	
					(298.15)	
5.58		E	253–283	$\log P_s = -(3616/T) + 12.875$	67.4	218
10.7		E (Kn)	283–323	$\log P_s = -(3476/T) + 12.687$	66.53	219
10.7		E (Kn)	226–263	$\log P_s = -(3883/T) + 14.052^a$	72.6	220
					(298.15)	
12.3		E (Kn,i)	282–297	$\log P_s = -(3798.571/T) + 13.829$	72.72	221
12.3		E (Kn, i)	283–303	$\log P_s = -(3444/T) + 12.641$	65.77	222
15.2		E (Kn)	283–303	$\log P_s = -(29820/T)$ $(200.682 \log T) + 597.767$	82.0	100
10.6		E	288–306	$\log P_s = -(3429/T) + 12.525$		223
13.7		GS (W), M(Hg)	273–403			103
14.0		GS (CO ₂)	273–313	$\log P_s = -(3566/T) + 13.107^a$		125
11.6		GS	289–323	$\log P_s = -(3722.5/T) + 13.549$	71.27	224
11.3		GS (GC)	302–352	$\log P_s = -(3801/T) + 13.8$		99
10.8		GS (CO ₂)	280–305	$\log P_s = -(3724/T) + 13.525$		124
10.9		GS (W)	323–343	$\log P_s = -(3738.6/T) + 13.577^a$		122
10.9		GS (CO ₂)	275	Miller	72.5	104
					(298.15)	
10.4		GS (HPLC)	283–323	$\log P_s = -(3960.03/T) + 14.299$	75.8	50
11.2		M (Baratron)	263–343	based on Chebyshev polynomial	72.42	69
					(298.15)	
11.3		M (Baratron)	274–353	Clarke and Glew	72.513	68
					(298.15)	
11.4		M (DB)	261–343	$\log P_s = -[2907.918/(236.459+t)]$ $+ 12.17748$		70
		M (DB)	353–363	$\log P_1 = -[76.496/(-25.09+t)]$ $+ 4.37665$		70
11.0		M (Hg)	313–353	$\log P_s = -[2619.91/(t+220.651)]$ $+ 11.70587$		66
		M (Hg)	353–453	$\log P_1 = -[1756.91/(t+204.937)]$ $+ 9.15867$		66
14.4		M (Rodebush)	292–308	$\log P_s = -[108.30/(t+27)] + 3.240$		225
10.8		HS	263–293	$\log P_s = -(3541/T) + 12.910^a$	67.8	146
		BP	419–613	$\log P_1 = -[1735.264/(T-70.820)]$ $+ 9.13400$		80
		BP	399–492	$\log P_1 = -[1606.529/(187.227+t)]$ $+ 8.97067$		226
10.8		BP	384–539	Wagner (Ref. 258)	72.7	81
7.71		Vs	276–283	$\log P_s = -(3462.6/T) + 12.501$	66.27	143
		Is (Hg)	373–473	$\log P_1 = -(2465/T) + 10.026$	43.72 ^b	74
		Is (Hg)	360–494	$\log P_1 = -(2493/T) + 10.093^a$		75
12.0		S×H	298			141
4.69		Pr (UNIFAC)	298			206
8.51		Pr (KLH)	298			11
17.2		Pr (Th)	298			192
6.45	22.7	GC (BP1)	313–353			157
8.04	28.2	GC (Apolane)	313–353			157
1-methyl-naphthalene: $MW=142.2$; $MP=-22$ °C						
	8.94	GS (CO ₂)	279–312	$\log P_1 = -(3011.1/T) + 11.0505$		124
		M	515–778	$\log P_1 = -(2430/T) + 9.7240^a$		227
	8.93	M (DB)	259–388	$\log P_1 = -[2006.862/(212.625+t)]$ $+ 9.39611$		70

TABLE 1. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PAHs—Continued

P_s	P_1	Method	ΔT (K)	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
		M (Ruska)	424–593	based on Chebishev polynomial		228
		BP	415–518	$\log P_1 = -[1826.948/(195.002+t)]$ $+ 9.16082$		226
	9.50	BP	282–473	$\log P_1 = -[2226.03/(230+t)] + 9.707^a$		78
	8.12	Pr (KLH)	298			11
	19.7	Pr (Th)	298			192
	7.42	GC (BP1)	313–363			157
	5.93	GC (Apolane)	313–363			157
Acenaphthene: $MW=154.2$; $MP=96.2$ °C						
3.36E-1		E (Kn)	290–323	$\log P_s = -(4496/T) + 14.606$	86.2	229
2.11E-1		E	258–308	$\log P_s = -(4264/T) + 13.625$	83.3	
3.83E-1		E (Kn,i)	327–356	$\log P_s = -(4422.921/T) + 14.4179$	84.68	221
2.87E-1		GS (HPLC)	283–323	$\log P_s = -(4535.39/T) + 14.669$	86.8	50
3.75E-1		M (IP)	338–366	$\log P_s = -(4353/T) + 14.174^a$		72
		M (IP)	368–413	$\log P_1 = -(3126/T) + 10.828^a$	59.2 ^b	72
		Is (Hg)	413–523	$\log P_1 = -(2835/T) + 10.158$	50.25 ^b	74
3.11E-1		Vs	291–311	$\log P_s = -(4290.5/T) + 13.883$	82.1	143
3.77E-1		S×H	298			141
1.22E-1		Pr (UNIFAC)	298			206
3.06E-1		Pr (KLH)	298			11
8.62E-1		Pr (Th)	298			192
Fluorene: $MW=166.23$; $MP=116$ °C						
5.75E-2		E (T)	280–300		80.3	96
8.85E-2		E (Kn, i)	306–323	$\log P_s = -(4324/T) + 13.450$	82.8	88
8.00E-2		GS (HPLC)	283–323	$\log P_s = -(4616.07/T) + 14.385$	88.4	50
		M (IP)	348–387	$\log P_s = -(4291/T) + 13.495^a$		72
8.51E-2		M (DB)	303–373	$\log P_s = -[4268.644/(262.656+t)]$ $+ 13.7691$		70
		M (DB)	383–428	$\log P_1 = -[2641.73/(230.963+t)]$ $+ 10.07324$		70
		Is (Hg)	423–573	$\log P_1 = -(2957/T) + 10.184$	52.34 ^b	74
7.92E-2		Pr (KLH)	298			11
2.43E-1		Pr (Th)	298			192
5.94E-2	4.73E-1	GC(BP1)	343–383			157
4.77E-2	3.80E-1	GC (Apolane)	343–383			157
Anthracene: $MW=178.24$; $MP=216.2$ °C						
1.39E-3		E (T)	328–346		90.0	96
8.32E-4		E (Kn, i)	339–354	$\log P_s = -(5320/T) + 14.763$	102.1	88
7.50E-4		E (T-W)	337–361	Clarke and Glew	100.4 104.5 (298.15)	91
1.44E-4		E	303–373	$\log P_s = -(5401/T) + 14.275$	101.7	218
3.31E-3		E (Kn, i)	365 (average)	$\log P_s = -(4795/T) + 13.545$	91.8	230
(average)		E (Kn, i)	364 (average)	$\log P_s = -(4820/T) + 13.736$	92.3	230
8.65E-4		E (Kn)	342–359	$\log P_s = -(5145/T) + 14.193$	98.49	89
1.10E-3		E (Kn)	353–432	$\log P_s = -(5277/T) + 14.741$	101.04	231
9.24E-4		E (Kn)	329–372	$\log P_s = -(5105/T) + 14.119$	97.74	232
(average)		E (Kn)	329–372	$\log P_s = -(5057/T) + 13.894$	96.82	232
2.49E-3		E (Kn)	290–358	$\log P_s = -(4397.60/T) + 12.1465$	84.1	233
1.44E-3		GS (CO ₂)	353–399	$\log P_s = -(4941.4/T) + 13.732$		123
1.84E-3		GS (GC)	323–354	$\log P_s = -(4763.3/T) + 13.24$		99
1.44E-3		GS (CO ₂)	358–393	$\log P_s = -(4951.8/T) + 13.766$		124
5.11E-3		GS (GC)	303–373	$\log P_s = -[3749.7/(t+238.6)] + 11.933$		128
1.06E-3		GS (GC)	313–373	$\log P_s = -(5157/T) + 14.322^a$	98.75	111
8.04E-4		GS (HPLC)	283–323	$\log P_s = -(4791.87/T) + 12.977$	91.8	50
6.93E-4		M (Rodebush)	378–398	$\log P_s = -(5263/T) + 14.493$	100.8	234
1.03E-3		M (Rodebush)	378–398	$\log P_s = -(5102.0/T) + 14.127$	97.634	225
4.84E-3		Is (Hg)	373–473	$\log P_s = -(4595/T) + 13.097$	83.6	74

TABLE 1. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PAHs—Continued

P_s	P_1	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
				(extrapolated)		
		Is (Hg)	496–614	$\log P_1 = -(3093/T) + 10.035$	54.8 ^b	74
		Is (Hg)	500–616	$\log P_1 = -(3112/T) + 10.074^a$		75
1.04E-3		F	396–421	$\log P_s = -(5102/T) + 14.127$	97.5	145
4.90E-4		Pr (TSA)	298			203
1.25E-3		Pr (UNIFAC)	298			206
1.29E-3	1.00E-1	GC (BP1)	343–383			157
8.25E-4	6.39E-2	GC (Apolane)	343–383			157
1.17E-3	9.10E-2	GC (BP1)	343–453	$\log P_1 = -(3642/T) + 11.18$		160
Phenanthrene: $MW=178.24$; $MP=101$ °C						
2.51E-2		E (T)	287–315		84.1	96
2.27E-2		E (Kn, i)	310–323	$\log P_s = -(4519/T) + 13.513$	86.6	88
1.80E-2		E (T-W)	315–335	Clarke and Glew	90.5	91
					92.5	
					(298.15)	
1.86E-2		E (T)	317–362	$\log P_s = -(4204/T) + 12.37$	80	93
2.13E-2		E	273–333	$\log P_s = -(5008/T) + 15.125$	92.9	216
1.02E-1		K (Kn, i)	315 (average)	$\log P_s = -(4740/T) + 14.905$	90.8	230
2.67E-2		GS (CO ₂)	325–363	$\log P_s = -(4553.2/T) + 13.698$		124
1.61E-2		GS (HPLC)	283–323	$\log P_s = -(4962.77/T) + 14.852$	95.0	50
		M (IP)	373–423	$\log P_1 = -(3601/T) + 11.138^a$	68.9 ^b	72
		Is (Hg)	473–623	$\log P_1 = -(2990/T) + 9.896$	53.0 ^b	74
		Is (Hg)	505–614	$\log P_1 = -(3099/T) + 10.067^a$		75
2.88E-2		S×H	298			141
2.27E-2		Pr (TSA)	298			203
1.81E-2		Pr (UNIFAC)	298			206
1.96E-2	1.11E-1	GC (BP1)	343–393			157
1.22E-2	6.88E-2	GC (Apolane)	343–393			157
1.73E-2	9.77E-2	GC (BP1)	343–453	$\log P_1 = -(3716/T) + 11.46$		160
Fluoranthene: $MW=202.26$; $MP=111$ °C						
1.68E-3		E (Kn)	329–354	$\log P_s = -(5332/T) + 15.108$	102.1	229
6.72E-4		E	298–358	$\log P_s = -(5357/T) + 14.795$	100	218
1.24E-3		GS (HPLC)	283–323	$\log P_s = -(4415.56/T) + 11.901$	84.7	50
		BP	470–657	$\log P_1 = -(3526/T) + 10.432^a$		235
2.18E-3	1.55E-2	GC (BP1)	343–383			157
9.39E-4	6.67E-3	GC (Apolane)	343–383			157
8.89E-4	6.31E-3	GC (BP1)	343–453	$\log P_1 = -(4040/T) + 11.35$		160
Pyrene: $MW=202.26$; $MP=156$ °C						
8.85E-4		E (Kn, i)	345–358	$\log P_s = -(4904/T) + 13.395$	93.9	88
3.34E-4		E	298–363	$\log P_s = -(5248/T) + 14.125$	100.5	218
3.06E-3		E (Kn, i)	352 (average)	$\log P_s = -(5230/T) + 15.028$	100.1	230
6.01E-4		E (Kn)	348–419	$\log P_s = -(5091/T) + 13.854$	97.5	236
					101.0	
					(298.15)	
9.26E-4		E (Kn, i)		$\log P_s = -(4840/T) + 13.200^a$		237
6.03E-4		GS (HPLC)	283–323	$\log P_s = -(4760.73/T) + 12.748$	91.2	50
		M (IP)	398–458	$\log P_1 = -(3990/T) + 11.254^a$	100.2	73
					(298.15)	
2.93E-4		M (DB)	353–413	$\log P_s = -[2967.129/(182.314+t)] + 10.77971$		70
		M (DB)	413–467	$\log P_1 = -[1553.755/(112.964+t)] + 7.75157$		70
		BP	473–668	$\log P_1 = -(4228/T) + 11.551^a$		235
8.80E-4		Pr (TSA)	298			203
1.73E-4		Pr (UNIFAC)	298			206
5.72E-4	1.13E-2	GC (BP1)	343–393			157
2.47E-4	4.89E-3	GC (Apolane)	343–393			157
7.13E-4	1.41E-2	GC (BP1)	343–453	$\log P_1 = -(4104/T) + 11.92$		160

TABLE 1. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PAHs—Continued

P_s	P_1	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
Benz(a)anthracene: $MW=228.3$; $MP=157\text{ }^\circ\text{C}$						
7.30E-6		E (T-W)	373-396	Clarke and Glew	113.5 123.3 (298.15)	91
2.81E-5		E (T)	377-426	$\log P_s = -(5430/T) + 13.66$	104	93
6.96E-6		E	333-393	$\log P_s = -(6250/T) + 15.805$	116.7	218
2.17E-5		E (Kn)	377-400	$\log P_s = -(5461/T) + 13.653$	104.6	89
1.51E-5		E (Kn, i)	330-390	$\log P_s = -(5925/T) + 15.0506$	113.5	97
1.50E-5		E (Kn, i)	245-310	$\log P_s = -(5926/T) + 15.051^a$		237
4.11E-7		E (Kn, i)	357-455	$\log P_s = -(6330/T) + 14.845$	120.5	238
2.76E-5		GS (HPLC)	283-323	$\log P_s = -(4246.51/T) + 9.684$	81.3	50
3.39E-5		Pr (UNIFAC)	298			206
5.29E-5	1.07E-3	GC (BP1)	343-403			157
1.48E-5	3.00E-4	GC (Apolane)	343-403			157
2.57E-5	5.21E-4	GC (BP1)	343-453	$\log P_1 = -(4742/T) + 12.63$		160
Benz(a)pyrene: $MW=252.32$; $MP=176\text{ }^\circ\text{C}$						
7.51E-7		E (Kn, i)	358-431	$\log P_s = -(6181/T) + 14.6066$	118.4	97
7.45E-7		E (Kn, i)	260-320	$\log P_s = -(6182/T) + 14.607^a$		237
7.01E-7		Pr (UNIFAC)	298			206
3.51E-6	1.12E-4	GC (BP1)	363-403			157
4.73E-7	1.51E-5	GC (Apolane)	363-403			157
2.25E-7	7.19E-6	GC (BP1)	343-453	$\log P_1 = -(4989/T) + 11.59$		160

^aEquations derived by the author from the vapor pressure data reported in the original papers.

^bReported values refer to $\Delta_{vap}H$.

where P is the vapor pressure, d the vapor density, R the molar gas constant, T the absolute temperature and M the molecular weight of the test compound.

GS methods show normally relative standard deviations between $\pm 0.5\%$ and $\pm 18\%$ in the range of vapor pressure of 10^{-8} – 10^4 Pa and in the range of temperature of 10–200 °C.^{50,62,112,115,126,128,131} A 9% measurement error has been calculated with the error propagation rule.^{50,102} The method precision, expressed as two times the standard deviation from the mean value at the 95% confidence limit, was $\pm 2\%$ and $\pm 3\%$ for lindane¹³² and triallate,¹³³ respectively and between $\pm 5\%$ and $\pm 10\%$ for ethyl and methyl parathion at various temperatures.⁵¹ A standard error of 5.2% has been found in the determination of the vapor pressure of 2,3,7,8-TCDD.¹¹⁹

The technique has been used also for the determination of the vapor density of pesticide-soil systems.⁶² The solid support was substituted with autoclaved soil and the vapor densities of dieldrin,^{35,101} lindan,³³ trifluralin,³⁴ DDT and related compounds¹³⁴ were measured as a function of the pesticide concentration, temperature, water content in soil and properties of soil.

2.1.5. Partition Coefficient

This method can be applied to water solutions of compounds of very low solubility (less than 10 ppm).⁴⁶

Air is passed through contact bubblers containing an aqueous solution of the compound (a pesticide labeled with ¹⁴C) under examination and, then, through two Arnold absorption bulbs in series containing a xylene-based scintillator solution, where the compound is trapped. At the end of the experiment the concentrations of compound in the gas phase and in the aqueous solution are measured by liquid scintillation counting.

The partition coefficient (p) is defined as

$$p = \frac{\text{(concentration of pesticide/cm}^3 \text{ aqueous phase)}}{\text{(concentration of pesticide/cm}^3 \text{ air)}} \\ = [(C_1 + C_2)V]/2A,$$

where C_1 and C_2 are the pesticide concentrations (counts $\text{min}^{-1} \text{cm}^{-3}$) at the start and at the end of the experiment respectively; V is the volume of air passed (cm^3); and A is the pesticide collected in the Arnold bulbs (counts min^{-1}).

Several determinations are carried out at 20 °C over a range of concentrations from very dilute to saturated solutions containing a suspension of the solid material. The plot of the partition coefficient versus concentration shows a constant value of the partition coefficient over a range of concentration of several orders of magnitude and then a sharp rise in the apparent value at the point of saturation. The value of solubility can be obtained from the point at which devia-

TABLE 2. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PCB congeners^c

P_s	P_1	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
Biphenyl: $MW = 154.21$; $MP = 71$ °C						
1.29		E (Kn, i)	288–314	$\log P_s = -(4262/T) + 14.407$	81.6	88
0.580		E (Kn)	278–308	$\log P_s = -(3799/T) + 12.505$	72.8	98
1.43		E (Kn, i)	298–323	$\log P_s = -(4367.436/T) + 14.8038$	83.60	221
0.969		E	287–307	$\log P_s = -(3918.2/T) + 13.128$	75.06	239
1.19		GS (GC)	278–298	$\log P_s = -(4402.1/T) + 14.84$	84.1	109
1.34	3.72	GS (GC)	348–453	$\log P_1 = -[2317.55/(T - 49.655)]$ $+ 9.89695$		240
		M	528–766	$\log P_1 = -(2507/T) + 9.7537$		227
1.29		M (DB)	283–338	$\log P_s = -[2921.175/(t + 217.243)]$ $+ 12.16848$	83.39	71
		M (DB)	333–393	$\log P_1 = -[2077.065/(t + 205.046)]$ $+ 9.54252$		71
1.97		HS	273–303	$\log P_s = -(3956/T) + 13.562^a$	75.7	146
1.03		Vs	279–299	$\log P_s = -(3959.4/T) + 13.293$	75.81	143
1.87		S×H	298			141
0.639		Pr (UNIFAC)	298			206
1.62		Pr (KLH)	298			11
4.32		Pr (Th)	298			192
0.422		Pr (MW)	298			179
0.594		Pr (TI)	298			179
1.00		Pr (TI)	298			200
0.703	2.03	GC	473			179,182
		(Apiezon L)				
2.54	7.04	GC (BP1)	313–363			157
2.25	6.22	GC (Apolane)	313–363			157
(1) 2-: $MW = 188.65$; $MP = 34$ °C						
0.301	0.367	E (T+Kn)	306–359	$\log P_1 = -(4149/T) + 13.48$	79.4 ^b	94
		E (T)	337–383			94
0.355		Pr (MW)	298			179
0.260		Pr (TI)	298			179
0.59		Pr (TI)	298			200
0.27		Pr (TI)	298			200
0.922		Pr (S×H)	298			204
0.755	0.926	GC	473			179,182
		(Apiezon L)				157
1.55	1.89	GC (BP1)	313–373			157
2.10	2.56	GC (Apolane)	313–373			157
1.57	1.91	GC		$\log P_1 = -(3366/T) + 11.57$		169
(2) 3-: $MW = 188.65$; $MP = 25$ °C						
3.62E-1		E(T+Kn)	310–359	$\log P_1 = -(3614/T) + 11.68$	69.2 ^b	94
		E (T)	341–402			94
4.36E-1		Pr (MW)	298			179
2.60E-1		Pr (TI)	298			179
2.20E-1		Pr (TI)	298			200
7.31E-1		Pr (S×H)	298			204
3.67E-1		GC	473			179,182
		(Apiezon L)				
9.79E-1		GC (BP1)	313–373			157
1.01		GC (Apolane)	313–373			157
9.80E-1		GC		$\log P_1 = -(3476/T) + 11.65$		169
(3) 4-: $MW = 188.65$; $MP = 77.7$ °C						
3.39E-1		E (T+Kn)	306–346	$\log P_s = -(3849/T) + 12.44$	73.7	94
7.88E-2	2.53E-1	E (T)	348–409	$\log P_1 = -(3541/T) + 11.28$	67.8 ^b	94
1.75E-1		GS (GC)	277–298	$\log P_s = -(4754.1/T) + 15.188$	90.8	109
1.31E-1		Pr (MW)	298			179
1.14E-1		Pr (TI)	298			179
1.22E-1		Pr (TI)	298			200
1.12E-1		Pr (S×H)	298			204
9.78E-2	3.20E-1	GC	473			179,182
		(Apiezon L)				

THE VAPOR PRESSURE OF ENVIRONMENTALLY SIGNIFICANT ORGANIC COMPOUNDS 167

TABLE 2. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PCB congeners^c—Continued

P_s	P_l	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
2.86E-1	9.18E-1	GC (BP1)	313-373			157
2.93E-1	9.42E-1	GC (Apolane)	313-373			157
8.7E-2	2.8E-1	GC (OV101)	423			170
2.92E-1	9.36E-1	GC		$\log P_1 = -(3488/T) + 11.67$		169
				(4) 2,2'-: $MW=223.1$; $MP=61$ °C		
1.34E-1		E (Kn)	310-328	$\log P_s = -(5019/T) + 15.962$	96.2 (298.15K)	241
6.03E-2	1.52E-1 (20 °C)	ET	293			140
1.84E-1	4.08E-1	S×H	298			135
6.91E-2		Pr (MW)	298			179
1.14E-1		Pr (TI)	298			179
3.15E-1		Pr (TI)	298			200
1.93E-1		Pr (S×H)	298			204
1.89E-1	4.24E-1	GC	473			179,182
		(Apiezon L)				
1.3E-1	2.8E-1	GC (OV101)	423			170
1.6E-1	3.6E-1	GC	373-518			170
		(SBOctyl 50)				
1.47E-1	3.27E-1	GC (OV101)	473			139
1.51E-1	3.35E-1	GC	473			139
		(Dexsil410)				
1.47E-1	3.27E-1	GC		$\log P_1 = -(3642/T) + 11.73$		169
				(9) 2,5-: $MW=223.1$; $MP=23$ °C		
	1.96E-1	S×H	298			135
	1.57E-1	Pr (MW)	298			179
	1.14E-1	Pr (TI)	298			179
	1.45E-1	Pr (TI)	298			200
	1.05E-1	Pr (TI)	298			200
	2.22E-1	Pr (S×H)	298			204
	2.02E-1	GC	473			179,182
		(Apiezon L)				
	1.84E-1	GC (BP1)	313-373			157
	2.0E-1	GC	373-518			170
		(SBOctyl 50)				
	2.31E-1	GC (OV101)	473			139
	2.32E-1	GC	473			139
		(Dexsil410)				
	1.85E-1	GC		$\log P_1 = -(3862/T) + 12.22$		169
				(11) 3,3'-: $MW=223.1$; $MP=29$ °C		
3.76E-2	4.10E-2	S×H	298			135
1.43E-1		Pr (MW)	298			179
1.14E-1		Pr (TI)	298			179
3.06E-2 (average)		Pr (TI)	298			200
9.39E-2		Pr (S×H)	298			204
6.11E-2	6.46E-2	GC	298			179,182,138
		(Apiezon L)				
7.94E-2	8.65E-2	GC (BP1)	313-373			157
8.74E-2	9.53E-2	GC (Apolane)	313-373			157
8.38E-2	9.14E-2	GC OV101)	473			139
6.97E-2	7.60E-2	GC	473			139
		(Dexsil410)				
2.7E-2		GC (Apolane)	333-403			162
7.97E-2	8.69E-2	GC		$\log P_1 = -(3936/T) + 12.14$		169
				(12) 3,4-: $MW=223.1$; $MP=50$ °C		
7.36E-4	1.28E-3	S×H	298			135
8.88E-2		Pr (MW)	298			179
4.99E-2		Pr (TI)	298			179
4.25E-2		r (S×H)	298			204
3.13E-2	5.32E-2	GC	473			179,182,138
		(Apiezon I.)				

TABLE 2. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PCB congeners^c—Continued

P_s	P_1	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
4.3E-2	7.4E-2	G (SBOctyl 50)	373-518			170
4.50E-2	7.83E-2	GC (OV101)	473			139
3.57E-2	6.22E-2	GC (Dexsil410)	473			139
4.46E-2	7.76E-2	GC		$\log P_1 = -(3885/T) + 11.92$		169
2.63E-3		E (Kn)	(15) 4,4'-: MW=223.1; MP=149 °C 303-360	$\log P_s = -(5416/T) + 15.585$	103.8 (298.15)	241
3.28E-3	5.11E-2	S×H	298			135
9.31E-3		Pr (MW)	298			179
2.19E-2		Pr (TI)	298			179
9.43E-3		Pr (TI)	298			200
4.17E-3		Pr (TI)	298			200
2.46E-3		Pr (S×H)	298			204
3.13E-3	5.08E-2	GC (Apiezon I)	473			179,182,138
4.58E-3	7.13E-2	GC (BP1)	313-373			157
5.38E-3	8.37E-2	GC (Apolane)	313-373			157
3.9E-3	6.0E-2	GC (OV101)	423			170
5.0E-3	7.8E-2	GC (SBOctyl 50)	373-518			170
4.85E-3	7.54E-2	GC (OV101)	473			139
3.79E-3	5.89E-2	GC (Dexsil410)	473			139
4.67E-3	7.26E-2	GC		$\log P_1 = -(3971/T) + 12.18$		169
2.03E-2	3.50E-2 (20 °C)	ET	(18) 2,2',5'-: MW=257.54; MP=44 °C 293			140
7.62E-2	1.16E-1	S×H	298			135
3.68E-2		Pr (MW)	298			179
3.30E-2		Pr (TI)	298			179
5.63E-2		Pr (S×H)	298			204
6.06E-2	9.04E-2	GC (Apiezon L)	473			179,182,138
3.9E-2	6.0E-2	GC (OV101)	423			170
5.6E-2	8.5E-2	GC (SBOctyl 50)	373-518			170
5.11E-2	7.76E-2	GC (OV101)	473			139
5.48E-2	8.33E-2	GC (Dexsil410)	473			139
5.13E-2	7.80E-2	GC		$\log P_1 = -(3935/T) + 12.09$		169
1.16E-2	1.82E-2 (20 °C)	ET	(26) 2,3',5'-: MW=257.54; MP=40 °C 293			140
3.23E-2	4.49E-2	S×H	298			135
4.02E-2		Pr (MW)	298			179
3.30E-2		Pr (TI)	298			179
2.96E-2		Pr (S×H)	298			204
2.62E-2	3.53E-2	GC (Apiezon L)	473			179,182,138
2.3E-2	3.2E-2	GC (OV101)	423			170
2.3E-2	3.2E-2	GC (SBOctyl 50)	373-518			170
2.96E-2	4.11E-2	GC (OV101)	473			139
2.96E-2	4.11E-2	GC (Dexsil410)	473			139
2.94E-2	4.09E-2	GC		$\log P_1 = -(4075/T) + 12$		169
6.43E-3	1.48E-2 (20 °C)	ET	(28) 2,4,4'-: MW=257.54; MP=57 °C 293			140
1.45E-2	2.95E-2	S×H	298			135

TABLE 2. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PCB congeners^c—Continued

P_s	P_l	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
2.73E-2		Pr (MW)	298			179
9.57E-3		Pr (TI)	298			179
9.97E-3		Pr (S×H)	298			204
1.36E-2	2.77E-2	GC (Apiezon L)	473			179,182,138
1.3E-2	2.6E-2	GC (OV101)	423			170
1.6E-2	3.2E-2	GC (SBOctyl 50)	373-518			170
1.66E-2	3.38E-2	GC (OV101)	473			139
1.67E-2	3.40E-2	GC (Dexsil410)	473			139
1.67E-2	3.40E-2	GC		$\log P_l = -(4075/T) + 12.20$		169
				(30) 2,4,6-: $MW=257.54$; $MP=62.5$ °C		
6.37E-2	1.46E-1	S×H	298			135
2.29E-2		Pr (MW)	298			179
1.30E-2		Pr (TI)	298			179
5.17E-2		Pr (TI)	298			200
6.15E-2		Pr (TI)	298			200
4.54E-2		Pr (S×H)	298			204
4.21E-2	9.46E-2	GC (Apiezon L)	473			179,182,138
4.17E-2	9.55E-2	GC (BP1)	343-383			157
6.29E-2	1.44E-1	GC (Apolane)	343-383			157
3.7E-2	8.5E-2	GC (SBOctyl 50)	373-518			170
4.85E-2	1.11E-1	GC (OV101)	473			139
5.89E-2	1.35E-1	GC (Dexsil410)	473			139
4.23E-2	9.68E-2	GC		$\log P_l = -(3886/T) + 12.02$		169
				(33) 2',3,4-: $MW=257.54$; $MP=60$ °C		
1.4E-2		GS (GC)	303-316	$\log P_s = -(1510/T) + 3.21$		114
4.84E-3	1.19E-2 (20 °C)	ET	293			140
2.72E-2		Pr (UNIFAC)	298			206
2.70E-2		r (MW)	298			179
2.43E-2		Pr (TI)	298			179
9.94E-3		Pr (TI)	298			200
1.14E-2		Pr (TI)	298			200
1.44E-2		Pr (S×H)	298			204
1.15E-2	2.43E-2	GC (Apiezon L)	473			179,182
9.7E-3	2.1E-2	GC (OV101)	423			170
1.4E-2	3.0E-2	GC (SBOctyl 50)	373-518			170
1.22E-2	2.64E-2	GC (OV101)	473			139
1.01E-2	2.19E-2	GC (Dexsil410)	473			139
1.1E-2		GC (Apolane)	333-403			162
1.22E-2	2.64E-2	GC		$\log P_l = -(4075/T) + 12.09$		169
				(40) 2,2',3,3'-: $MW=291.99$; $MP=121$ °C		
4.73E-4	4.50E-3 (20 °C)	ET	293			140
1.09E-3	8.91E-3	S×H	298			135
2.29E-3		Pr (MW)	298			179
9.57E-3		Pr (TI)	298			179
1.12E-3		Pr (S×H)	298			204
1.34E-3	1.12E-2	GC (Apiezon L)	473			179,182
1.20E-3	9.79E-3	GC (BP1)	313-373			157
8.3E-4	6.8E-3	GC (OV101)	423			170
1.5E-3	1.2E-2	GC	373-518			170

TABLE 2. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PCB congeners^c—Continued

P_s	P_1	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{\text{sub}}H$ (kJ/mol)	Ref.
1.08E-3	8.86E-3	(SBOctyl 50)				
1.05E-3	8.61E-3	GC (OV101)	473			139
		GC	473			139
		(Dexsil410)				
1.22E-3	9.98E-3	GC		$\log P_1 = -(4271/T) + 12.32$		169
				(52) 2,2',5,5'-: $MW=291.99$; $MP=87$ °C		
2.5E-3		GS (GC)	303-313	$\log P_s = -(4920/T) + 13.92$		114
1.99E-3	9.01E-3	ET	293			140
		(20 °C)				
1.30E-2	5.12E-2	S×H	298			135
4.97E-3		Pr (MW)	298			179
9.59E-3		Pr (TI)	298			179
6.60E-3		Pr (TI)	298			200
1.06E-2		Pr (TI)	298			200
3.70E-3		Pr (S×H)	298			204
4.92E-3	1.93E-2	GC	473			179,182,138
		(Apiezon L)				
4.03E-3	1.59E-2	GC (BP1)	343-393			157
5.80E-3	2.29E-2	GC (Apolane)	343-393			157
3.3E-3	1.3E-2	GC (OV101)	423			170
5.1E-3	2.0E-2	GC	373-518			170
		(SBOctyl 50)				
4.66E-3	1.84E-2	GC (OV101)	473			139
4.36E-3	1.72E-2	GC	473			139
		(Dexsil410)				
2.01E-3	7.91E-3	GC (BP1)	343-453	$\log P_1 = -(4127/T) + 11.74$		160
7.3E-3		GC (Apolane)	333-403			162
4.08E-3	1.61E-2	GC		$\log P_1 = -(4220/T) + 12.36$		169
				(53) 2,2',5,6'-: $MW=291.99$; $MP=104.5$ °C		
1.61E-3	1.07E-2	ET	293			140
		(20 °C)				
6.71E-3	3.85E-2	S×H	298			135
2.04E-2		Pr (MW)	298			179
9.57E-3		Pr (TI)	298			179
7.77E-3		Pr (S×H)	298			204
6.15E-3	3.56E-2	GC	473			179,182,138
		(Apiezon L)				
4.72E-3	2.73E-2	GC (BP1)	313-373			157
3.6E-3	2.1E-2	GC (OV101)	423			170
6.0E-3	3.5E-2	GC	373-518			170
		(SBOctyl 50)				
4.63E-3	2.68E-2	GC (OV101)	473			139
5.72E-3	3.31E-2	GC	473			139
		(Dexsil410)				
4.78E-3	2.77E-2	GC		$\log P_1 = -(4114/T) + 12.24$		169
				(54) 2,2',6,6'-: $MW=291.99$; $MP=198$ °C		
2.27E-3	1.04E-1	S×H	98			135
3.96E-4		Pr (MW)	298			179
2.19E-2		Pr (TI)	298			179
2.87E-3		Pr (S×H)	298			204
1.32E-3	6.59E-2	GC	473			179,182,138
		(Apiezon L)				
8.54E-4	3.92E-2	GC (OV101)	473			139
1.13E-3	5.17E-2	GC	473			139
		(Dexsil410)				
8.45E-4	3.88E-2	GC		$\log P_1 = -(3751/T)$		169
				(77) 3,3',4,4'-: $MW=291.99$; $MP=180$ °C		
1.82E-5	4.71E-4	S×H	298			135
5.97E-4		Pr (MW)	298			179
8.04E-4		Pr (TI)	298			179

THE VAPOR PRESSURE OF ENVIRONMENTALLY SIGNIFICANT ORGANIC COMPOUNDS 171

TABLE 2. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PCB congeners^c—Continued

P_s	P_l	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
3.48E-5		Pr (S×H)	298			204
4.46E-5	1.40E-3	GC (Apiezon L)	473			179,182,138
7.12E-5	2.19E-3	GC (BP1)	313-373			157
6.37E-5	1.96E-3	GC (Apolane)	313-373			157
4.6E-5	1.4E-3	GC (OV101)	423			170
6.2E-5	1.9E-3	GC (SBOctyl 50)	373-518			170
6.92E-5	2.13E-3	GC (OV101)	473			139
4.68E-5	1.44E-3	GC (Dexsil410)	473			139
7.15E-5	2.20E-3	GC		$\log P_l = -(4552/T) + 12.61$		169
				(101) 2,2',4,5,5'-: MW=326.43; MP=77 °C		
9.6E-4		GS (GC)	303-313	$\log P_s = -(4840/T) + 13.22$		114
4.04E-4	1.46E-3 (20 °C)	ET	293			140
5.27E-4	1.67E-3	S×H	298			135
1.52E-3		Pr (UNIFAC)	298			206
2.25E-3		Pr (MW)	298			179
8.04E-4		Pr (TI)	298			179
7.84E-4 (average)		Pr (TI)	298			200
7.17E-4		Pr (S×H)	298			204
1.18E-3	3.58E-3	GC (Apiezon L)	473			179,182,138
1.06E-3	3.36E-3	GC (BP1)	343-383			157
1.27E-3	4.02E-3	GC (Apolane)	343-383			157
8.2E-4	2.6E-3	GC (OV101)	423			170
1.3E-3	4.0E-3	GC (SBOctyl 50)	373-518			170
1.14E-3	3.61E-3	(OV101)	473			139
1.28E-3	4.04E-3	GC (Dexsil410)	473			139
9.46E-4	2.99E-3	GC (BP1)	343-453	$\log P_l = -(4369/T) + 12.13$		160
1.2E-3		GC (Apolane)	333-403			162
1.07E-3	3.39E-3	GC		$\log P_l = -(4514/T) + 12.67$		169
				(128) 2,2',3,3',4,4'-: MW=360.88; MP=150 °C		
5.25E-6	9.80E-5 (20 °C)	ET	293			140
2.9E-6	4.2E-5	S×H	298			135
1.54E-4		Pr (MW)	298			179
6.76E-5		Pr (TI)	298			179
8.53E-6		Pr (S×H)	298			204
2.31E-5	3.59E-4	GC (Apiezon L)	473			138,179,182
2.15E-5	3.41E-4	GC (BP1)	313-373			157
1.1E-5	1.8E-4	GC (OV101)	423			170
2.1E-5	3.3E-4	GC (SBOctyl 50)	373-518			170
2.32E-5	3.67E-4	GC (OV101)	473			139
1.84E-5	2.92E-4	GC (Dexsil410)	473			139
2.18E-5	3.46E-4	GC		$\log P_l = -(4881/T) + 12.91$		169
				(153) 2,2',4,4',5,5'-: MW=360.88; MP=103 °C		
3.90E-5	2.53E-4 (20 °C)	ET	293			140
3.2E-5	1.8E-4	S×H	298			135
4.48E-4		Pr (MW)	298			179
6.76E-5		Pr (TI)	298			179
4.09E-5		Pr (S×H)	298			204
1.24E-3	6.63E-3	GC	473			138,179,182

TABLE 2. Vapor pressure (Pa) at 25 °C and enthalpy of sublimation of selected PCB congeners^c—Continued

P_s	P_l	Method	$\Delta T(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
		(Apiezon L)				
1.21E-4	6.79E-4	GC (BP1)	313-373			157
1.28E-4	7.19E-4	GC (Apolane)	313-373			157
1.0E-4	5.6E-4	GC (OV101)	423			170
1.3E-4	7.2E-4	GC	373-518			170
		(SBOctyl 50)				
1.26E-4	7.08E-4	GC (OV101)	473			139
1.45E-4	8.13E-4	GC	473			139
		(Dexsil410)				
1.22E-4	6.84E-4	GC		$\log P_l = -(4775/T) + 12.85$		169
		(155) 2,2',4,4',6,6'-: MW=360.88; MP=114 °C				
4.80E-4	3.44E-3	S×H	298			135
3.49E-4		Pr (TI)	298			179
5.37E-4		Pr (S×H)	298			204
8.05E-4		Pr (TI)	298			179
2.85E-4		Pr (TI)	298			200
6.41E-4	4.43E-3	GC	473			138,179,182
		(Apiezon L)				
1.6E-3		GC (Apolane)	333-403			162
5.41E-4	3.87E-3	GC		$\log P_l = -(4303/T) + 12.02$		169
		(202) 2,2',3,3',5,5',6,6'-: MW=429.77; MP=162 °C				
2.90E-5		GS (GC)	302-334	$\log P_s = -(5307.3/T) + 13.262$	101.7	109
5.96E-6		Pr (UNIFAC)	298			206
1.52E-5		Pr (MW)	298			179
2.95E-5		Pr (TI)	298			179
2.73E-5		Pr (TI)	298			200
2.41E-6		Pr (S×H)	298			204
2.69E-5	5.40E-4	GC	473			179,182
		(Apiezon L)				
1.2E-5	2.4E-4	GC	373-518			170
		(SBOctyl 50)				
8.34E-6	1.73E-4	GC (OV101)	473			139
1.88E-5	3.90E-4	GC	473			139
		(Dexsil410)				
2.53E-5	5.25E-4	GC (BP1)	343-453	$\log P_l = -(4851/T) + 12.99$		160
		(209) Decachlorobiphenyl: MW=498.66; MP=305 °C				
5.30E-8		GS (GC)	324-363	$\log P_s = -(6358.0/T) + 14.049$	121.8	109
1.4E-5		RV	293			153
(20 °C)						
2.20E-8		Pr (UNIFAC)	298			206
7.58E-8		Pr (MW)	298			179
4.02E-8		Pr (TI)	298			179
1.01E-7		Pr (TI)	298			200
2.89E-9		Pr (S×H)	298			204
5.36E-8	2.75E-5	GC	473			179,182
		(Apiezon L)				
1.14E-8	5.58E-6	GC (OV101)	473			139
2.69E-8	1.32E-5	GC	473			139
		(Dexsil410)				
2.90E-8	1.42E-5	GC (BP1)	343-453	$\log P_l = -(5402/T) + 13.27$		160

^aEquation derived by the author from the vapor pressure data reported in the original paper.

^bReported values refer to $\Delta_{vap}H$.

^cPCB congeners are identified by the B&Z number (Ref. 259) and by the chlorine substitution.

TABLE 3. Vapor pressure (Pa) at ambient temperatures and enthalpy of sublimation of selected pesticides

P_s	P_l	Method	$\Delta T/(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
Aldrin: $MW=364.9$; $MP=104\text{ }^\circ\text{C}$						
<u>20 °C</u>						
1.0E-2		E ^a				14
8.47E-3		GS (GC)	309-343	$\log P_s = -(4796.4/T) + 14.29$		99
8.18E-3		GS (GC)				242
(average)						
1.0E-3		RV	293			153
6.64E-3	4.51E-2	GC (BP1)	343-453	$\log P_l = -(3924/T) + 12.04$		160
4.2E-3		GC				243
<u>25 °C</u>						
1.60E-2		GS (GC)	309-343	see 20 °C		99
5.3E-3		Pr (C-C, M1)	298			187
1.1E-4		Pr (C-C, M2)	298			187
3.78E-3	2.29E-2	GC (BP1)	343-383			157
5.50E-3	3.33E-2	GC (Apolane)	343-383			157
1.25E-2	7.57E-2	GC (BP1)	343-453	see 20 °C		160
Diazinon: $MW=304.3$; liquid						
<u>20 °C</u>						
	9.75E-3	GS				244
	6.56E-3	GS (GC)	298-318	$\log P_l = -(4014.67/T) + 11.5120$		131
	1.9E-2	B	283-308			148
	2.4E-3	GC (SE30)	408-453			131
	2.53E-3	GC				243
	(average)					
<u>25 °C</u>						
	1.11E-2	GS (GC)	298-318	see 20 °C		131
	2.0E-2	GC (BP1)	343-453			160
	8.5E-3	GC (SE30)	373-443			131
p,p'-DDT: $MW=354.5$; $MP=109\text{ }^\circ\text{C}$						
<u>20 °C</u>						
2.01E-5		E (T)	339-373	$\log P_s = -(6160/T) + 16.316$	118	90
2.52E-5		GS (S)	323-363	$\log P_s = -(6010/T) + 15.903$	115	106
6.58E-4		GS (W)	313-363	$\log P_s = -(4370/T) + 11.725$	84	116
2.9E-5		GS (¹⁴ CO ₂)	293-353		110	108
1.98E-5		GS (GC)	293-313	$\log P_s = -(6176/T) + 16.365$	118	134
1.7E-5		GS (¹⁴ C)	293-373			113
3.3E-5		PC	293			46
4.3E-5		RV	293			153
2.0E-5		RV	293-333			155
2.7E-3		Pr (C-C, M1)	293			187
2.7E-5		Pr (C-C, M2)	293			187
3.50E-5	2.66E-4	GC (BP1)	343-453	$\log P_l = -(4865/T) + 13.02$		160
1.5E-4		GC				243
<u>25 °C</u>						
4.52E-5		E (T)	339-373	see 20 °C		90
5.56E-5		GS (S)	323-363	see 20 °C		160
1.17E-3		GS (W)	319-363	see 20 °C		116
5.8E-5		GS				245
5.7E-5		GS (¹⁴ CO ₂)	293-353			108
4.47E-5		GS (GC)	293-313	see 20 °C		134
1.3E-5		RV	298			150
1.22E-4	8.29E-4	GC (BP1)	353-403			157
6.91E-5	4.69E-4	GC (Apolane)	353-403			157
7.44E-4	5.05E-4	GC (BP1)	343-453	see 20 °C		160

TABLE 3. Vapor pressure (Pa) at ambient temperatures and enthalpy of sublimation of selected pesticides—Continued

P_s	P_l	Method	$\Delta T/(K)$	Vapor pressure equation	$\Delta_{sub}H$ (kJ/mol)	Ref.
<u>30 °C</u>						
9.91E-5		E (T)	339-373	see 20 °C		90
1.20E-4		GS (S)	323-363	see 20 °C		106
2.04E-3		GS (W)	319-363	see 20 °C		116
1.2E-4		GS ($^{14}CO_2$)	293-353			108
9.82E-5		GS (GC)	293-313	see 20 °C		134
1.7E-3		GS (GC)				162
1.55E-4	9.38E-4	GC (BP1)	343-453	see 20 °C		160
1.9E-3		GC (Apolane)	333-403			162
Dieldrin: $MW=380.9$; $MP=175$ °C						
<u>20 °C</u>						
4.1E-4		E ^a				14
4.09E-4		GS (GC)	308-348	$\log P_s = -(4901/T) + 13.33$		99
3.40E-4		GS (GC)	293-313	$\log P_s = -(5178/T) + 14.195$	99.1	101
3.9E-4		PC	293			46
2.5E-4		DL	293			147
1.3E-4		Pr (C-C, M1)	293			187
1.3E-5		Pr (C-C, M2)	293			187
1.68E-4	5.73E-3	GC (BP1)	343-453	$\log P_l = -(4310/T) + 12.46$		160
8.9E-4		GC				243
<u>25 °C</u>						
7.80E-4		GS (GC)	308-348	see 20 °C		99
6.73E-4		GS (GC)	293-313	see 20 °C		101
1.7E-4	5.3E-3	GC (BP1)	343-393			157
2.0E-4	6.0E-3	GC (Apolane)	343-393			157
3.3E-4	1.0E-2	GC (BP1)	343-453	see 20 °C		160
Dimethoate: $MW=229.2$; $MP=52$ °C						
<u>20 °C</u>						
3.86E-4		GS (GC)	298	$\log P_s = -(4241.13/T) + 11.0539$ (estimated)		131
3.7E-4		RV	298			154
4.3E-4		RV	298			154
4.1E-3	8.5E-3	GC (SE30)	408-453			131
6.67E-3 (average)		GC				243
<u>25 °C</u>						
6.74E-4		GS (GC)	298	see 20 °C		131
7.7E-3	1.4E-2	GC (SE30)	373-443			131
Hexachlorobenzene: $MW=284.79$; $MP=230$ °C						
<u>20 °C</u>						
1.14E-3		E				63
1.14E-3		GS (GC)	288-318	$\log P_s = -(5279/T) + 15.065$	101.3	107
2.6E-3		GS (GC)				63
1.50E-3		GS (GC)	314-373	$\log P_s = -(4948/T) + 14.054$ ^b		209
1.48E-3		M (Rodebush)	369-397	$\log P_s = -(4793.6/T) + 13.522$		225
4.6E-4		RV	298			153
7.39E-4		RV	293-333			155
6.49E-4	7.78E-2	GC (BP1)	343-353	$\log P_l = -(3582/T) + 11.11$		160
<u>25 °C</u>						
2.29E-3		GS (GC)	288-318	see 20 °C		107
2.87E-3		GS (GC)	314-373	see 20 °C		209
2.78E-3		M (Rodebush)	369-397	see 20 °C		225
5.4E-3		Pr (UNIFAC)	298			206
1.49E-3	1.59E-1	GC (BP1)	343-383			157

TABLE 3. Vapor pressure (Pa) at ambient temperatures and enthalpy of sublimation of selected pesticides—Continued

P_s	P_1	Method	$\Delta T/(K)$	Vapor pressure equation	$\Delta_{\text{sub}}H$ (kJ/mol)	Ref.
1.14E-3	1.22E-1	GC (Apolane)	343-383			157
1.11E-3	1.19E-1	GC (BP1)	343-353	see 20 °C		160
γ -Hexachlorocyclohexane: $MW=290.8$; $MP=112$ °C						
20 °C						
1.27E-3		E (T)	333-365	$\log P_s = -(6020/T) + 17.640$	115	90
3.68E-3		GS (GC)				242
4.27E-3		GS (GC)	294-365	$\log P_s = -(5288/T) + 15.669$	101.1	132
8.42E-3		S (HCl)	313-343	$\log P_s = -(4685/T) + 13.907$	89.66	126
4.0		M	293-333			246
4.1E-3		PC	293			46
2.8E-3		DL	293			147
1.3E-3		B	283-308			148
2.6E-3		RV	293			152
2.3E-3		RV	293-333			155
6.7E-2		Pr (C-C, M1)	293			187
1.1E-3		Pr (C-C, M2)	293			187
4.85E-3	3.95E-2	GC (BP1)	343-353	$\log P_1 = -(3680/T) + 11.15$		160
25 °C						
2.8E-3		E (T)	333-365	see 20 °C		90
5.6E-3		GS	297			247
(24 °C)						
8.41E-3		GS (GC)	294-365	see 20 °C		132
1.56E-2		GS (HCl)	313-343	see 20 °C		126
1.47E-2	1.07E-1	GC (BP1)	343-383			157
9.00E-3	6.53E-2	GC (Apolane)	343-383			157
8.83E-3	6.41E-2	GC (BP1)	343-353	see 20 °C		160
Malathion: $MW=330.3$; $MP=2.85$ °C						
20 °C						
	6.07E-4	GS (GC)	298	$\log P_1 = -(4241.13/T) + 11.2501$ (estimated)		31
	7.3E-4	RV	293			154
	6.7E-4	GC (SE30)	373-443			131
	9.2E-4	GC				243
25 °C						
	1.06E-3	GS (GC)	298	see 20 °C		131
	4.7E-3	GC (BP1)	343-453			160
	1.1E-3	GC (SE30)	373-443			131
Methyl-parathion: $MW=263.2$; $MP=35$ °C						
20 °C						
8.35E-4		GS (GC)	298-318	$\log P_s = -(6538/T) + 19.224^b$		131
1.13E-3		GS (GC)	298-308	$\log P_s = -(5700/T) + 16.495$	109.2	51
9.3E-4		B	283-308			148
1.8E-3		RV	293-333			155
2.34E-3		GC				243
(average)						
25 °C						
2.0E-3		GS (GC)	272-373	see 20 °C		131
2.38E-3		GS (GC)	298-318	see 20 °C		51
1.8E-2	2.3E-2	GC (BP1)	343-353			160
2.5E-3	3.2E-3	GC (SE30)	373-443			131
Parathion: $MW=291.3$; $MP=6$ °C						

TABLE 3. Vapor pressure (Pa) at ambient temperatures and enthalpy of sublimation of selected pesticides—Continued

P_s	P_1	Method	$\Delta T/(K)$	Vapor pressure equation	$\Delta_{\text{sub}}H$ (kJ/mol)	Ref.
20 °C						
	5.07E-3	E (Kn)	298-339	$\log P_1 = -(3395/T) + 9.286$	65 °	248
	7.00E-4	GS (GC)	298-318	$\log P_1 = -(4645.07/T) + 12.6903$		131
	6.23E-4	GS (GC)	298-318	$\log P_1 = -(5274/T) + 14.785$	101 °	51
	2.52E-3	GS				249
	2.60E-3	GS (S)	297-344	$\log P_1 = -(4400/T) + 12.425$		115
	5.9E-4	ET	293			37
	6.7E-4	B	283-308			148
	5.9E-4	RV	298			12
	6.4E-4	RV	293-333			155
	8.1E-4	GC (SE30)	408-453			131
25 °C						
	7.92E-3	E	298-339	see 20 °C		248
	1.29E-3	GS (GC)	298-318	see 20 °C		131
	1.25E-3	GS (GC)	298-318	see 20 °C		51
	4.65E-3	GS (S), D	297-344	see 20 °C		115
	6.7E-3	GC (BP1)	343-353			160
	1.52E-3	GC (SE30)	373-443			131

^aValues supplied by "Schell" Research.

^bEquation derived by the author from the vapor pressure data reported in the original papers.

^cReported values refer to $\Delta_{\text{vap}}H$.

tion from the straight line occurs, while the vapor pressure can be calculated from the values of the partition coefficient and the solubility using the expression

$$p = (S \times 10^{-6} \times 760 \times 22400 \times 293) / (VP \times M \times 273),$$

where p is the partition coefficient at 20 °C; VP is the saturation vapor pressure (mm Hg) at 20 °C; M is the molecular weight; and S is the solubility (ppm) at 20 °C.

2.1.6 Other Methods

Some other methods have been proposed for the determination of low vapor pressures of chemicals. They can be summarized as follows:

(1) $S \times H$. Vapor pressure (P) and solubility (S) in water are related through the Henry's law constant (H); therefore P can be calculated by the knowledge of S and H . This procedure has been used to obtain the vapor pressure at 25 °C of some PCB congeners¹³⁵ as solids, which are then converted into subcooled liquids. H has been measured by the gas purging technique¹⁰² and S by the column generation technique^{136,137} which are considered both very accurate. A comparison of the data for subcooled liquids with the literature data, predicted¹³⁸ or experimental,^{139,140} has shown a general agreement, except that for hexachlorobiphenyls.

A similar procedure has been proposed by Mackay *et al.*¹⁴¹ Vapor pressures of three PAHs and biphenyl can be calculated from the S values determined by the shake flask-fluorescence method¹⁴² and H values determined by the batch stripping method.¹⁴¹

(2) Measurement of the vapor in the head space in equilibrium with an excess of Aroclor mixture dissolved in water.¹⁴⁰ This system, termed "Equilibration Technique" has been used to measure by gas chromatography both vapor pressure and solubility in water at room temperature of the single compounds in the Aroclor mixture (1242, 1254, or 1260) at equilibrium in a closed bottle. It allows one to calculate H for each compound in the mixtures and S , P , and H for each mixture.

(3) Measurement of the vapor viscosity.¹⁴³ The apparatus has also been termed *vibration gauge*.¹⁴⁴ It is based on the principle that the vibration of a Λ shaped fine quartz fiber¹⁴³ or a 10-cm strip of molybdenum¹⁴⁴ is proportional to the vapor pressure inside a measurement cell. This system must be calibrated with an absolute manometer. It has been used to measure vapor pressures of the order of 10^{-3} – 10^{-4} mm Hg (0.133 – 1.33×10^{-2} Pa).

(4) Measurement of the *fluorescence* of the vapor, which is proportional to the vapor pressure.¹⁴⁵ It has been used for some PAHs.

(5) Measurement of the concentration in the *head space* which is proportional to the vapor pressure.¹⁴⁶ The vapor in equilibrium with the condensed phase is collected, dissolved in hexane and analyzed by IR or UV spectroscopy. It has been used for biphenyl, naphthalene, and other compounds.

(6) Application of *diffusion law* to the determination of the vapor pressure of some pesticides.¹⁴⁷ This simple method is based on the determination of the diffusion-rate of the test compound (Lindane and Dieldrin) from the bottom of a Sovirel flask to the top, where a filter paper soaked with oil is

TABLE 4. Vapor pressure at 25 °C and enthalpy of sublimation of selected PCDDs and PCDFs

P_s	P_1	Method	$\Delta T(K)$	Vapor pressure equation $\log P_s$	$\Delta_{sub}H$ (kJ/mol)	Ref.
6.4E-6		GS (GC)	333-393	1,2,3,4 - DD: $MW=322.0$; $MP=188-190$ °C	118	111,121, 210,211,212
2.48E-6	1.04E-4	GC (DB5)	363-423			161
5.4E-4 (20 °C)		GS (^{14}C)	293-373	1,3,6,8 - DD: $MW=322.0$; $MP=219.0-219.5$ °C		113
7.0E-7		Pr (Th)	298		125.8	211,212
9.9E-8		GS ($^{14}CO_2$)	298	2,3,7,8 - DD: $MW=322.0$; $MP=305-306$ °C		119
2.02E-7		GS (GC)	303-344		$-(6472.495/T) + 15.01395$	112,250
1.3E-7		Pr (corr. RI)	298			161
(3.5-6.3)E-6		Pr (corr. Cl)	298			111,121
2.0E-7		Pr (Th)	298			210
6.2E-7		Pr (Th)	298		119.0	211,212
1.30E-7	1.74E-5	GC (DB5)	363-423	1,2,3,7,8 - DD: $MW=356.4$; $MP=240-241$ °C		161
1.58E-7	2.11E-5	GC (DB5) ^a	333-553			186
5.8E-8		Pr (Th)	298		134.0	211,212
1.36E-9	3.96E-6	GC (DB5)	363-423	1,2,3,4,7,8 - DD: $MW=391.0$; $MP=273-275$ °C		161
1.87E-8	5.43E-6	GC (DB5) ^a	333-553			186
5.1E-9		Pr (Th)	298		140.8	211,212
4.41E-9	1.02E-6	GC (DB5)	363-423	1,2,3,4,6,7,8 - DD: $MW=425.2$; $MP=264-265$ °C		161
5.15E-9	1.19E-6	GC (DB5) ^a	333-553			186
7.5E-10		Pr (Th)	298		149.8	211,212
1.1E-10		GS(GC)	384-474	Octachloro - DD: $MW=460.0$; $MP=330-332$ °C	151.1	111,210, 211,212
8.7E-6 (20 °C)		GS (^{14}C)	293-373			113
1.8E-5 (20 °C)		RV	293			153
2.62E-10	2.77E-7	GC (DB5)	363-423			161
2.56E-10	2.72E-7	GC (DB5) ^a	333-553			186
1.23E-6	1.23E-4	GC (DB5)	363-423	2,3,7,8 - DF: $MW=306.0$; $MP=227-228$ °C		161
1.13E-6	1.13E-4	GC (DB5) ^a	333-553			186
2.0E-6		Pr (Th)	298		119.7	211,212
3.71E-7	3.64E-5	GC (DB5)	363-423	1,2,3,7,8 - DF: $MW=340.4$; $MP=225-227$ °C		161
3.33E-7	3.27E-5	GC(DB5) ^a	333-553			186
2.3E-7		Pr (Th)	298		129.0	211,212
				2,3,4,7,8 - DF: $MW=340.42$; $MP=196.0-196.5$ °C		

TABLE 4. Vapor pressure at 25 °C and enthalpy of sublimation of selected PCDDs and PCDFs—Continued

P_s	P_l	Method	$\Delta T(K)$	Vapor pressure equation $\log P_s$	$\Delta_{sub}H$ (kJ/mol)	Ref.
4.43E-7	2.17E-5	GC (DB5)	363-423			161
4.96E-7	2.43E-5	GC(DB5) ^a	333-553			186
3.5E-7		Pr (Th)	298		130.4	211,212
1,2,3,4,7,8- DF: MW=374.87; MP=225.5-226.5 °C						
8.41E-8	8.09E-6	GC (DB5)	363-423			161
3.68E-8	3.54E-6	GC(DB5) ^a	333-553			186
3.2E-8		Pr (Th)	298		137.4	211,212
1,2,3,6,7,8- DF: MW=374.87; MP=232-234 °C						
7.10E-8	8.09E-6	GC (DB5)	363-423			161
6.42E-8	7.32E-6	GC(DB5) ^a	333-553			186
2.9E-8		Pr (Th)	298		137.1	211,212
2,3,4,6,7,8- DF: MW=374.87; MP=239-240 °C						
3.81E-8	4.99E-6	GC (DB5)	363-423			161
4.45E-8	5.82E-6	GC(DB5) ^a	333-553			186
2.6E-8		Pr (Th)	298		136.8	211,212
1,2,3,4,6,7,8- DF: MW=409.31; MP=236-237 °C						
1.83E-8	2.24E-6	GC (DB5)	363-423			161
1.58E-8	1.93E-6	GC(DB5) ^a	333-553			186
4.7E-9		Pr (Th)	298		144.6	211,212
1,2,3,4,7,8,9 - DF: MW=409.31; MP=221-223 °C						
1.48E-8	1.31E-6	GC (DB5)	363-423			161
1.14E-8	1.01E-6	GC(DB5) ^a	333-553			186
6.2E-9		Pr (Th)	298		145.2	211,212
Octa- DF: MW=443.76; MP=258-260 °C						
5.0E-10		GS (GC)	373-474		149.4	111,121, 210,211,212
1.26E-9	2.60E-7	GC(DB5) ^a	333-553			186

^aTemperature programmed GC.^bCompounds identified by the chlorine substitution, DD = dibenzo-p-dioxin, DF = dibenzo furan.

placed. The content of the test compound in oil is determined at time intervals and plotted as a function of time. From the slope of the curve, the diffusion coefficient, and the height of the flask, it is possible to obtain the vapor density and, then, the vapor pressure. The relative standard deviation of the measurements is 10-15%.

(7) Application of a *Bioassay* technique, based on insect mortality, to the determination of the vapor pressure of some pesticides.¹⁴⁸

2.2. Indirect Experimental Methods

These methods require calibration with compounds of known vapor pressure, measured with a suitable direct method. The preferred reference compounds are those which belong to the same class of the compounds under examination.

2.2.1. Relative Volatilization Rate

The measurement of the relative loss rates of chemicals can be a means of estimating vapor pressures, provided the vapor pressure of one of the components is known.¹⁴⁹

One method is based on the principle that, with compounds insoluble in water, the vapor pressure of an immiscible phase is substantially unchanged by the presence of water. Thus, the vapor pressure of the insoluble compound can be calculated from the amount of water and compound volatilized after distillation of the aqueous suspension. On this basis Bowman *et al.*¹⁵⁰ determined the vapor pressure of DDT. They used the general equation relating the volatility of two materials (A and B) to molecular weight and vapor pressure

$$W_A/W_B = (M_A P_A)/(M_B P_B),$$

TABLE 5. Vapor pressure at 25 °C and enthalpy of vaporization of some reference compounds in GC

P_1	Method	$\Delta T(K)$	Vapor pressure equation $\log P_1$	$\Delta_{\text{vap}}H$ (kJ/mol)	Ref.
n-Octadecane: $MW=254.4; MP=28.18\text{ }^\circ\text{C}$					
2.59E-2	GS (CO ₂)	318-361	$-(4414.6/T) + 13.220$		124
5.49E-2	BP	356-586	$-[3031.11/(230+t)] + 10.626^a$		78
n-Eicosane: $MW=282.6; MP=36.8\text{ }^\circ\text{C}$					
2.67E-3	GS (CO ₂)	344-380	$-(4877.1/T) + 13.785$		124
1.72E-3	M (DB)	363-467	$-[2607.622/(177.32+t)] + 10.12382$		70
8.38E-3	BP	395-615	$-[3278.8/(230+t)] + 10.781^a$		78
Dibutyl-phthalate: $MW=278.35$; liquid					
3.45E-3	E (Kn, i)	313-370	$-(4871/T) + 13.875$ $-(1666/T + 547700/T^2) + 9.190^b$	93.3	251
3.17E-2	E	298-353	$-(5204/T) + 15.955$	96.7	218
3.64E-3	E (Kn, i)	288-313	$-(4790/T) + 13.627$	91.67	252
4.1E-4	E (Kn)	298			253
1.54E-3	GS (GC)	333-433	$-(4865/T) + 13.506$	93.3	254
	GS (GC)	360-418	$-(4741/T) + 13.446^a$		129
4.03E-3	GS (GC)	283-423	$-(3795.49/T + 143618/T^2) + 11.9509$		127
9.7E-3	GS (HPLC)	298			110
6.08E-3	GS (HPLC)	333-433	$-(4501/T) + 12.88^a$	90.0	255
1.18E-3	M	399-475	$-(1011/T + 720,000/T^2)$ $+ 8.564$	81.7	256
2.5E-3	M (IG)	298			257
5.6E-3	M (IG)	298			65
3.43E-3	E,PT	313-368	$-(5122/T) + 14.714$	98.07	86
4.40E-3	PT	323-373	$-(4680/T) + 13.340$	89.5	84
6.02E-3	PT	328-375	$-(4450/T) + 12.705$	84.9	85
7.58E-4	D, Te	343-463	$-[2872/(t + 176.5)] + 11.133$		83
	BP	397-430		86	76
	BP	362-449	$-(2200/T) + 7.513^a$		79
1.3E-3	D	333-373		106.7	87
2.44E-2	Pr (UNIFAC)	298			206
5.6E-3	GC (BP1)	343-453			160
1.03E-3 (20 °C)	RV	293-333			155

^aEquation derived by the author from the data reported in the original paper.

^bEquation reported in the original paper, derived from a pool of literature data.

where W is the weight of distillate, M the molecular weight, and P the vapor pressure.

Other methods generally use simple experimental devices to measure the vapor pressure of a compound from its loss rate and the loss rate of a reference compound of known vapor pressure under the same experimental conditions.

The volatilization rate of a compound, k , is closely approximate to¹⁵¹

$$k = cP(\sqrt{M}),$$

where c is a constant determined by the air-flow characteristics for the system and P is the vapor pressure of the compound which has a molecular weight of M . The volatilization rate, k , can be determined from the gradient of the linear regression of $\ln W$, where W is the weight of material remaining in the deposit, versus exposure time. The vapor pressures and volatilization rates of two chemicals under the same experimental conditions are related as follows

$$P_1 = k_1 P_2 (\sqrt{M_2}) / k_2 (\sqrt{M_1}).$$

This equation can be used to estimate unknown vapor pressures by comparison of the rates of loss of the two chemicals.

The procedure is very simple.^{149,152,153} Aliquots of a solution of the test and reference compounds were evaporated on several watch glasses. After evaporation three glasses were removed for extraction and analysis and the remainder were carefully transferred to the middle shelves of a temperature controlled laboratory oven (20 °C ± 0.5). The oven had a circulating fan with heating and cooling coils, and featured wide mesh shelves to assist free air circulation (air change rate of 12 per hour). Three watch glasses were selected at random from the array at different periods and removed for extraction and analysis by GC-ECD or by HPLC. The results from each of the three replicate watch glasses were averaged to give the best estimate of the amount of chemical remain-

ing at the time of sampling: the coefficient of variation for the separate watch glasses was generally <10%. The ratio of loss rates has been found to be relatively insensitive to changes in the solvent used to prepare the deposit, the deposit density, the purity of the chemicals in the deposit or the environmental conditions.

Other authors⁵¹ used a slightly different procedure which allowed trapping of the vapor with polyurethane to further control the amount of compound initially present.

Gückel *et al.*^{12,154} employed a roughened glass measuring plate, on which the compound was deposited, attached to one arm of a highly accurate, self-recording electric balance in a fully thermoregulated case. The weight of the measuring plate was registered continuously by an electronic control. The flow rate of air could be fixed at any point between 0.2 and 300 ℓ h⁻¹. Measurements could be made between +15 °C and +80 °C. The gradual reduction in weight of the compound at given temperature and air flow rate was registered automatically as a measure of the volatility of a substance.

The evaporation rates of 22 chemically pure substances, including pesticides, were determined at 20 ± 0.1 °C and at an air flow rate of 50 ± 1 ℓ /h. For the same substances, the vapor pressures at 20 °C were gathered from the literature.

The relationship between vapor pressure, P , and evaporation rate, V , is of the type

$$\log P = a \log V + \log b.$$

Plotting $\log P$ versus $\log V$ for the 22 substances, a straight line with gradient a was obtained.

This investigation has shown that the figures given in the literature for vapor pressures of dimethoate, chlorfenvinphos, malathion, and two alcohols should be revised. It also demonstrates a functional link between the evaporation rate and the temperature for each substance, expressed as

$$\log V = (-A/T) + B. \quad (1)$$

The same technique has been employed¹⁵⁵ to measure the evaporation rates, in the temperature range 20 to 60 °C, of 19 substances, including pesticides, for which the vapor pressure equation was known from the literature. For each substance the constants A and B of Eq. (1) were determined by a linear regression calculation.

The vapor pressures and the evaporation rates were then calculated, using the vapor pressure equation and Eq. (1) respectively, for all 19 substances at the temperatures of 20, 30, 40, 50, and 60 °C and the resulting values were correlated through the relationship

$$\log P_t = A_t + (B_t \log V_t).$$

The constants A_t and B_t were derived at the same five temperatures. These relationships were used to obtain vapor pressures from measurements of the evaporation rates at temperatures of 20, 40, and 60 °C on ten chemical substances. The calculated vapor pressures were compared with the literature values; a very good agreement was found.

2.2.2. Chromatographic Methods

The gas chromatographic (GC) techniques are based on the concept that the retention times (volumes) of single compounds are inversely correlated to their respective vapor pressures.

Herington¹⁵⁶ derived the fundamental equation relating retention time (volume) and vapor pressure

$$\log(t_{s2}/t_{s1}) = \log(P_1/P_2) + \log(\gamma_{1sp}/\gamma_{2sp}), \quad (2)$$

where the indices 1 and 2 refer to component 1 and component 2; t_s is the retention time; P is the saturation vapor pressure; γ_{sp} is the activity coefficient in the stationary phase.

Equation (2) includes entropy effects of the retention related to the partition in the liquid phase. A minimization of these effects can be achieved using a non-polar stationary phase for which separation depends only upon vapor pressure differences. With this approach Eq. (2) becomes

$$t_{s2}/t_{s1} = P_1/P_2.$$

Thus, from the knowledge of the vapor pressures of some reference compounds, it is possible to obtain the vapor pressures of test compounds at the same conditions.

Di-n-butyl phthalate,¹⁵⁷⁻¹⁵⁹ octadecane and eicosane,^{157,160} p,p'-DDT,^{160,161} 2,4,5-trichlorophenoxyacetic acid, isobutyl ester (2,4,5-TIB)¹⁶² have been used as reference compounds. Kim *et al.*¹³¹ studied the effect of various variables, including the temperature range of measurement, the nature of the liquid phase in either packed or capillary columns, and the nature of the reference compound in the determination of the vapor pressures of pesticides. The agreement between the experimental vapor pressures determined by GS and those determined by GC is improved when the polarity of the GC reference compound approximates that of the test compounds.

The importance of the capillary columns in obtaining better resolutions has been stressed by Bidleman.¹⁵⁷

The vapor pressure of test compounds can be calculated by the Hamilton's procedure,¹⁵⁹ through the equation

$$\ln P_1 = L_1/L_2 \ln P_2 + C, \quad (3)$$

which relates the vapor pressure of two substances at the same temperature. Indices 1 and 2 refer to the test compound and the reference compound respectively, and L is the enthalpy of vaporization. Both L_1/L_2 and the constant C can be obtained from the GC data using the relation

$$\ln(V_R)_1/(V_R)_2 = (1 - L_1/L_2) \ln P_2 - C,$$

where V_R is the retention volume. The values of $\ln(V_R)_1/(V_R)_2$ are reported as a function of $\ln P_2$ at various temperatures and the slope $(1 - L_1/L_2)$ and the intercept $(-C)$ are obtained by linear regression. These values are used to calculate, through Eq. (3), the vapor pressure of the test compound, P_1 , at the temperature of interest. This treatment of the data assumes that the ratio of the enthalpy of vaporization is constant in the range of temperature taken into consideration.

Bidleman¹⁵⁷ evaluated the accuracy of a method based on capillary GC¹⁵⁹ to estimate the vapor pressure of non-polar solid compounds (24 organochlorines, PAHs, and pesticides) by comparing vapor pressures measured by capillary GC with the literature values of the corresponding subcooled liquids. Two 1.0 m long fused silica columns were used, a poly(dimethylsiloxane) bonded phase column (BP-1) and a wall-coated open-tabular hydrocarbon phase column (Apolane-87). GC measurements were carried out by using octadecane and eicosane hydrocarbons as vapor pressure reference compounds. The author found, from the data of the high melting compounds (anthracene and hexachlorobenzene), that the vapor pressure determined by GC (P_{gc}) corresponds to the vapor pressure of the subcooled liquid (P_1), although the GC experiments were carried out at temperatures below the melting point. Systematic errors between P_{gc} and P_1 were observed. On the BP-1 column, P_{gc} was too low by a factor of 2.3 at $P_1 = 10^{-1}$ mm Hg (13.3 Pa), and too high by a factor of 3.5 at $P_1 = 10^{-7}$ mm Hg (1.33×10^{-5} Pa). The Apolane-87 column showed more nearly ideal behavior. On this column, P_{gc} underestimated P_1 by a factor of 1.9 at $P_1 = 10^{-1}$ mm Hg (13.3 Pa), and the error decreased for lower P_1 . Corrections for these systematic errors were made by relating P_{gc} to P_1 through regression equations of the type

$$\log P_{gc} = m \log P_1 + b,$$

where m and b are constants.

The GC method was applied to evaluate the vapor pressure of 30 PCB isomerids containing one to seven chlorines. The average P_1 decreased by a factor of 4.5 for each Cl added to the biphenyl core. Mackay *et al.*²⁰ found that the addition of a chlorine to the biphenyl reduces solubility and vapor pressure of a factor of about 3.

Bidleman¹⁵⁷ also found large differences in vapor pressure for isomers of a particular chlorination level. In particular, isomers with the greater number of "ortho" chlorines within each chlorinated level have the higher vapor pressures. This effect has been found by other authors¹³⁹ and is related to the fact that the retention times of the PCB isomers in gas chromatography increase when the number of "ortho" substituted chlorine decreases.^{163,164} PCB congeners not containing a high degree of "ortho" chlorine substitution have the higher degree of planar conformation, show more biodegradation,¹⁶⁵ and are more toxic¹⁶⁶⁻¹⁶⁸ compared to the non-planar PCBs having chlorine in "ortho" position.

Hinckley *et al.*¹⁶⁰ determined, by capillary GC using the same BP-1 column, vapor pressures of several test compounds, including organochlorines, phthalate esters, and pesticides. Organochlorines, PAHs, and pesticides as standard compounds, most of which already used in the previous work,¹⁵⁷ were chromatographed along with two reference compounds (eicosane and p,p'-DDT). A plot of $\log P_1$ vs $\log P_{gc}$ was made to establish a correlation between measured and literature values, and this correlation was then used to compute P_1 of test compounds from their measured P_{gc} . This method provides vapor pressures within a factor of 2 of average literature values for non-polar compounds, well

within the interlaboratory precision of other techniques. GC tends to overestimate vapor pressures of moderately polar compounds.

Following the previous works,^{157,160} the GC retention data available for 32 PCB congeners were used to derive the parameters for calculating saturation liquid-phase vapor pressures of other PCB congeners as functions of temperature and ortho-chlorine substitution.¹⁶⁹ The parameters were slopes (m_1) and intercepts (b_1) of the equation

$$\log P_1 = m_1/T + b_1.$$

The slope for each of 32 PCB congeners was calculated from L_1/L_2 , the ratio of the heats of vaporization of test (1) and standard (2) substances ($m_1 = -L_1/2.303R$), from the knowledge of L_2 (93.4 kJ mol⁻¹ for eicosane, 84.5 kJ mol⁻¹ for octadecane, and 88.9 kJ mol⁻¹ for p,p'-DDT) and b_1 was derived from values of P_1 at the experimental temperatures.^{157,160} The slopes varied regularly with homolog (number of total chlorines) and also with the number of ortho-chlorines. From this information, m_1 and b_1 values were estimated for 148 other PCBs whose vapor pressures were reported at only a fixed temperature.^{139,170}

The retention behavior in gas chromatography, for a homogeneous class of compounds having the same basic structure, can be interpreted exclusively from the substituents influence on molecular interactions.¹⁷⁰⁻¹⁷² On this basis the retention data can be compared. Kovats¹⁷³ proposed an isothermal retention index, RI , for the homogeneous series of n-alkanes, defined with the following equation

$$RI = 100 \frac{n + 100[\log t_s(x) - \log t_s(n)]}{[\log t_s(n+1) - \log t_s(n)]},$$

where n is the carbon number of n -alkane eluting before substance x and $n+1$ is the carbon number of n -alkane eluting after substance x .

For homogeneous series of compounds, such as PCBs,^{163,170,174,175} PAHs,¹⁷² chlorinated dibenzo-p-dioxins¹⁷⁶ and dibenzofurans,¹⁷¹ the retention indices of the single compounds for each series has been derived.

Sissons and Welti¹⁷⁷ considered that the RI of a compound is directly proportional to its free energy of solution in a stationary phase, which in turn is an approximately additive function of the groups constituting the molecule. Consequently, any PCB molecule can be thought of as consisting of two chloro-substituted phenyl groups each with its own $1/2(RI)$ value. All PCBs are composed of twenty such basic groups and the RI of any PCB can therefore be estimated by adding together the $1/2(RI)$ values of the two component phenyl groups. Half-indices can be derived by taking half of the retention index for a PCB having the same number of chlorine atoms in the two rings or by subtracting half of the retention index for biphenyl from the retention index of a chlorinated biphenyl having only one ring substituted.

Albro *et al.*¹⁷⁸ computed retention indices for all of the 210 possible chlorinated biphenyls on 13 gas chromatographic liquid phases by summing pairs. They found that the

retention indices derived from the rough additivity of $1/2(RI)$ values are within 0.03% of those observed for all PCBs. Caution should be exercised in applying the predicted retention indices to PCBs having more than three chlorine atoms in one ring and less than three in the other. However, this group is seldom, if ever, seen in environmental samples.

The experimental vapor pressure data for each compound in a series in the liquid state can be related to the retention indices through an equation of the form

$$-\log P_1 = a RI + b,$$

where a and b are constants.

Burkhard *et al.*¹⁷⁹ examined eleven methods to predict vapor pressures (Pa) of 15 PCBs at 25 °C. One of these methods correlated the Gibbs energy of vaporization ($\Delta_{\text{vap}}G$) with gas-liquid chromatographic retention indices.

The standard compounds used in this investigation were 15 PCB congeners with solid vapor pressures (P_s) ranging from 10^{-8} to 1 Pa. These literature values, accepted as being "correct," were converted to subcooled liquid (P_l) values, using melting point (T_m) and entropy of fusion data ($\Delta_{\text{fus}}S$), through the equation¹⁸⁰

$$\ln P_l/P_s = \Delta_{\text{fus}}S(T_m - T)/(RT), \quad (4)$$

where P_l/P_s is termed fugacity ratio, R is the gas constant, and T is the measurement temperature.

$\Delta_{\text{fus}}S$ was assumed to be constant for all compounds and equal to 13.1 (cal mol⁻¹ K⁻¹) or 54.8 (J mol⁻¹ K⁻¹), the average of 16 individual PCB values obtained by Miller *et al.*¹⁸¹

The values of $\Delta_{\text{vap}}G$ were calculated from these P_l values through the relationship

$$\Delta_{\text{vap}}G = -RT \ln P_l$$

and correlated to the Albro *et al.*¹⁷⁸ retention indices for a Apiezon L stationary phase column. They found the following correlation equation

$$\Delta_{\text{vap}}G = 5.44(RI) - 1711.9, \quad r^2 = 0.955.$$

This equation was used to predict $\Delta_{\text{vap}}G$ values. With these predicted values, vapor pressures were estimated by using the melting points of the literature. The authors have finally reported a comparison between the vapor pressures obtained with this procedure and the literature experimental data extrapolated at 25 °C. The average error for all compounds is about 1.75, defined as the ratio of the predicted to experimental vapor pressures.

The same procedure was then adopted to predict the Henry's law constants of PCB congeners using the subcooled liquid vapor pressure data derived in this way and the predicted values of solubility.^{138,182}

Foreman and Bidleman¹³⁹ plotted the liquid phase vapor pressures (mm Hg) at 25 °C of 27 PCBs estimated by Bidleman¹⁵⁷ versus published retention indices (RI) by Albro *et al.*^{178,183} on two GC stationary phases. Good fits were obtained for data based on measurements with an intermedi-

ate polarity (Dexsil-410) capillary column and a non polar (OV-101) packed column. The correlation equations are

$$-\log P_1 = (-3.974 \times 10^{-3})RI + 4.434, \quad r^2 = 0.996,$$

using the RI data on Dexsil-410, and

$$-\log P_1 = (-4.189 \times 10^{-3})RI + 4.184, \quad r^2 = 0.999,$$

using the RI data on OV-101.

The same equations have been used to determine the vapor pressure of 134 PCBs found in five commercial Aroclor fluids. Vapor pressure estimates of the five fluids were calculated using individual PCB vapor pressures and Aroclor compositional information,^{183,184} assuming Raoult's law.

Fischer *et al.*¹⁷⁰ determined vapor pressures at 25 °C for 133 individual PCB congeners as subcooled liquids, on the basis of GC retention indices obtained with two different methods. In the first method the retention indices were those obtained with *n*-alkyltrichloroacetates as reference homologues on a methyl-50% octyl polysiloxane phase (SB Octyl 50) with a single-stage linear temperature program. Using vapor pressure reference data for 20 individual PCB congeners in the subcooled-liquid state,¹⁸⁵ the following correlation was obtained for the range of the di- to heptachlorobiphenyls

$$-\log P_1 = 3.689 \times 10^{-3}RI - 5.712, \quad r^2 = 0.998.$$

From this equation, P_1 (Pa) data for 133 congeners were calculated.

In the second method the retention indices were obtained on a methyl polysiloxane phase (OV 101) at 150 °C and reference vapor pressure data taken from the *n*-alkanes of the retention index system. The first method should yield more accurate results.

Eitzer and Hites¹⁶¹ determined the subcooled liquid vapor pressures of five PCDD and nine PCDF by the Hamilton's¹⁵⁹ GC method. The reference compound was *p,p'*-DDT. The experimentally determined vapor pressures (mm Hg) at 25 °C were highly correlated to published GC retention indices of dioxins¹⁷⁶ and dibenzofurans,¹⁷¹ through the following equation

$$\log P_{\text{gc}} = (404 - RI)/319, \quad r^2 = 0.99.$$

This equation allows the calculation of vapor pressures of all chlorinated dioxins and dibenzofurans; these predicted vapor pressures correlate with vapor pressures determined or predicted by other methods.

Subcooled liquid vapor pressures of the same class of compounds were also determined with a similar procedure, using a temperature programmed DB-5 fused silica columns with mass spectrometry detector.¹⁸⁶

The average precision of the GC methods, expressed as relative standard deviation on repeated measurements, was 9%¹⁵⁷ for 24 organochlorines and PAH, between 1.9 and 21% for pesticides¹³¹ and between 7 and 36% for PCBs.¹⁶²

3. Prediction Methods

Vapor pressure data are often scarce for chemicals of environmental concern, especially for those with low vapor pressures (<1.0 Pa), due to analytical difficulties.¹⁷⁹ Also, chemical products are often mixtures of many compounds; the vapor pressure determinations of each component in the mixture are difficult, when they are not available in pure form. The prediction methods in these cases may offer a valuable means to predict vapor pressures.

Some of these methods are derived from the Clapeyron–Clausius equation. Generally, they require information regarding the critical temperature, the critical pressure, the enthalpy of vaporization, the vapor pressure at least at one reference temperature (normal or reduced boiling point) and, for the solids, also the melting point or the enthalpy of melting.^{2,187} When the normal boiling point or the melting point are not available, they can be estimated from the structure of the compound.¹⁸⁷

Other theoretically based methods use correlation equations between vapor pressure and some topological indices derived from the chemical structure of the compounds.

These techniques show several difficulties when applied to low vapor pressure (<1.0 Pa) compounds which are solid at ambient temperature.

3.1 Clapeyron–Clausius Equation

The Clapeyron–Clausius equation in the general form is

$$d \ln P / dT = \Delta_{\text{vap}} H / (\Delta Z R T^2), \quad (5)$$

where P is the vapor pressure, T is the absolute temperature, $\Delta_{\text{vap}} H$ is the enthalpy of vaporization, R is the gas constant and ΔZ is the compressibility factor given by

$$\Delta Z = P \Delta V / RT,$$

where ΔV is the volume increment in the vaporization of one mole of substance. ΔZ is dimensionless and has a value of 1 for an ideal gas; it can be ignored if the pressure is low and considering that the molar volume of the condensed phase is relatively small.

The simplest equation obtained by integration Eq. (5) is

$$\ln P = A_1 - B_1 / T, \quad (6)$$

where A_1 and B_1 can be expressed in terms of the parameters in Eq. (5). Equation (6) is generally used for small ranges of temperature, where $\Delta_{\text{vap}} H / \Delta Z$ can be assumed constant. More complex equations can be derived assuming an analytical form for the temperature dependence of $\Delta_{\text{vap}} H$.

Grain¹⁸⁷ proposes two methods for the evaluation of the vapor pressure of organic compounds. The first is based on the Antoine equation¹⁸⁸ which can be applied to the liquids and gases in the range of 10^{-3} –760 mm Hg (0.133–1.01 $\times 10^5$ Pa); the second is based on the modified Watson correlation¹⁸⁹ and can be applied to liquids and solids in the range 10^{-7} –760 mm Hg (1.33×10^{-5} – 1.01×10^5 Pa). Both methods require as input data the experimentally determined or predicted normal boiling point (T_b). None is able to esti-

mate vapor pressures below 10 mm Hg (1.33×10^3 Pa) within a 10% deviation from the experimental data, however in many problems of environmental concern, as the evaluation of volatilization of a chemical from an open spill, an order of magnitude is usually sufficient.

Method 1 (Antoine) is based on the equation

$$\ln P = A_2 - B_2 / (T - C_2)$$

which, in the explicit form, yields

$$\ln P = [\Delta_{\text{vap},b} H (T_b - C_2)^2 / (\Delta_b Z R T_b^2)] \times [1 / (T_b - C_2) - 1 / (T - C_2)]. \quad (7)$$

T_b (K) is the absolute boiling point; $\Delta_b Z$ is the compressibility factor at the boiling point (0.97); C_2 is a constant which can be estimated via Thomson's rule⁶¹

$$C_2 = -18 + 0.19 T_b.$$

$\Delta_{\text{vap},b} H$ is the heat of vaporization at the boiling point, which can be evaluated by the Fishtine¹⁹⁰ equation

$$\Delta_{\text{vap},b} H / T_b = \Delta_{\text{vap},b} S = K_F (8.75 + R \ln T_b),$$

where K_F is derived taking into account the dipole moments of polar and nonpolar molecules. K_F values are listed¹⁸⁷ for various compound classes.

Method 2 (Watson–Grain), reported also by Lyman,² takes into consideration the possibility of introducing into Eq. (5) the temperature dependence of $\Delta_{\text{vap}} H$, expressed as

$$\Delta_{\text{vap}} H = \Delta_{\text{vap},b} H [(1 - T/T_c) / (1 - T_b/T_c)]^m,$$

where m is a constant. If for the critical temperature, T_c , the approximation $T_c \approx 3 T_b / 2$ is used

$$\Delta_{\text{vap}} H \approx \Delta_{\text{vap},b} H (3 - 2 T_{\rho b})^m, \quad (8)$$

where $T_{\rho b} = T / T_b$. Substituting Eq. (8) into Eq. (5) and integrating, the final result is

$$\ln P_{\text{vp}} \approx [\Delta_{\text{vap},b} H / (\Delta_b Z R T_b)] \{ [1 - (3 - 2 T_{\rho b})^m / T_{\rho b}] - [2m(3 - 3 T_{\rho b})^{m-1} \ln T_{\rho b}] \}, \quad (9)$$

where m depends upon the physical state at the temperature of interest. For all liquids $m = 0.19$. For solids the following values are recommended

$$T_{\rho b} > 0.6; \quad m = 0.36,$$

$$0.6 > T_{\rho b} > 0.5; \quad m = 0.8,$$

$$T_{\rho b} < 0.5; \quad m = 1.19.$$

The errors for method 1 have been evaluated to be 2.7% for vapor pressures between 10 and 760 mm Hg (1.33×10^3 and 1.01×10^5 Pa) and 87% between 10^{-3} and 10 mm Hg (0.133 and 1.33×10^3 Pa). For method 2 they are 2.5% and 39% respectively for the same previous ranges of vapor pressure and 47% between 10^{-7} and 10^{-3} mm Hg (1.33×10^{-5} and 0.133 Pa).

Lyman² recommends also the equation derived by Mackay *et al.*¹¹ (Kistiakowsky Linear ΔH (KLH)), which requires only the boiling point and the melting point

$$\ln P = -(4.4 + \ln T_b)[1.803(T_b/T - 1) - 0.803 \ln(T_b/T)] - 6.8(T_m/T - 1), \quad (10)$$

where the symbols have the same meaning and units as above. The last term of Eq. (10) can be ignored for liquids ($T_m < T$). The term 0.803 (K) is introduced to obtain the dependence of the heat of vaporization on the temperature. It has been found valuable for aliphatic and aromatic hydrocarbons and for aliphatic and aromatic halogenated compounds.

The mean ratio between the values obtained with this method and the literature values, for 72 compounds (hydrocarbons and halocarbons) having vapor pressures between 10^{-5} and 1 atm (1.01 and 1.01×10^5 Pa), is 1.25.¹¹ Using the Watson-Gray equation² for the same test set of chemicals the average method error was about 20% for liquids and about 30% for solids. Below 10^{-5} atm (1.01 Pa) errors will rise rapidly and may, on average, be expected to exceed a factor of 10 near 10^{-8} atm (1.01×10^{-3} Pa).

Burkhard *et al.*¹⁷⁹ report that this method is the best of the noncorrelative methods they tested with several PCBs.

Other authors^{191,192} developed, on the basis of Eq. (5), an accurate and thermodynamically sound equation for the estimation of vapor pressure of organic solids and liquids. This equation utilizes improved estimation schemes for the entropies of vaporization and melting over Trouton's rule and Walden's rule. It also utilizes improved estimation of the heat capacity changes associated with vaporization and melting. The final form of this equation is

$$\begin{aligned} \ln P = & -[(T_m - T)/T](8.5 - 5.0 \log \sigma + 2.3 \log \phi) \\ & -[(T_b - T)/T](10 + 0.08 \log \phi) + [(T_b - T)/T \\ & - \ln(T_b/T)](-6 - 0.9 \log \phi). \end{aligned} \quad (11)$$

Equation (11) describes the vapor pressure in terms of T , T_m , T_b , and only two molecular descriptors, σ , the rotational symmetry number and ϕ , the conformational flexibility number of the molecule. It was shown to successfully estimate the vapor pressures of a large number of organic compounds.

3.2. Estimation of Vapor Pressure Using Indices of Molecular Structure

One of the most important approaches in estimating a large number of properties, e.g., water solubility, octanol-water partition coefficient, vapor pressure, Henry's law constant, etc. is represented by the methods of the fragment constants. These methods assume that each property of a compound is the sum of contributions of single atoms or group of atoms (fragments) or structural factors (e.g., type of bond).

The method of fragment contribution to evaluate the octanol-water partition coefficient of many organic compounds has been highly developed.^{193,194} Fragment constants for over 160 atoms or fragments have been derived together with several structural factors (type of bond, branching,

rings, chain length, halogenation, etc.). The log of the property is calculated from the contribution of the fragment values and of the structural factors.

On this basis the linear free-energy relationship (LFER) model has been proposed assuming that the effect of substituents on the interactions drug-receptor is an additive combination of the hydrophobic, electronic, steric and dispersive factors. The same concept has been applied to the relationships between the octanol-water partition coefficient and the solubility of organic compounds.¹⁹⁵

Several investigations have reported development of predictors, related to molecular topology, which require only the knowledge of the chemical structure and therefore are particularly suitable for new chemical products, when only the chemical structure is known. They can be accurately calculated and account for the structural differences between chemicals. Methods based on quantitative structure-activity relationships (QSARs) have been extensively used in the field of pharmacology to evaluate some biological effects (enzyme induction, biodegradation, toxicity, etc.) through correlations with topological indices.¹⁹⁶ Only recently QSARs have been used in predicting also parameters of environmental interest (solubility, Henry's law constant, partition coefficients, etc.); for these investigations they have been referred to sometimes as quantitative structure-property relationships (QSPRs). Molecular surface area and molecular connectivity indices (MCI) belong to this class of predictors.

Molecular connectivity indices,^{197,198} χ , are derived from the assignment of a numerical adjacency value to each atom other than hydrogen in the molecular skeleton. This value corresponds to the bond number or the valence of each atom. Four classes of bonding are identified: paths, chains, clusters, and path-clusters. Different orders are assigned to each class. The molecular connectivity index can be calculated by summing the negative square roots of the product of the atom valences relative to each group of adjacent atoms in the molecule.

Burkhard *et al.*¹⁹⁹ developed QSPRs for a test family consisting of *n*-alkanes (methane to pentacontane), biphenyls and all PCB congeners, with new variables obtained from a principal component analysis of the MCI. These new variables have similar meaning for all the compounds and reflect physical characteristics of the molecule.

The same authors¹⁷⁹ used eleven methods to predict vapor pressures at 25 °C for 15 PCBs with known experimental values. Two methods were correlative based on MCI, the molecular topological indices of Kier and Hall.¹⁹⁷ The final regression equation for the first method is

$$\log P = 2.781 - 0.413(\text{NP10}), \quad r^2 = 0.953,$$

where P is the saturation vapor pressure (Pa) (for the standard state at the temperature of interest) and NP10 is the number of paths of order 10 MCI.

The second method is an extension of the previous MCI approach.¹⁹⁹ The predictive equation is

$$\log P = -6.792 - 2.649(\text{PCA1}), \quad r^2 = 0.910,$$

where PCA1 is the first principal component variable.

The mean values of the ratios of the predicted to experimental vapor pressures are 2.53 and 4.44 for the two methods respectively. According to the authors, this study demonstrated that the variables derived from the MCIs employed in the second method have a better physical meaning over the MCIs used by the first method but have less specificity for each compound.

In an attempt to correlate the vapor pressure of PCBs with their molecular structure, Rouvray and Tatong²⁰⁰ used a number of topological indices²⁰¹ at two temperatures, 25 and 100 °C. Included in this study were the Wiener index, W , the Balaban distance sum connectivity index, J , several of the Randic molecular connectivity indices, χ , and the chlorine number, n_{Cl} . They used the vapor pressures of 15 different PCBs at 25 °C, the same reported in the work by Burkhard *et al.*¹⁷⁹ The vapor pressures of 10 PCBs at 100 °C were compiled by means of interpolation and extrapolation from a variety of sources. The best relationship obtained for the 15 PCBs between the vapor pressure (Pa) at 25 °C and the several different topological indices was

$$\ln P = 8.73 + 1.21 \chi_{pc} - 0.08W, \quad r = 0.9787.$$

For the data set of the 10 PCBs with vapor pressures (Pa) at 100 °C, the best regression equation was

$$\ln P = 14.23 - 2.20 \chi_p, \quad r = 0.9787.$$

Stepwise regression analysis on the data set of 15 PCBs having vapor pressures (Pa) determined at 25 °C, yielded as the best regression equation

$$\ln P = -20.70 - 0.06W + 11.48J, \quad r = 0.9768.$$

The main conclusions of the study are that (i) the vapor pressures of PCBs correlate very well with topological indices; (ii) the vapor pressures of PCBs at 25 °C and 100 °C are also highly correlated; and (iii) different indices need to be employed to obtain the best correlation at each of the two temperatures.

The relationships between the logarithms of subcooled vapor pressure (P_1) and Henry's law constant (H) for PCB congeners with planar total surface area (TSA) have been investigated.²⁰² Linear regression of $\log P_1$ (Pa) for the literature data^{114,140,157,179} against planar TSA (Å or 10^{-20}m^2) gives a significant linear relationship expressed by

$$\log P_1 = -4.88 \times 10^{-2} \text{ planar TSA} + 9.40, \quad r = 0.962.$$

From this equation vapor pressures of sufficient reliability for use in environmental modeling were derived for all congeners.

The "group surface area" approach has been developed by Amidon and Anik;²⁰³ it has been used to estimate the Gibbs energy changes for the following processes: (i) pure (supercooled) liquid to aqueous solution; (ii) pure (supercooled) liquid to gas; (iii) gas to aqueous solution. The vapor pressures at 298 K of some alkyl aromatic hydrocarbons are calculated from the free energy changes of process (ii).

QSPR models have been developed to accurately calculate the congener-specific aqueous solubilities and Henry's law constants of many PCBs.²⁰⁴ From the predicted values of the two parameters, the vapor pressures can be estimated.

Kamlet *et al.*²⁰⁵ proposed the linear solvation energy relationship (LSER) model to estimate the toxicity of various compounds. This model has been applied to the estimation of the solubility and of other properties. It uses linear combinations of three free energy contributions of the cavity term, the dipolar term, and the hydrogen bonding term.

Banerjee *et al.*²⁰⁶ found that vapor pressure (mm Hg) of 53 compounds could be correlated with the Kamlet's solvatochromic parameters through the empirical relationship

$$\log P = 7.82 - 7.29(V_I/100) - 6.41\pi^* + 3.25\pi^{*2} - 0.01(\text{mp} - 25), \quad r = 0.98,$$

where V_I is the molecular volume, π^* is a measure of solute dipolarity/polarizability and mp is the melting point in °C. This equation implicitly assumes that the entropy of vaporization is constant. The melting point term is an entropy-of-fusion correction which allows both liquids and solids to be covered by the same equation. Liquids are assigned a melting point of 25 °C to remove the last term from the equation.

The UNIFAC approach,^{207,208} which offers access to a wider range of structures, was also attempted by the same authors.²⁰⁶ For the UNIFAC based equation, solute self-association in the liquid phase is modeled by calculating the interaction of the solute with a reference matrix of methyl groups. It was applied to a wide range of compounds with different chemical characteristics and vapor pressures ranging over 12 orders of magnitude. They obtained the following correlation for 118 compounds

$$\log P = 6.94 - (2.25 V_U + 4.23 \log \gamma_C) - 0.577 \log \gamma_R - 0.01(\text{mp} - 25), \quad r = 0.95,$$

where V_U is related to $\log \gamma_C$. The activity coefficient, γ , of a component is expressed as

$$\gamma = \gamma_C \gamma_R,$$

where γ_C (the combinatorial), represents size/shape differences between the component and its environment, and γ_R (the residual) reflects interactive effects.

Dunnivant and Elzerman¹³⁵ reported that currently available QSPRs are ineffective for predicting solubilities, Henry's law constant and vapor pressures, when compared to experimentally determined results, while an empirical data fitting approach based on coefficients related to chlorine substitution patterns appears promising.

In a more recent paper Dunnivant *et al.*²⁰⁴ developed QSPR models which accurately calculate the congener-specific aqueous solubilities (S) and Henry's law constants (H) of polychlorinated biphenyls. The S and H data can be used to derive the vapor pressure values of the same PCB congeners.¹⁶⁹

Rordorf^{111,121,209} measured the vapor pressures at several temperatures of ten chlorinated dibenzo-p-dioxins and of ten

chlorinated benzenes by a gas saturation method. He found linear dependencies of the $\log P$ values on the chlorine substitution number for fixed temperatures. Corresponding correlations for the enthalpies and entropies of sublimation allowed the estimation of the vapor pressure curve of 2, 3, 7, 8-tetrachloro-dibenzo-p-dioxin.

The same determinations of vapor pressure were then used as data base to predict thermal properties of dioxins and furans²¹⁰ and vapor pressures, boiling points and enthalpies of fusion of several halogenated dioxins.²¹¹ The correlation method uses the liquids as reference states. Boiling points and enthalpies of fusion were deduced for the measured compounds and were correlated with the degree of halogenation. The two correlations were used to predict boiling points and enthalpies of fusion for related dioxins of known melting points, and these values served as starting point for the vapor pressure predictions. Other thermal properties, such as molar heat capacities of the gaseous and the liquid phases, enthalpies and entropies of evaporation, of sublimation and of fusion were also estimated for the investigated halogenated dibenzo-p-dioxins. This work has been extended to other halogenated dioxins and furans.^{212,213}

Similar correlations for solubility, octanol-water partition coefficient, vapor pressure, and Henry's law constants of polychlorinated dioxins give predictions of the first two parameters within a factor of 2 for most of congeners, while the last two parameters can be predicted within a factor of 5.²¹⁴ The vapor pressure data experimentally obtained by Rordorf for ten dioxins and referred to subcooled liquids tend to fall by a factor of 8 per chlorine added.²¹⁴

4. Analysis of the Data and Comments

The vapor pressure data, interpolated or extrapolated at ambient temperature (Tables 1–5), were collected together with the vapor pressure equations and with the enthalpy of sublimation or vaporization in the temperature range of measurement. All the data were converted to common units, vapor pressures to Pa and enthalpy values to kJ mol^{-1} .

The vapor pressure equations were those reported in the original papers, but, sometimes, were derived from the literature experimental data.

When the range of temperature measurement was above the melting point and too far from the ambient temperature, only the vapor pressure equation was given, because the extrapolation at ambient temperature could not be considered reliable. The range of temperature measurement in gas chromatography was that corresponding to the column temperature. For prediction methods, only the temperature at which the prediction was made has been indicated.

The values of vapor pressure obtained for the subcooled liquids have been converted to those of the corresponding solids for ease of comparison, using the already mentioned Eq. (4). $\Delta_{\text{fus}}S$ was assumed to be equal to $54.8 \text{ J mol}^{-1} \text{ K}^{-1}$ for the PCB congeners, as calculated from the experimentally determined values by Miller *et al.*,¹⁸¹ and to 56.5

$\text{J mol}^{-1} \text{ K}^{-1}$ for the other compounds, as estimated from Walden's rule by Yalkowsky for the rigid PAHs.²¹⁵ Thus, for $\Delta_{\text{fus}}S/R$, a value of approximately 6.59 was taken in the first case and 6.79 in the second.

More accurate values of P_s could be obtained using actual $\Delta_{\text{fus}}S$'s, when available, relative to each compound.¹⁶⁰

The data of Tables 1–3 and 5 have been examined with a simple statistical analysis, choosing the data set containing a minimum number of four values for a single compound. The results are reported in Tables 6 and 7. The data of Table 4, regarding chlorinated dioxins and furans, have not been taken into consideration, because of the lack of values available for each compound. However, the reproducibility of these values seems satisfactory.

Table 6 shows an analysis of the data obtained with direct experimental methods for some PAHs, biphenyl, some pesticides, and dibutyl phthalate. It gives the ratio between the maximum and the minimum value, the average, the standard deviation, and the relative standard deviation for each compound. Often, the number of data obtained with each experimental method is not sufficient to calculate the respective averages. However, when possible, individual sets have been examined separately. Also, the data obtained with different methods have been combined and averaged. Thus, Table 6 offers the chance of some general remarks:

(1) The max/min ratio of the values obtained by effusion (E) and gas saturation (GS) is sometimes greater than ten, indicating that differences of an order of magnitude are possible also with these methods. Sometimes (DDT and dibutyl phthalate) these differences depend on single values, that have a large effect on the average.

(2) No significant differences between averages for each compound are observed, on the basis of the Student's $t_{0.05}$ test on the available data sets. Moreover, the RSDs, corresponding to individual or combined sets, are substantially constant for each compound. These results suggest that the data sets for each compound can be treated as belonging to the same statistical population.

(3) The uncertainty in the vapor pressure measurements increases as vapor pressure decreases. A quantitative evaluation of this trend may be obtained by linear regression of $\log \text{RSD}$ against $\log P_{\text{av}}$, for the combined E, GS sets at 25°C of the compounds reported in Table 6. It gives the following equation: $\log \text{RSD} = -0.146 \log P_{\text{av}} + 1.511$, with $r^2 = 0.586$.

Naphthalene shows a good reproducibility of the data obtained by E and GS, with a difference within 7% of the average values relative to these two methods. When the data obtained with other methods are included, the differences among the global average (28 values) and those relative to E and GS are 2.6% and 4.1% respectively. As a matter of fact naphthalene has been proposed as reference material for evaluation of methods for measurement of low vapor pressures.^{70,104} Sinke¹⁰⁴ recommended a value of 0.0820 Torr (10.9 Pa) for the vapor pressure of naphthalene at 298.15 K; this value is very close to the average of data obtained by E and different of about 3% from the global

TABLE 6. Analysis of the vapor pressure data obtained with direct experimental methods

Method	Number of data points	Max/Min	Average \pm SD (Pa)	RSD (%)
Naphthalene (25 °C)				
E	11	2.72	10.96 \pm 2.30	21.0
GS	8	1.35	11.70 \pm 1.38	11.8
E, GS	19	2.72	11.27 \pm 1.95	17.3
M	5	1.31	11.86 \pm 1.43	12.1
E, GS, M, HS, BP, S \times H, Vs	28	2.72	11.24 \pm 1.85	16.4
Acenaphthene (25 °C)				
E, GS	4	1.82	3.04E-1 \pm 0.74E-1	24.2
E, GS, M, S \times H, Vs	7	1.82	3.26E-1 \pm 0.63E-1	19.3
Fluorene (25 °C)				
E, GS, M	4	1.54	7.78E-2 \pm 1.40E-2	18.0
Anthracene (25 °C)				
E	9	23.0	1.31E-3 \pm 0.98E-3	74.8
GS	6	6.36	1.95E-3 \pm 1.59E-3	81.5
E, GS	15	35.5	1.57E-3 \pm 1.25E-3	79.6
E, GS, M, Is, F	19	35.5	1.64E-3 \pm 1.37E-3	83.5
Phenanthrene (25 °C)				
E	6	5.67	3.46E-2 \pm 3.31E-2	95.7
E, GS	8	6.34	3.13E-2 \pm 2.88E-2	92.0
E, GS, S \times H	9	6.34	3.10E-2 \pm 2.69E-2	86.8
Pyrene (25 °C)				
E	5	9.16	11.61E-4 \pm 10.88E-4	94.0
E, GS	6	9.16	10.68E-4 \pm 10.00E-4	93.6
E, GS, M	7	10.44	9.57E-4 \pm 9.58E-4	100.1
Benz(a)anthracene (25 °C)				
E	7	68.5	1.35E-5 \pm 0.95E-5	70.4
E, GS	8	68.5	1.53E-5 \pm 1.01E-5	66.0
Biphenyl (25 °C)				
E	4	2.47	1.07 \pm 0.38	35.5
E, GS	6	2.47	1.13 \pm 0.31	27.4
E, GS, M, HS, Vs	10	3.40	1.30 \pm 0.41	31.5
p,p'-DDT (20 °C)				
GS	5	38.7	1.50E-4 \pm 2.84E-4	189.3
E, GS	6	38.7	1.28E-4 \pm 2.60E-4	203.1
E, GS, PC	7	38.7	1.14E-4 \pm 2.40E-4	210.5
(25 °C)				
GS	5	26.2	2.77E-4 \pm 4.99E-4	180.1
E, GS	6	26.2	2.38E-4 \pm 4.56E-4	191.6
Dieldrin (20 °C)				
E, GS, PC, DL	5	1.64	3.60E-4 \pm 0.68E-4	18.9

TABLE 6. Analysis of the vapor pressure data obtained with direct experimental methods—Continued

Method	Number of data points	Max/Min	Average \pm SD ^a (Pa)	RSD ^b (%)
Hexachlorobenzene (20 °C)				
E, GS	4	2.28	1.60E-3 \pm 0.69E-3	43.1
E, GS, M	5	2.28	1.57E-3 \pm 0.61E-3	38.9
γ -Hexachlorocyclohexane (20 °C)				
E, GS	4	6.63	4.41E-3 \pm 2.97E-3	67.3
E, GS, PC, DL, B	7	6.63	3.69E-3 \pm 2.42E-3	65.6
Parathion (20 °C)				
GS	4	4.17	1.61E-3 \pm 1.10E-3	68.3
E, GS	5	8.14	2.30E-3 \pm 1.82E-3	79.1
E, GS, ET, B	7	8.59	1.83E-3 \pm 1.69E-3	92.3
Dibutylphthalate (25 °C)				
E	4	77.3	9.80E-3 \pm 14.68E-3	150.0
GS	4	6.30	5.34E-3 \pm 3.45E-3	64.6
E, GS	8	77.3	7.57E-3 \pm 10.15E-3	134.0
E, GS, M, PT, D, Te	16	77.3	5.36E-3 \pm 7.43E-3	139.0

^aSD = standard deviation from the average.^bRSD = percent relative standard deviation from the average.

average (28 values). Also the values of enthalpy at 298.15 K, obtained by several authors (72.5–72.8 kJ⁻¹ mol⁻¹), using E, GS, and M, are strongly reproducible, indicating the general good accuracy of these measurements.

Gas chromatography (GC) is the most important indirect method. Unfortunately only for the PCB congeners (Table 2)

a statistical analysis of the available data is possible. Table 7 shows that the max/min ratio for all compounds is less than 5, indicating a high precision of the method. Unfortunately the accuracy of these average values cannot be evaluated by comparison with those obtained by direct experimental methods, due to the lack of these data in Table 2.

TABLE 7. Analysis of the vapor pressure data obtained by GC for selected PCB congeners

(No)	Compound	Data (N)	Max/Min	Average \pm SD ^a (Pa)	RSD ^b (%)
(3)	4-	4	3.36	1.91E-1 \pm 1.14E-1	59.7
(4)	2,2'-	5	1.45	1.55E-1 \pm 0.22E-1	14.2
(9)	2,5-	5	1.26	2.10E-1 \pm 0.21E-1	10.0
(11)	3,3'-	6	3.24	6.81E-2 \pm 2.23E-2	32.7
(12)	3,4-	4	1.44	3.88E-2 \pm 0.64E-2	16.5
(15)	4,4'-	7	1.72	4.38E-3 \pm 0.79E-3	18.0
(18)	2,2',5-	5	1.55	5.23E-2 \pm 0.82E-2	15.7
(26)	2,3',5-	5	1.29	2.63E-2 \pm 0.33E-2	12.5
(28)	2,4,4'-	5	1.28	1.52E-2 \pm 0.18E-2	11.8
(30)	2,4,6-	6	1.70	4.85E-2 \pm 1.03E-2	21.2
(33)	2',3,4-	6	1.44	1.14E-2 \pm 0.16E-2	14.0
(40)	2,2',3,3'-	6	1.81	1.17E-3 \pm 0.24E-3	20.5
(52)	2,2',5,5'-	9	3.63	4.61E-3 \pm 1.49E-3	30.3
(53)	2,2',5,6'-	6	1.71	5.14E-3 \pm 0.99E-3	19.3
(77)	3,3',4,4'-	7	1.60	5.76E-5 \pm 1.15E-5	20.0
(101)	2,2',4,5,5'-	9	1.59	1.13E-3 \pm 0.16E-3	14.2
(128)	2,2',3,3',4,4'-	6	2.11	1.97E-5 \pm 0.46E-5	23.3
(153)	2,2',4,4',5,5'-	7	1.45	1.25E-4 \pm 0.13E-4	10.4
(202)	2,2',3,3',5,5',6,6'-	5	3.24	1.83E-5 \pm 0.81E-5	44.3
(209)	Deca-	4	4.70	3.02E-8 \pm 1.75E-8	57.9

^aSD = standard deviation from the average.^bRSD = percent relative standard deviation from the average.

TABLE 8. Accuracy of the vapor pressure data obtained with indirect and prediction methods

Compound	T(°C)	Average	Maximum deviation factors ^a		
			Pr	RV	GC
Naphthalene	25	11.24	2.4		1.7
1-methyl naphthalene	25	9.12 ^b	-2.2		1.5
Acenaphthene	25	3.26E-1	2.7		
Fluorene	25	7.78E-2	-3.1		1.6
Anthracene	25	1.64E-3	3.3		2.0
Phenanthrene	25	3.10E-2	1.7		2.5
Fluoranthene	25	1.20E-3 ^b			-1.8
Pyrene	25	9.57E-4	5.5		3.9
Benz(a)anthracene	25	1.53E-5	-2.2		-3.5
Benz(a)pyrene	25	7.48E-7 ^b	1.1		-4.7
Biphenyl	25	1.30	-3.3		-2.0
Di-butyl phthalate	25	5.36E-3	-4.6		1.0
Aldrin	20	8.88E-3 ^b		8.9	2.1
Diazinon	20	1.18E-2 ^b			4.9
p,p'-DDT	20	1.14E-4	-24	5.7	3.3
	25	2.38E-4		18	3.5
Dieldrin	20	3.60E-4	28		-2.5
	25	7.27E-4 ^b			4.3
Hexachlorobenzene	20	1.57E-3		3.4	2.4
	25	2.65E-3 ^b	-2.0		2.4
γ-Hexachlorocyclohexane	20	3.69E-3	-18	1.6	-1.3
	25	8.94E-3 ^b			-1.6
Methyl parathion	20	9.65E-4 ^b		-1.9	-2.4
	25	2.19E-3 ^b			-8.2
Parathion	20	1.83E-3		3.1	2.3
	25	3.78E-3 ^b			2.5

^aDeviation factor is calculated from the ratio of the average obtained with direct experimental methods to single values. When this ratio is less than 1, its negative reciprocal is reported. Values of deviation factor are the maximum found for each compound.

^bAverage of the experimental values reported in Tables 1-3 and 5 and not included in Table 6.

However a comparison is possible between single GC values of Tables 1-3 and 5 and the averages of Table 6. The maximum deviations, calculated as the ratio between the averages and the single GC values, are shown in Table 8. The range of the values obtained is generally less than one order of magnitude, sometimes better than the deviations shown by single values obtained by other experimental methods.

It has been observed that GC has several advantages over the other techniques for determining vapor pressures: speed, tolerance to relatively impure compounds, the ability to determine vapor pressures of several compounds simultaneously, and small sample size requirements.¹⁶² For all these reasons this method can be recommended as one of the most suitable for the determination of the vapor pressure of low volatility compounds.

A similar analysis has been carried out with the data obtained by relative volatilization rate (RV) and prediction (Pr) methods (Table 8).

The results of the RV indicate that the maximum deviation is about 18, but more data would be necessary for a better evaluation of this method.

Pr methods also give satisfactory results (Table 8), with deviations of a maximum value of 5.5 for PAHs, biphenyl,

TABLE 9. Vapor pressure ranges of measurement of the most important experimental methods employed with environmental contaminants

Method	Range (Pa)
Direct	
Gas saturation	10 ⁻⁸ -10 ⁴
Effusion (Kn and T)	10 ⁻⁴ -10 ²
Manometry	10 ⁻¹ -10 ⁵
Boiling point	10 ⁻¹ -10 ⁵
Pendulum tensimeter	10 ⁻² -10 ³
Indirect	
Gas chromatography	10 ⁻⁸ -10 ¹
Relative volatilization rate	10 ⁻⁵ -10 ⁻¹
Prediction	
Various	10 ⁻⁸ -10 ³

and dibutyl phthalate. However, the values of vapor pressure for pesticides, obtained with the methods based on Clapeyron-Clausius equation using the Antoine (method 1) or Watson-Grain (method 2) approximations (Sec. 3.1), can deviate from the average of the data obtained with direct experimental methods of factors greater than ten.

Finally, Table 9 shows a general view of the literature information concerning the vapor pressure ranges, where the measurements with the most important methods were carried out.

The direct experimental methods can cover a very wide range of vapor pressure. GS is the most suitable for measuring very low vapor pressure at ambient temperature. E shows a more restricted range of vapor pressure. The other methods can measure only high vapor pressures.

Among the indirect methods, GC has been employed for the determination of very low vapor pressures in different experimental conditions, such as type and dimensions of the column, nature of the stationary phase, temperature of the column and injector.

The RV method has given good results in measuring low vapor pressure down to 10⁻⁵ Pa at ambient temperature.

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6. List of Symbols

B	bioassay
BP	boiling point at reduced pressures
D	dew point tensimeter
DL	diffusion law
E	effusion
	(Kn) Knudsen cell
	(Kn,i) Knudsen cell, internal balance
	(T) torsion
	(T+Kn) combined torsion and Knudsen cell
	(T-W) simultaneous torsion and weighing
ET	equilibration technique
F	fluorimetry

ΔG	Gibbs energy (J mol^{-1}); $\Delta_{\text{vap}}G$ Gibbs energy of vaporization
GC	gas chromatography (stationary phase)
GS	gas saturation (HCl) determination of hydrochloric acid produced by decomposition of the chlorinated compound (CO_2) determination of carbon dioxide produced by combustion (^{14}C) β -counting of the ^{14}C -labeled compound ($^{14}\text{CO}_2$) β -counting of carbon dioxide produced by combustion of the ^{14}C -labeled compound (GC) determination by gas chromatography (HPLC) determination by high pressure liquid chromatography (S) spectrophotometric determination (W) determination by weight
H	Henry's law constant ($\text{Pa m}^3 \text{mol}^{-1}$)
HS	head space
ΔH	enthalpy (J mol^{-1}); $\Delta_{\text{sub}}H$ enthalpy of sublimation; $\Delta_{\text{vap}}H$ enthalpy of vaporization; $\Delta_{\text{sub}}H$ (in tables) enthalpy of sublimation in the range of measurement or, when indicated, at 298.15 K
Is	isoteniscope(Hg) mercury manometer
M	manometry (Baratron, Rodebush, Ruska) manometric systems (DB) Datametric Barocel (Hg) mercury manometer (IG) ionization gauge (IP) inclined piston
MP	melting point
MW	molecular weight
PC	partition coefficient
P	vapor pressure (Pa); P_1 liquid or subcooled liquid vapor pressure; P_s solid vapor pressure
Pr	prediction (C-C, M1 or M2) Clapeyron–Clausius, Method 1 or Method 2, see the text (corr. Cl) correlation vapor pressure-chlorine substitution (corr. RI) correlation vapor pressure-retention indices in GC (KLH) Kistiakowsky Linear ΔH (MW) molecular weight, correlation (QSPR) Quantitative Structure Property Relationship (S×H) vapor pressure data obtained from S and H values predicted with QSPR (Th) thermodynamic approach (TI) topological indices, correlation (TSA) total surface area, correlation (UNIFAC) indices, correlation
PT	pendulum tensimeter
R	gas constant ($8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$)
RI	retention index
RV	relative volatilization rate
ΔS	entropy ($\text{J mol}^{-1} \text{ K}^{-1}$); $\Delta_{\text{fus}}S$ entropy of fusion; $\Delta_{\text{vap}}S$ entropy of vaporization

S	aqueous solubility (g m^{-3} or mol m^{-3})
$S \times H$	solubility \times Henry's law constant
t	temperature ($^{\circ}\text{C}$)
T	temperature (K)
Te	tensimeter
VG	vibration gauge
VR	relative volatilization rate
V_s	viscosity

Conversion factors

Vapor pressure: $1 \mu\text{m} = 0.133322 \text{ Pa}$; $1 \text{ mm Hg} = 1 \text{ torr} = 133.322 \text{ Pa}$; $1 \text{ atm} = 101,325 \text{ Pa}$ (or Nm^{-2}) Heat: $1 \text{ cal} = 4.184 \text{ J}$

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