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PERMEABILITY OF ORGANIC COMPOUNDS THROUGH VARIOUS
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PERMEABILITY OF ORGANIC COMPOUNDS THROUGH VARIOUS PACKAGING POLYMERS DATABASE

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ABSTRACT

PERMEABILITY OF ORGANIC COMPOUNDS THROUGH VARIOUS PACKAGING POLYMERS DATABASE

By

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The flexibility and cost effectiveness of plastic has resulted in increased usage in recent years. Although much information is known on polymer/organic penetrant mass transport systems, it is spread over many mediums and formats making access difficult. The loss/gain of aromas in food product/package systems is inherently related to product quality and package costs.

The objective of this project is to create a comprehensive database of mass transfer (permeability, diffusion, and sorption coefficients) which would be readily accessible to technical product/packaging professionals.

The proposed database would serve as a design, quality, and safety tool, dramatically improving project turnaround time. The significance of estimating the degree of flavor loss will ultimately lead to an optimization of quality and functionality.

This thesis is dedicated to the late Dr. Jack Giacin whose wonderful smile, wealth of knowledge and giving nature made this world a better place.

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Symbol	Significance
P	Permeability
D	Diffusion
S	Solubility
F	Fahrenheit
C	Celsius
K	Kelvin
ppm	parts per million
m^2	meters squared
hrs	hours
Pa	pascals
Sec	seconds
SI	standard international units
Wt	weight
V	volume
Tg	glass transition temperature
KPa	kilo pascals
L	liters
STP	standard temperature and pressure
RH	relative humidity

INTRODUCTION

Over the years, the number of polymeric packaging materials available to industry has steadily increased. Currently there is substantial knowledge on many of the polymer/organic penetrant mass transport systems. This information is sprawled over numerous mediums and written in many forms. There is great practical interest in knowing the loss/gain of aromas in a food product/package system for several reasons. In today's competitive global marketplace, companies as well as consumers demand high quality products. The quality of food products, as well as other consumer goods products, is directly related to product/package interaction. Due to this symbiotic relationship, permeability of organic compounds must be an integral part of the package design process.

At this time a comprehensive database of permeability is not available. The creation of a comprehensive database will enable the product/package designer to optimize quality and functionality while simultaneously minimizing cost. For example, this database would be useful in the design of various products containing volatile, organic constituents, such as confectionary products, beverages, flavored dairy products, soups, and culinary products.

Because a database of this nature needs to be flexible in design and of considerable magnitude, it is necessary to approach this project in several stages.

The objective of this thesis is to create a comprehensive database using Microsoft Access 97 coupled with Visual Basic for Application programming to compile permeability data which would be readily accessible to technical product/packaging professionals. The proposed database would serve as a design, quality, and safety tool, allowing for estimation of the degree of flavor loss which could be expected from a given product/package system design.

Zobel

Copious amounts of research pertaining to saturated vapors has been published since 1948. While this work is useful in estimating how well a package will withstand an accidental high level of contamination, it is not an authentic use of data to estimate permeation rates because of the considerably lower levels of vapor encountered in a retailing situation Zobel (1982). In response to this determination, Zobel devised an isostatic technique coupled with a flame ionization detector. This methodology is partially based on the work of Niebergal's (1978) sophisticated method. Since Zobel suggested that real life situations would require vapor concentrations down to 1 ppm, he chose to use a flame ionization technique as his detection method.

The flame ionization method assured the possibility of measuring within these low ppm vapor concentration ranges which the previous vapor sampling methods did not. However, the flame ionization detector is limited to simple test vapors; therefore, it cannot be used to test complex natural odors.

Later, Zobel (1984) modified the detection technique by incorporating a sorption desorption cycle before the test vapor entered the detector. This resulted in an increase in detection accuracy because it improved discrepancy between a real signal and a baseline drift when testing at the more "realistic" low vapor concentration levels. At these low vapor concentration levels, permeability became virtually constant, allowing for possible extrapolation at even lower levels. Zobel (1984) concluded that the results showed that the rate of change of permeability coefficient with concentration was small provided that the odorant was kept below 10% of the saturated vapor pressure.

Gilbert

Gilbert, the Head of the Rutgers Food Science Department, is another significant contributor to the science of mass transfer. The famous paper by Gilbert and Pegaz (1969) is a milestone in this area of science. The quasi isostatic procedure utilizing a gas chromatograph equipped with a flame ionization detector was developed and reviewed. As recent as 1987, Gilbert uses this quasi isostatic procedure, and it is the platform which Baner and Hernandez from Michigan State's School of Packaging based their quasi-isostatic methodology on in the mid-80s.

Gilbert was a strong believer in pre-conditioning the samples before testing; and he reported all results after gelbo flex testing the film samples for 20 cycles as stated in ASTM F-392-74 adding another dimension to the results. In the case of flexed glassine, the extremely high values are attributed to the presence of pinholes or macro voids in the film which sharply increase the permeation rate. An exception to the normal increased permeability of flexed films was found. PE/NYLON/PE responded positively to flexing by decreasing the permeability values. This can be attributed to orientation of polymer chains on flexing with consequent increase in "packing" of these macromolecules Gilbert and al. (1987).

Allied, a nylon film converter, established a collaborative study with Gilbert. The results of the study include an interesting quantitative to qualitative analysis for determining if a particular polymer/penetrant combination was excellent, good, or poor. The results are as follows and are based on permeability units of $\frac{grams}{24hrs*m^2*100ppm}$ at 70°F, Gilbert's standard measurement of permeability. An excellent rating was conferred on polymer/penetrant combinations with 0.1 or less permeability, good in the range of 0.1 to 1, and poor for any polymer/penetrant combination over 1. The film materials tested included: nylon, polyvinylidene chloride (PVDC), ethyl vinyl alcohol(EVOH), and glassine McKinley (1984).

The results indicate that nylon provides good to excellent protection against the permeation of flavors and aromas, and offers the most economical barrier per-mil thickness. In addition, nylon provides excellent grease, and oil resistance, and high temp performance, as well as impact puncture and tear resistance. Coextruded films with thin nylon cores proved to have the broadest range of performance properties of the films tested with optimum flavor and aroma barrier McKinley (1984).

In 1987 Gilbert conducted another extensive lamination study. The effect of water interacting with nylon laminations was studied. Nylon, a hydrophobic material containing hydrogen bonds, acts adversely when in contact with water, causing the polymer matrix to swell; this results in film platicization and an increase in permeability. However, Gilbert discovered that with proper laminations which protect the nylon from outside conditions by utilizing a polyolefin layer this plasticizing effect could be nearly eliminated. Consequently, it was found that the best barrier properties at both 0% RH and 75% RH were awarded to the nylon and polyethylene vinyl alcohol laminations rather than the PET-G and polyvinylidene chloride (PVDC) laminations. It should be noted that Gilbert developed a new set of test cells: one for low barrier testing, and one for high barrier Gilbert (1987).

DeLausses

DeLausses, an engineer for the Dow Chemical company, has established another isosatic testing method for determining the mass transfer characteristics of various organic polymer/penetrant combinations. Polymer penetrant combinations cannot reliably be ranked by their oxygen permeabilities DeLausses (1994). DeLausses claims many packaging engineers unfortunately have this misconception. Permeability has consistently been reported as a modified Zobel unit, or SI $(\frac{kg*m}{m^2*\sec*Pa})^{-20}$ with the logic being to simplify reporting of permeability.

In his earlier testing DeLausses used a photoionization detector to quantify polymer/penetrant mass transfer data. Later, it was determined that photoionization detectors were not as accurate as initially thought. The potential coating of the window of the photoionization detector from permeating molecules proved to reduce sensitivity.

DeLausses(1994) did a case study seeking to understand the importance of barrier layer placement for both rigid containers and thin films in aroma barrier packaging. D-limonene was used as the model flavor component establishing an interest in keeping the flavor in the package, instead of studying the adverse affects of a volatile migrating into the package. The barrier layer on the inside for both the rigid container and thin film greatly reduced the permeability of d-limonene through the package. This can be attributed to the increased time needed to saturate the barrier layer on the inside since the diffusivity is very low as opposed to the barrier on the outside where the d-limonene would diffuse much more rapidly, inadvertently increasing permeation. Once again, it was found that EVOH permeability and diffusivity can be up to 1000 times greater for flavor and aroma mass transport when subjected to high humidity than under dry conditions. This same study also displayed the lack of sensitivity of vinylydene chloride to high levels of humidity compared with dry conditions.

Later, DeLausses (1988), used a novel mass spectrometer as the means of detection of aromas/volatiles in all tests. This detection system was chosen so that the user could evaluate the effect of multiple mixtures of organic penetrants, an option not available with the popular flame ionization detection method.

A study was undertaken by Dow to determine the applicability of aroma barrier properties for its Saran (PVDC) film. DeLausses found that the permeability of aromas was up to 9000 times lower than in polyolefins. DeLausses interestingly noted that the solubility coefficients were found to be similar in magnitude.

DeLausses also utilized an equation for predicting the permeabilities of various compounds at different temperatures. This equation has proved useful because investigators are increasingly testing higher barrier materials which require increased test temperatures to bring permeability measurements within detection range of mass spectrometers. This is necessary in order to increase both the diffusion and permeability coefficient, thus keeping test times reasonable.

It should also be noted that DeLausses specifically mentioned the inability to use this temperature dependent equation through Tg or with polymer/penetrant combinations which strongly react, and/or glassy polymers. In other words, caution should be used when utilizing this equation.

A simple explanation of the mass spectrometer unit used in 1988 is as follows: It could be programmed to look for the most populous ion fragments of the permeant. Multiple permeants could be tested simultaneously by avoiding significant degeneracies when selecting ion fragments for monitoring. The response could be monitored and stored for later analysis. The importance of using a partial pressure gradient more true to life was emphasized DeLausses (1988).

In a later study, DeLausses (1990) defined the necessary improvement of flavor/volatile testing in relation to inorganic substances. It is known that vegetable and tomato sauces can only tolerate 1-5 ppm oxygen loss on a wt/wt loss. There is a much smaller flavor movement allowed. Often a few parts per billion of flavor are enough to change the taste or smell of a food.

It was discovered in this project that by using the flow through hollow fiber probe, parts per billion sensitivity can be reached for monitoring volatile organics in air or nitrogen. This sensitivity increase allows the use of conventional electron impact for aroma/flavor permeation measurements. The electron impact mass spectrometer is known for its wider dynamic range, broader range of application to a variety of chemicals, and more commercial availability. It should be noted that this technique could be used to test below ambient temperatures, another advantage over previously used units DeLausses (1990) Zobel's (1982) earlier flame ionization technique was found to be accurate to $3 * 10^{-12}$ kg * m^{-2} * sec^{-1}.

Giacin, Hernandez, Baner

Mass Transfer, as it relates to packaging issues, has been studied at The School of Packaging, Michigan State University, for many years. Dr. Jack Giacin, and Dr. Ruben Hernandez have established one of the most well known labs for the advancement of this scientific quest.

Giacin (1981) developed a quasi-isostatic procedure utilizing a "snoopy" detector, which was based on decreased electrical resistance of the sensing element. The "snoopy" detector was deemed to have sensitivity similar to the popular flame ionization detector. The difference between the upper and lower cell sensors determined the transmission rate. Permeability was calculated from this result by incorporating the carrier gas flow rate, and permeation concentration at steady state. LDPE with isopropanol was tested under constant 23°C with a partial pressure gradient of 28.5 ppm wt/v. Giacin, at this time, reported permeability in $\frac{gm*mil}{m^2*24hr*mmHg}$.

Baner (1984) reviewed the concept of concentration dependencies for permeability and diffusion coefficients. (Baner's contribution to the development of the quasi and isostatic procedures is more thoroughly covered in the methodology's section.) Permeance was reported in $\frac{gm*structure}{m^2*day*100ppm}$ along with concentration in ppm wt/v.

At the same time, Hernandez (1984) studied the importance of Tg in permeance which was earlier described by Meares (1954). Both a quasi-isostatic (accumulating) and isostatic (continuous) methodology were developed to quantify the mass transfer characteristics of toluene, a volatile organic substance often chosen to model petroleum substances. The study of this parameter identifies the investigator as interested in the migration of harmful substances from the outside environment into the product, as opposed to the transfer of a flavor simulated by another chosen organic penetrant in relation to its mass transfer parameters for a specific polymer.

This particular study also defines a series of equations to mathematically model mass transfer parameters and their use. These equations are valid only when the system follows fickian type behavior, a phenomenon frequently not upheld in many organic penetrant/polymer systems.

Hernandez (1984) has also determined that between 23-60°C the behavior of the polymer/penetrant system changes from fickian to non-fickian for the toluene/PET system studied. The completion of this database can be a valuable tool useful in determining how the transition from fickian to non-fickian behavior occurs, whether gradual or dramatic.

Threshold is defined as a situation where no permeation has occurred at a given temperature and partial pressure gradient for a specific polymer/pentrant system after the period of 6 months. Hernandez (1984) determined that there exists a 76 ppm threshold for PET/toluene at 23°C

Two methods were utilized to determine the effects of water on the permeability of toluene vapor through a multi-layer film containing hydrophilic layers Liu, Hernandez, Giacin (1986). The testing of the mass transport characteristics of a multi-component mixture through a high barrier polymer proved too much for the automated sampling of the isostatic system. The testing of high barrier material greatly increased the time to reach steady state. This can be attributed to the difficulties associated with keeping a constant partial pressure gradient over an extended period of time, an attribute the quasi-isostatic system was not plagued with. Permeance was measured in $(\frac{(g * structure * 10^2)}{m^2 * day * 100 ppm})$. Permeance over permeability is the desired measurement for any multilayer structure due to the unpredictable nature and many times unknown thickness of the various layers of the structure. The polymer tested was a multi-layer structure consisting of PE/Nylon/EVAL/Nylon/PE. All tests were conducted at 23°C.

Method I consisted of pre-conditioning the samples at a specified humidity for the test until equilibrium was reached. At that point the samples were moved to the permeability testing apparatus and affixed. The organic penetrant, in this case, toluene, was flowed in a carrier gas, N2, along with a relative humidity level set to duplicate the pre-conditioning of the film.

Method II pre-conditioned the film over desiccant, effectively eliminating moisture. Afterwards, the sample was affixed to the permeation cell where it was flowed with the organic penetrant kept at desired relative humidity level. This test evaluates the effect of water vapor as a co-permeant to toluene, the organic volatile penetrant.

The permeability of multi-component penetrant systems (toluene/water) through multilayer structures is a complex phenomenon. The permeability of toluene(method I) through this multilayer structure as compared to toluene/water vapor(method II) through the same multilayer structure proved to be 3-4 times greater magnitude under a particular temperature, concentration, and relative humidity. The thermodynamics of the permeation of multi-component organic penetrants through polymer structures is not well understood at this time and will be the subject of future investigation Liu, Giacin, Hernandez (1987). (Hensley, Giacin, Hernandez (1991) undertook this investigation).

Another important discovery was made. There is a threshold relative humidity value, above which toluene permeation proceeds at a measurable rate, which signifies the permeation process as concentration dependent Liu, Giacin, Hernandez (1987.)

Studies of organic penetrant/polymer systems have overwhelmingly been focused on single penetrant/polymer systems. However, the simultaneous permeation of binary mixtures is a more accurate representation of real life situations where the product aroma profile can contain a number of volatile components Hensley, Hernandez, Giacin (1991). The permeation experiments were conducted at 23°C at vapor activities between .21 and .5 using an isostatic technique described earlier by Hernandez (1984). This isostatic procedure was modified from Baner's quasi-isostatic procedure. The permeability of ethyl acetate and limonene, both individually and as a binary mixture, were evaluated through polypropylene. The permeabilities for all experiments whether coincidental or not for binary mixtures were substantially higher than for single component tests, holding variables constant. At the lowest vapor activity, a 500% increase in the permeability of ethyl acetate vapor was reported as compared to the binary mixture of ethyl acetate vapor and limonene. Units of $(\frac{kg*m}{m^2*s*Pa})^{-6}$ were used for permeability.

During the same time frame as Hensley, Takashi (1991) studied the permeation of ethyl acetate vapor through deposited polyethylene terephalate film and composite structures. This marks the onset of a series of students studying the aroma barrier properties for surface modified high barrier films.

The Japanese market in 1988 made commercially available a silica deposited PP and PET film for retort pouches. This film has a number of desirable properties. It has a high barrier to O_2 and water, is non-temperature sensitive, transparent, retortable, and microwaveable. Takashi, Hernandez, Giacin (1991) Film samples of EVOH, MXD-6 (Nylon), and Silica deposited PET high barrier structures along with composite structure PET/PET/OPP, PET/SiOxPET/CPP and PET/EVOH/CPP retortable pouch structures were selected for this study.

A quasi-isostatic procedure was designed for this study as well. Probably based on Baner, Hernandez, Giacin (1986). Permeance units of $\frac{g}{m^2 * day * 100ppm}$ were calculated from the quasi-isostatic procedure. A table of SI units results was also presented as $\frac{g}{m^2 * \sec * Pa}$.

At 56% humidity, ambient temperature (22°C) and 190 ppm of ethyl acetate, both the EVOH and silica deposited PET film showed no permeation after 500 hours of continuous testing. However, raising the humidity to 86% while keeping the other parameters constant adversely affected the EVOH, causing high transmission rate while still not showing any measurable permeation of ethyl acetate through the silica deposited PET Takashi, Hernandez, Giacin (1991). Retort temperature (120,125,130°C) and holding time (20,40,60 minutes) effect on the permeation rate was studied. As expected, an increase in temperature and holding time is synonymous with an increase in permeation. However, this increase is not linear and can be attributed to the point at which the SiOx layer is cracked resulting in macrovoids. Takashi has studied and reported these adverse cracking effects using an optical microscope. It is therefore very important to understand the impact of macrovoids on the shelf life of a product. The presence of macrovoids (pinholes, cracking, poor seal integrity, etc) has to be well understood and under control. Otherwise, assuring good barrier properties (microvoids) for a particular product/package system is considered a waste of time.

Wangwiwatsilp, Hernandez, Giacin (1993) studied the mass transfer parameters of toluene and ethyl acetate surface sulfonated PP, PET, and nylon. Baner's now classic quasi-isostatic methodology was utilized for these experiments, along with keeping in tact SI units for permeability $\frac{kg*m}{m^2*\sec*Pa}$.

Corona discharge, gas plasma, and flaming are all processes which improve the adhesion properties, along with fluorination, sulfonation, polymer blends, coextrusion and coating that can be used to impart increased hydrogen barrier properties when applied to polymers. A well-written and extensive review of surface modifications is covered by Wangwiwatsilp's (1993) literature review.

The results of these studies have shown the effectiveness of the sulfonated layer in reducing the rates of transmission, and the effective diffusion coefficient values of ethyl acetate and toluene through the sulfonated

PP film. The surface sulfonated PET had little or no effect on the barrier properties of ethyl acetate, and the sulfonation process on nylon proved unsuccessful all together Wangwiwatsilp (1993).

Future studies of the effects of water were deemed useful for this venture along with addressing food contact issues. An important point was also made to watch other industries for breakthroughs and possible applications for packaging/polymer industry; the electronics industry, in particular, ought to be watched as it works extensively with deposition for microchips Wangwiwatsilp (1993).

Lin, Harte, Giacin (1995) developed an isostatic procedure to measure taints and off-flavors in foods and confectionery packaging. A good overview of threshold values for volatile compounds in foods and explanatory references for such information is included. Timely information on the threshold values for organic vapors in air and foods from the International Standards Organization (ISO) and the American Conference of Governmental Industrial Hygienist are additional sources of current information.

(Georgia) Gu, Hernandez, Giacin (1997) studied the aroma barrier properties of clay/polyimide nanocomposites. When nanocomposites are used as a packaging material, the composite enhanced strength and barrier properties make it possible to produce a package with a lower amount of material. Also, clay resources abound in nature and are cheap in cost. For a more thorough explanation of nanocomposites the reader is referred to this excellent literature review of the subject Gu, Hernandez, Giacin (1997).

Two companies have recently developed commercially available permeation testing mechanisms for testing organic vapors through packaging materials. Both are isostatic procedures and are based on the assumption that the permeation process follows Ficks's first and second law as well as Henry's law. Modern Control's, MAS 2000 comes commercially equipped for testing under dry conditions only, with a temperature range from room - 200°C. Mocon provides the consumer with two available options, the Aromatran 1A and 2. Aromatran 1A can test a single permeant at dry conditions or a specific relative humidity with a temperature range from 5-65°C and is fully automated. The Aromatran 2 is a semi-automatic version and has a built in cryotrap for the increased sensitivity necessary for testing higher barrier materials. Recently, the MAS 2000 system was modified with a device for trapping the permeated organic aromas/volatiles. In this modified configuration, the trapping system was designed to ensure that the sample cell chamber is continuously flushed with the carrier gas and the permeated vapor is conveyed to the trapping tube attached. The dynamic purge and trap/thermal desorption procedure showed an increase in sensitivity of three to four orders of magnitude over the continuous flow isostatic procedure Chang, Hernandez, Giacin (1996).

Permeability measurements were compared to a non clay/polyamide coated polymer and a 2.5% clay/polyamide polymer. At 3.2 kPa and 23°C and 0% relative humidity the non clay/ polyamide structure showed a permeability of .12 $\frac{kg*m}{m^2*\sec*Pa}$ compared with a permeability of 0.019 $\frac{kg*m}{m^2*\sec*Pa}$ for 2.5% (volume/volume)Clay/Polyamide, respectively. Organic concentration did NOT significantly affect permeability coefficient values for the respective polyamide films at 3.2 kPa and 1.7 kPa tested. Also, test temperature does NOT markedly affect the permeation of ethyl acetate through clay loaded polyimide films over the temperature range studied Gu, Hernandez, Giacin (1997).

A significant study was undertaken by Huang, Hernandez and Giacin to better understand the relationship and application of Baner's now classic quasi-isostatic procedure to the new commercial MAS 2000 isostatic system.

Penetrants of ethyl acetate, toluene, limonene, methyl ethyl keone and α-pinene at 24°C were evaluated through glassine, HDPE, Oriented Polypropylene, Saran coated OPP, and Acrylic coated OPP. Values between the two testing methodologies were considered within acceptable limits. However, the limitation of 44 hr run with the MAS 2000 excluded some permeation measurements for high barriers. The following organic penetrant/polymer combinations had no measurable permeation after 44 hours of continuous testing with the MAS 2000: Ethyl acetate through Saran coated OPP and Acrylic coated OPP, toluene through Saran coated OPP and Acrylic coated OPP, limonene through oriented PP, Saran coated OPP, acrylic coated OPP, methyl ethyl ketone through Saran coated OPP, acrylic coated OPP and α-pinene through HDPE, oriented PP Saran coated OPP and acrylic coated OPP Huang, Hernandez, Giacin (1996).

A mathematical consistency test for permeation measurements was developed by Hernandez and Gavara (1993). From the consistency analysis of the continuous flow permeability data, it can be concluded that the diffusion processes were fickian and the parameters of the experiment were under control Huang, Hernandez, Giacin (1996).

Over the temperature range studied, the relationship between permeance and temperature follow well the Arrhenius expression Huang, Hernandez, Giacin (1996).

Concentration levels greatly affected the permeance values but not the diffusion coefficients of flavor and aroma compounds in the barrier films Huang, Hernandez, Giacin (1996).

The barrier properties of the six polymer structures evaluated, in order of decreasing barrier performance, are as follows: metallized PET/OPP, Acrylic coated OPP, Saran coated OPP, OPP, HDPE and Glassine. The MAS 2000 has a low limit of detectability ranging between 0.4 mg/hr for toluene permeability to 0.2 mg/hr for the permeability of ethyl acetate for continuous running 44 hours Huang, Hernandez, Giacin (1996).

Absolute Pressure Method

There are two variations to the absolute pressure method: the manometric, high vacuum/time-lag technique, and volumetric, or constant volume/variable pressure, and constant pressure/variable volume. The first is the classical method defined by Barrer and Skirrow 1948. The general equations and setup of Barrer's manometric technique are as follows.

The whole diffusion cell is first thoroughly degassed at a fairly high temperature and the thermostat adjusted to the required temperature. By means of the Toepler pump (T), gas is introduced to the unsupported side of the membrane, the pressure being indicated by the barometer (B). Throughout the experiment the pressure is kept constant by manipulation of the Toepler pump. The gas is permeated through the membrane into a vacuum chamber of known volume and the increase in pressure with tie is followed by a McLeod gage, and a pressure vs. time plot is made. The experiment is continued until the slope becomes constant when the steady state of flow has been established. From the steady state the permeability constant P may be calculated Barrer (1948):

$$P = \frac{273}{T} * \frac{V}{p_1} * \frac{l}{a} * \frac{1}{76}$$

The majority of mass transport testing initially was done with inorganic gases, rubbers, or ethylene. The famous "Dow cell" was also based on Barrer's method and was successfully used to test O_2 and water permeabilities for many years (ASTM D1434). The cell however was not capable of measuring organic vapors without modifications. Barrer's classical technique was modified to enable it to measure organic substances as well. The absolute pressure method is limited also because it does not determine the permeability of gases at different relative humidities. Since an absolute pressure differential across the membrane is used, it is plagued with leakage problems, and cannot be used with pressure sensitive or easily deformable films Talwar (1974). A more fundamental problem with the method also exists because the detection system cannot differentiate between co-permeating vapors. The method is therefore restricted to measuring the permeation of pure vapor only. The effects of co-permeants, in particular, water vapor, cannot be evaluated Baner (1987).

Gravimetric Method

Variations of the gravimetric technique have been utilized by many researchers to study the mass transport characteristics of organic vapors through various polymer structures. The nature of the gravimetric procedure makes it necessary to thoroughly understand the polymer/permeant mass transport characteristics before selecting this method for determining the permeability of organic compounds through a polymer. The gravimetric procedure, unlike the absolute pressure method and quasi-isostatic/isostatic methods, indirectly determines the permeability coefficient. This makes it necessary for the mass transport system to follow fickian behavior, thus enabling $P = D * S$, where P = the permeability coefficient, D = the diffusion coefficient, and S = the solubility coefficient. (An explanation of fickian behavior is out of the scope of this project and the reader is referred to Hernandez (1986) for a thorough explanation of this subject.)

Until now the only way to determine if the polymer/penetrant combination has followed fickian type behavior was to compare the results of Crank's (1975) sorption equation with calculated results. However, the development of a database for mass transfer, the main objective of this research, provides an additional tool to determine if the polymer/penetrant combination is fickian in behavior.

Currently, the preferred apparatus for conducting sorption experiments is an electrobalance because this system continually records the weight gain or loss of the sample as a function of time. In addition, this system is often interfaced with a vapor generator system, allowing sorption measurements to be conducted over a range of penetrant vapor concentration levels (Barr 1997).

General state of the art gravimetric electrobalance technique is described as follows by Barr 1997: Using the gravimetric electrobalance technique, the solubility coefficient value can be obtained by first suspending a film sample weighing approximately 30mg in the electrobalance hangdown tube, where it surrounds the polymer sample. The weight change of the sample is continuously recorded as a function of time, using either a trip chart recorder or computer. Once steady state level of sorption has been obtained, the solubility coefficient value can be determined from the following expression:

$$S = \frac{M_\infty}{w \cdot b}$$

Where S is the solubility coefficient value, expressed as mass of vapor sorbed at equilibrium per mass of polymer per driving force. M_∞ represents the total mass of vapor sorbed by the polymer at equilibrium at a given temperature, w is the initial weight of the polymer test sample, and b is the value of the permeant driving force.

Experimental sorption data is usually presented graphically as a plot of M_t / M_∞ as a function of the square root of time, with the initial portion of the curve being linear (Meares, 1965). The diffusion equation appropriate for the sorption of penetrant by a polymer sample in film or sheet form was described by Crank (1975) as:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi_2}[\exp(\frac{-D \cdot \pi_2 \cdot t}{\ell_2}) + \frac{1}{9}\exp(\frac{-9D \cdot \pi_2 \cdot t}{\ell_2})]$$

Where M_t and M_∞ are the amount of penetrant sorbed by the polymer film sample at time t and the equilibrium sorption after infinite time, respectively; t is the time required to reach M_t, and ℓ represents the film thickness. If the experimental and calculated curves are in good agreement, the diffusion process is usually considered Fickian, and an accurate estimation of D can be made (Nielson and Giacin 1994). This is achieved by setting M_t / M_∞ = 0.5 and calculating the sorption diffusion coefficient as follows:

$$D_s = \frac{0.049\ell^2}{t_{0.5}}$$

Where D_s is sorption diffusion coefficient, and $t_{0.5}$ is the time required to attain half of the sorption level at steady state. Once the solubility and diffusion coefficient values have been determined, the permeability coefficient value, P, can be obtained from Equation

$$P = D \times S$$

Where P is the permeability coefficient value, and D is the diffusion coefficient value, and S represents the solubility coefficient value.

If the reader is interested in solubility coefficients, Fayoux (1996) who has done an extensive literature review on the subject is recommended. Another good explanation of the applicability of the gravimetric procedure is given by Mohney, Hernandez, and al. (1988).

Database Overview

A database can be defined as an extensive list of information systematically categorized for easy and fast sorting. In today's fast paced, information intensive society, databases are the engines which drive many of these new software platforms. One prominent example is the Yahoo search engine, which is backed by a database.

Microsoft Access 97 was utilized to program the Permeability of Organic Compounds Through Various Packaging Polymers Database. Unlike traditional programming methods, Microsoft Access 97 uses object-oriented programming. For this reason, it is not possible to print out a list of code for the entire program. The use of Access 97 can be understood and applied at various levels. The capabilities of Microsoft Access 97 are further extended by the use of macros, visual basic for applications programming (VBA), and standard query language (SQL).

A working knowledge of the following topics is necessary in order to understand the mechanics of the database developed for this thesis.

1) Forms
2) Tables
3) Modules
4) Macros

5) Visual Basic for Applications

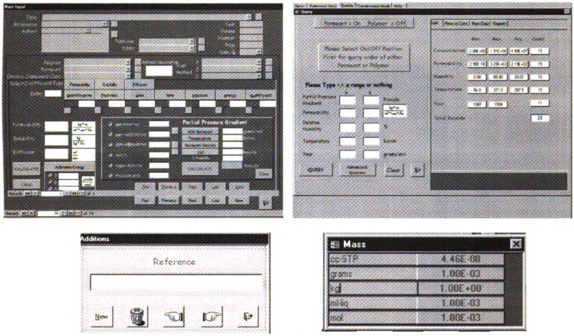
6) Standard Query Language

7) Security

It should be taken into consideration that a successful database design relies greatly on the initial planning period where the problem must be clearly defined.

Three Database Form Types Used

Forms are the visual storefront of the database. A well-designed form should be both functional and visually appealing. In order to execute functions, forms are linked with tables and sometimes queries. There are three basic form types used in this thesis. The main input form Figure 1, pop-up forms (used for both calculations and addition of new information), and the main and advanced query form.



cc-STP	4.46E-08
grams	1.00E-03
kg	1.00E+00
ml-liq	1.00E-03
mol	1.00E-03

Figure 1. 1) Main Input Form, 2) Query Form and 3) Pop-Up Addition and Calculation Form.

Database Forms

When designing a new form there are two basic options: Manual "design view" or various automated "form wizards". Figure 2. The database developed for this thesis was completely fabricated in "design view" due to the specific needs of this database.

After selecting "design view", the user arrives at the screen in Figure 3. As can be seen, there are many options to both configure and design a new or existing form. Figure 4 depicts a possible form in design view.

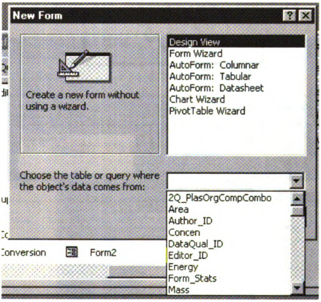
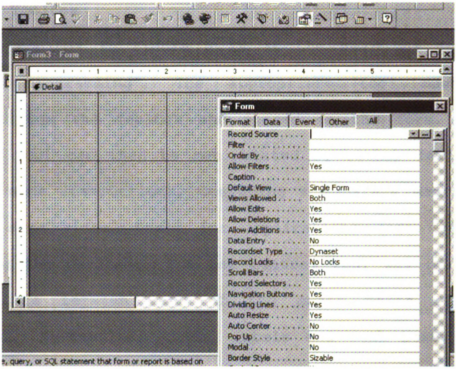


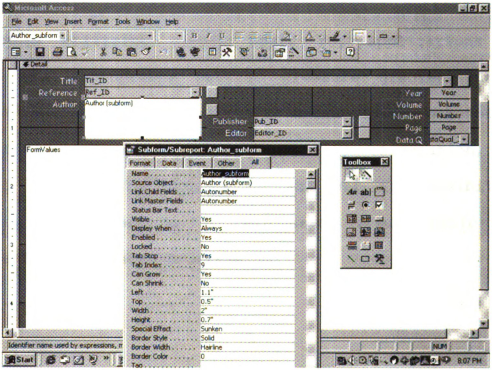
Figure 2. New Form, "design view" and "wizards"



Record Source	
Filter	
Order By	
Allow Filters	Yes
Caption	
Default View	Single Form
Views Allowed	Both
Allow Edits	Yes
Allow Deletions	Yes
Allow Additions	Yes
Data Entry	No
Recordset Type	Dynaset
Record Locks	No Locks
Scroll Bars	Both
Record Selectors	Yes
Navigation Buttons	Yes
Dividing Lines	Yes
Auto Resize	Yes
Auto Center	No
Pop Up	No
Modal	No
Border Style	Sizable

e, query, or SQL statement that form or report is based on

Figure 3. "Design view" new form



Name	Author_subform
Source Object	Author (subform)
Link Child Fields	Autonumber
Link Master Fields	Autonumber
Status Bar Text	
Visible	Yes
Display When	Always
Enabled	Yes
Locked	No
Tab Stop	Yes
Tab Index	9
Can Grow	Yes
Can Shrink	No
Left	1.1"
Top	0.5"
Width	2"
Height	0.7"
Special Effect	Sunken
Border Style	Solid
Border Width	Hairline
Border Color	0
Tag	

Identifier name used by expressions, m

Figure 4. "Design view" modification

Database Toolbox

The toolbox in Figure 5 is at the heart of "object oriented programming". The appropriate tool must be selected from the toolbox and placed on the form. The selected tool can then be manipulated by either following the pre made instructions, designing a separate macro, or writing some visual basic for applications code. While designing the database, the tab control tool was utilized to navigate between each of the major parts of the database. Rectangles, lines, labels and text boxes were all employed numerously to define forms. Combo boxes were also implemented in the database design to select items from more than one drop down list. Option buttons were programmed utilizing visual basic for applications to select the appropriate partial pressure gradient unit. Command buttons were frequently actuated to accomplish everything from a complex permeability calculation, to closing a form, to turning on and off the visibility property of various cells, both using visual basic for applications and macro programming.

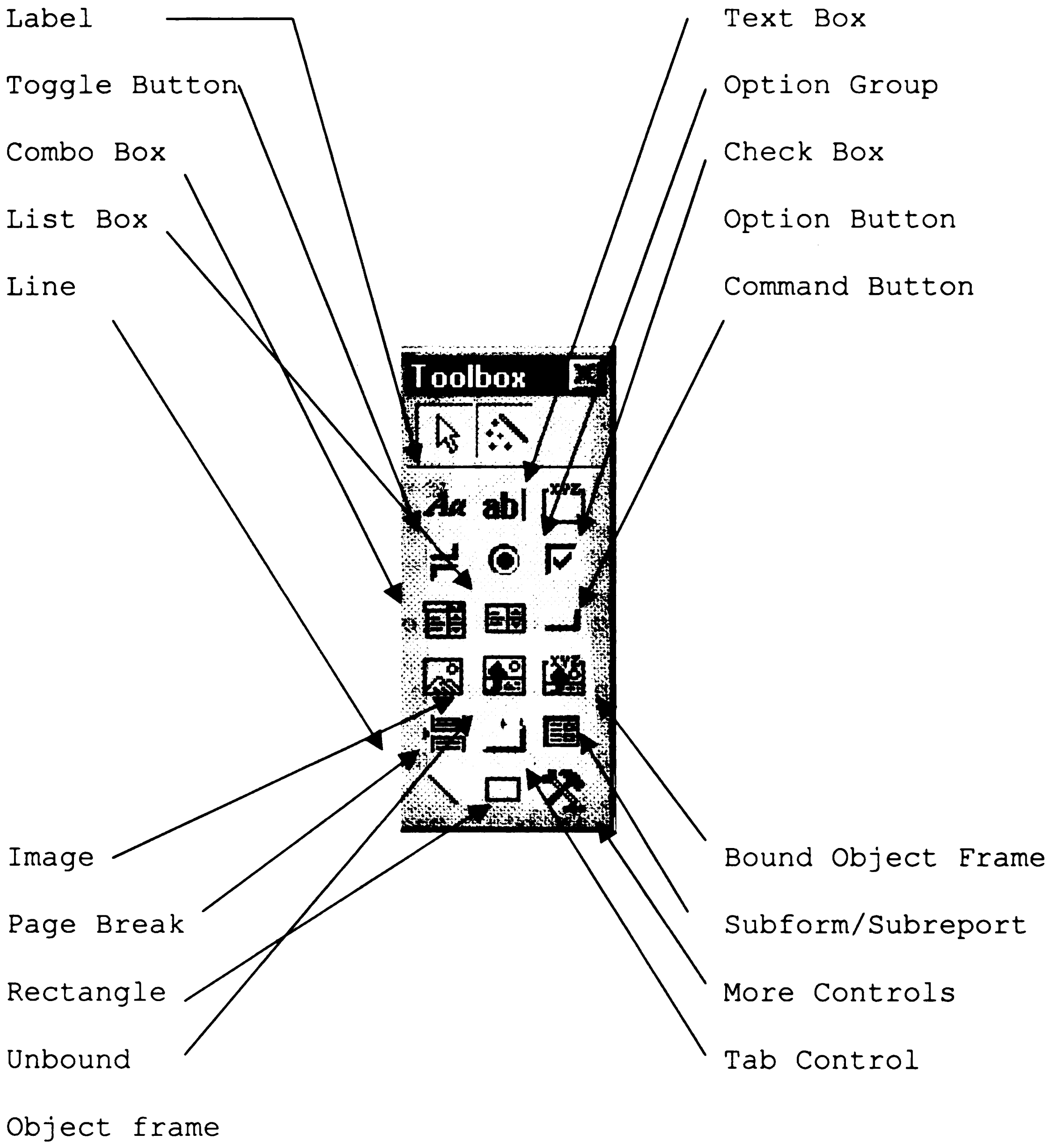
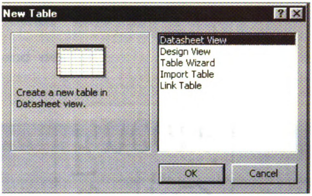


Figure 5. Toolbox

Database Tables

A database table can be imagined as lists of information separated into appropriate categories. Interestingly enough, the database table is never seen by the user of a well-designed database, but is affixed to a more elegantly designed form. The planning stage requires the database constructor to define clearly the "fields", or categories, which the data should be divided into. These fields will determine how information can be entered into the database, later sorted and retrieved via a query. In order to speed up the query of the database and to minimize errors, numerical identification fields are assigned to each of the text-based fields. This practice becomes increasingly important as the database acquires more information.

How does the design of a table work? As with a new form design, the table "wizard" functions have not been used in the design of this database. Tables can be both imported from other databases and linked. The permeability database designed for this database uses the linking feature. There were, therefore, two databases developed. One with all tables, and the other with the rest of the information. This system allows different database fronts to be used later, and offers the optimum framework for expansion.

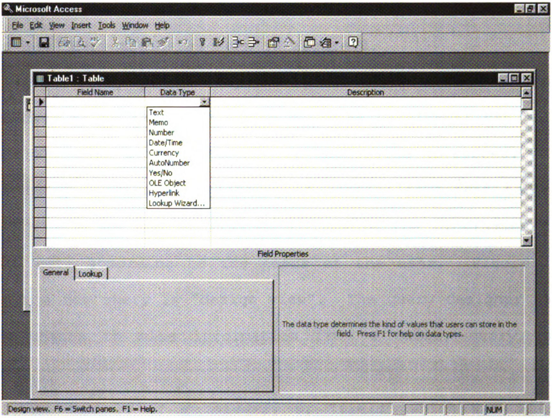


Create a new table in Datasheet view.

Figure 6. New Table

The two different table types created in this database include the main table and individual function, or calculation tables. The main table is the place where all the "quereable information" is stored after conversion in the main input page. Permeability, solubility, diffusion coefficients had to be converted into Standard International Units in order to be available for later purposes. This was one of the biggest challenges faced designing this database. The second types of tables used were created for use as conversion calculators for the mass transfer calculations.

Figure 7 is the screen which arrives after selecting design view. For the design of this database only text and number data types were used. As can be seen from Figure 7, there are many other ways and possible applications for table functions and design.



The data type determines the kind of values that users can store in the field. Press F1 for help on data types.

Design view. F6 = Switch panes. F1 = Help.

Figure 7. Table design view

Database Queries

Queries are used to sort data from a table or another query according to the question raised. The query can ask information from multiple tables and combine the results into one. Queries are also non-visible to the user and are attached to a more user accessible form. As with the design of new forms and tables, the "design view" was used for new query design as seen in Figure 8.

The query proves why the preliminary design of the database is so important. The database programmer can only sort the data by the "fields" or categories developed. In the query process, the linking of various pertinent tables and/or queries can be created to enable the programmer to sort data according to the needs of the user. Figure 10 shows a new query in "design view". The query designer has the chance to mine information from a table, query, or both.

An example of a category or "field" which was added into this database to expand the searching capabilities is the penetrant/permeant compound class. This addition enables the user to search not only a specific compound but also a complete compound class. If this had not have been included during the initial design process, adding it later would be comparable to redesigning a car chassis in the late stages of its manufacturing. Not only would it be necessary to update each record, but the tables, forms and queries would all have to be modified.

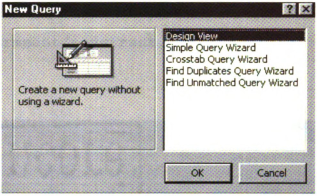


Figure 8. New Query

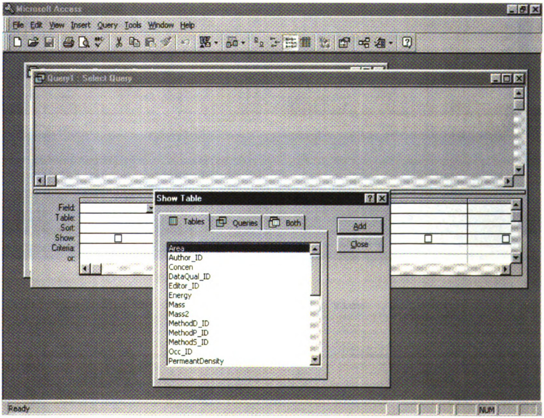
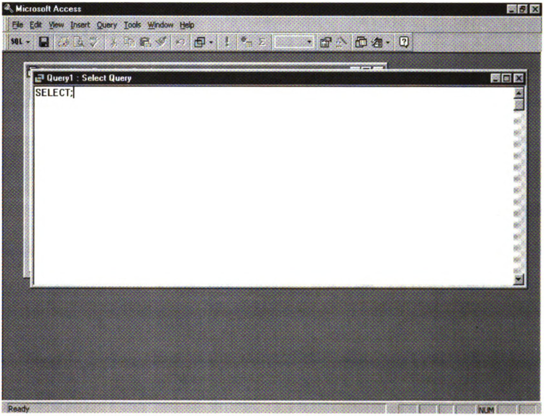


Figure 9. New Query Design View

Standard Query Language (SQL) can be applied to assist the user for more complex sorting requirements. Figure 10 depicts the SQL "query view". The use SQL programming was needed to enable the user to start the query with either a polymer or a permeant/penetrant.



SELECT;

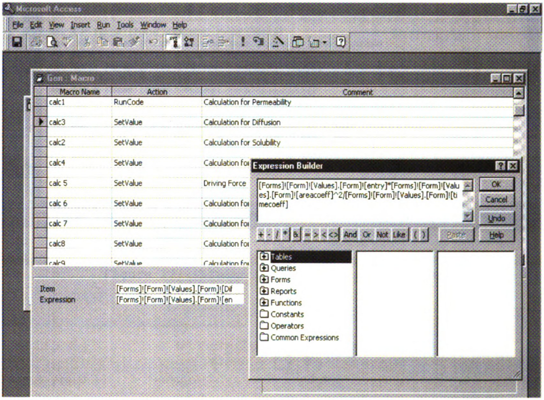
Figure 10. SQL Query view

Database Macros, Visual Basic for Applications, and Modules

A database macro is programmed to perform a specific function. The use of macros is one of the features which is possible with object oriented programming. While macros are not as complicated to program as Visual Basic for Applications, they are slower. Both macros and Visual Basic for Applications were used to drive the functions of this database.

When designing a new macro, the first step is to choose which action will be performed. This having been determined, the expression builder is used to combine various cell values into a calculation as shown in Figure 11. The solubility, diffusion and activation energy were calculated in this manner. It is interesting to note that the permeability constant could not be calculated with a macro. This particular calculation exceeded the limits of the macro. In this case a module was designed using VBA code as viewed in Figure 12. However, a macro was still used to run the module.

It would be possible to program the code directly into the calculation button for permeability, solubility, diffusion, activation energy, etc. by using either macros or Visual Basic for Applications code. One advantage of programming in this manner is that it offers the ability to use these macros and modules for other applications or calculations within the database. Another advantage is that it provides an improved organization of the calculations. This becomes increasingly important as the complexity of the database evolves.



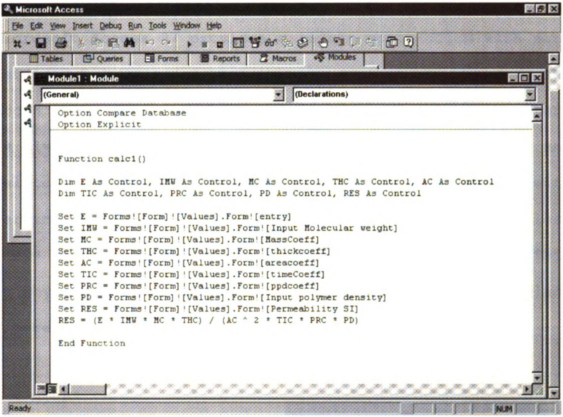
Macro Name	Action	Comment
calc1	RunCode	Calculation for Permeability
calc3	SetValue	Calculation for Diffusion
calc2	SetValue	Calculation for Solubility
calc4	SetValue	Calculation fo
calc 5	SetValue	Driving Force
calc 6	SetValue	Calculation fo
calc 7	SetValue	Calculation fo
calc8	SetValue	Calculation fo
calc9	SetValue	Calculation fo

Item [Forms]![Form]![Values].[Form]![Dif

Expression [Forms]![Form]![Values].[Form]![en

```
[Forms]![Form]![Values].[Form]![entry]*[Forms]![Form]![Valu
es].[Form]![areacoeff]^2/[Forms]![Form]![Values].[Form]![ti
mecoeff]
```

Figure 11. Macro builder



```
Option Compare Database
Option Explicit


Function calc1()

Dim E As Control, IMW As Control, MC As Control, THC As Control, AC As Control
Dim TIC As Control, PRC As Control, PD As Control, RES As Control

Set E = Forms![Form]![Values].Form![entry]
Set IMW = Forms![Form]![Values].Form![Input Molecular weight]
Set MC = Forms![Form]![Values].Form![MassCoeff]
Set THC = Forms![Form]![Values].Form![thickcoeff]
Set AC = Forms![Form]![Values].Form![areacoeff]
Set TIC = Forms![Form]![Values].Form![timeCoeff]
Set PRC = Forms![Form]![Values].Form![ppdcoeff]
Set PD = Forms![Form]![Values].Form![Input polymer density]
Set RES = Forms![Form]![Values].Form![Permeability SI]
RES = (E * IMW * MC * THC) / (AC ^ 2 * TIC * PRC * PD)

End Function
```

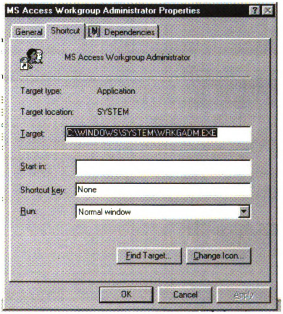
Figure 12. Permeability Calculation Module

Database Security

Database security is a very important issue. Microsoft Access 97 provides a secure application with many levels of permission possible. Figure 13 pictures the Login menu before entering into a secured database. There is always one administrator with the possibility to add and delete an unlimited number of users and user groups with varying levels of permissions. If the password is lost there is NO possibility for retrieving the database. This is why the wrkgadm information must be kept in a safe place Figure 14.

Name: JonAdmin
Password:

Figure 13. Security Login



Target type: Application
Target location: SYSTEM
Target: C:\WINDOWS\SYSTEM\WRKGADM.EXE
Start in:
Shortcut key: None
Run: Normal window

Figure 14. MS Access Workgroup Admin.

Database Layout

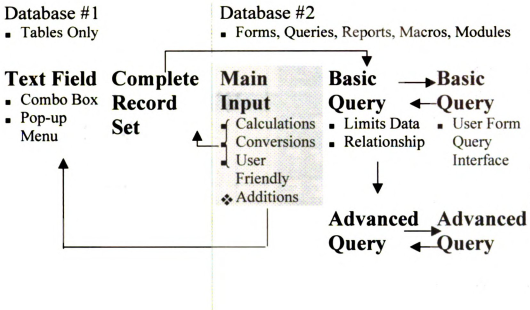


Figure 15. Schematic of Database Mechanics #1

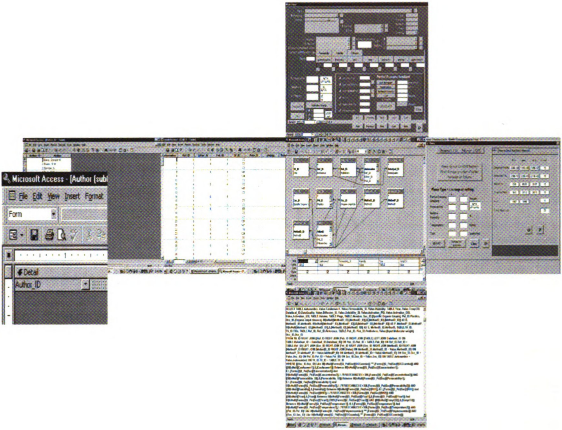


Figure 16. Schematic of Database #2

Overview Input Reference

One page input was developed to improve the reliability of inputting all information from a given reference. This input page is meant to be used only by administration and can be limited by security options to users. Multiple pop up menus and extensive programming and planning have been used to make this page as straight forward and error free as possible.

The page can be divided into two distinct areas: the literature reference section and the permeant/penetrant, mass transfer calculation section. Since there are more calculations than literature references the calculation section was designed as a subform of the literature reference. This makes it possible for more than one entry per literature reference. It also eliminates needing to enter the literature reference each time new polymer/penetrant combinations are entered into the page. Visual Basic for Applications programming has been used to improve the speed and accuracy of the permeability, solubility, diffusion, activation energy and partial pressure gradient conversion calculations. It makes them more straightforward. Because the selection of the desired calculation is possible, only the appropriate fields to be filled in are left "active", greatly reducing errors and speeding up the tedious input process.

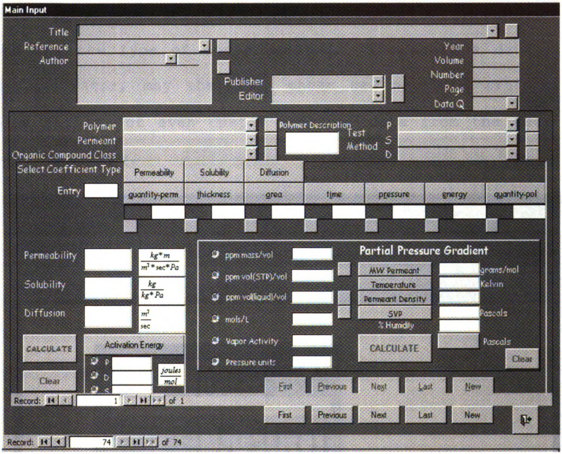


Figure 17. 1 page Input Reference

Literature Reference

The literature reference as shown in Figure 18 is a section of the 1 page input reference page. Its leaves complete flexibility with additional buttons available to add any new type of entry desired. The user, a database administrator, may therefore enter new magazine articles, book titles, or even custom internal data from the user's own laboratory.

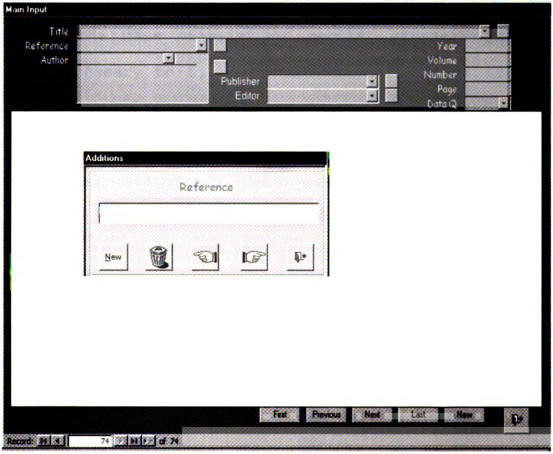


Figure 18. Literature Reference Section of the Reference Input

Input Reference Mass Transfer

Mass Transfer is a function of the partial pressure gradient. The user is expected to enter the polymer, permeant/penetrant desired, organic compound class, mass transfer test method, and any additional information in the polymer description field as can be seen in Figure 21. The user then selects one of the mass transfer functions along with one partial pressure gradient function as seen in Table 1. The software has been designed to leave only "active" the mass transfer or partial pressure gradient fields necessary to fill in for each calculation desired. Standard International Units (SI) are calculated for each function. Both the "active" fields and SI conversions were accomplished using Visual Basic for Applications programming.

Table 1. Input reference mass transfer

Mass Transfer	*Partial Pressure Gradient*
Permeability	ppm mass/vol
Solubility	ppm vol(STP)/vol
Diffusion	ppm vol(liquid)/vol
Activation Engergy	mol/L
	Vapor Activity
	Pressure Units

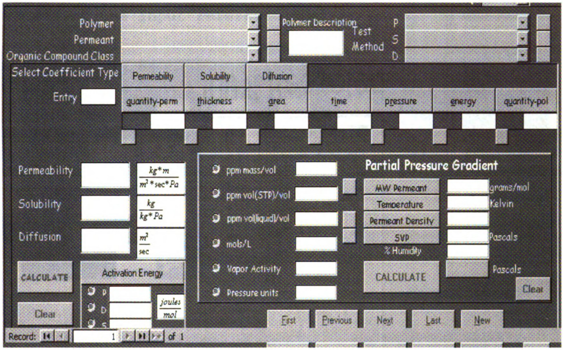


Figure 19. Mass Transfer Input Reference

Mass Transfer Calculations

Figure 20 isolates the mass transfer calculation section of the input reference section of the database.

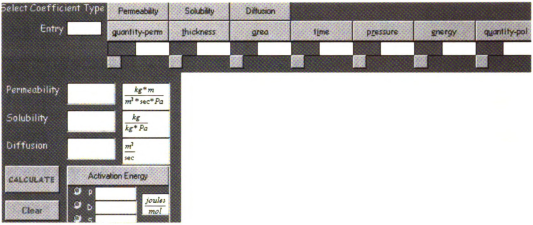


Figure 20. Mass Transfer Section of the input reference

Visual Basic for Applications programming was used to manipulate Microsoft Access 97. Figures 21, 22 and 23 depict how the calculations of permeability, solubility and diffusion are setup. Table 2 lists the Visual Basic for Applications code used to calculate each of the mass transfer functions. The code was written using case statements. As an example, case 1 was written as the permeability calculation. Table 3 lists the Visual Basic for Applications code used to "activate", "freeze", hide and show each of the functions seen in Figures 21, 22 and 23.

Table 2. VBA mass transfer calculation code

```
Private Sub Button_masstranscalc_Click()
    Select Case Frame_MassTransfer.value
    Case 1
        [Permeability SI].value = entry.value *
((MassCoeff.value * PermMW.value * thickcoeff.value) /
(areacoeff.value * timeCoeff.value * ppdcoeff.value *
PolyDensity.value))
    Case 2
        [Solubility SI].value = entry.value *
((MassCoeff.value * PermMW.value * PermDensity.value) /
(mass2coeff.value * PolyDensity.value * ppdcoeff.value))
    Case 3
        [Diffusion SI].value = entry.value *
(areacoeff.value / timeCoeff.value)
    Case 4
 [Forms]![Form]![Values].[Form]![Frame_Activation].SetFocus
    Case Else
    Dim strMsg As String, strInput As String
    ' Initialize string.
    strMsg = "Please select a calculation type before"
 End Select
End Sub
```

Table 3. VBA written for switching active cells on/off

```
Private Sub Frame_MassTransfer_AfterUpdate()

    Select Case Frame_MassTransfer.value

    Case 1

        [Permeability SI].Enabled = True

        Toggle_Permeability.Enabled = True

        [Solubility SI].Enabled = False

        Toggle_Solubility.Enabled = True

        [Diffusion SI].Enabled = False

        Toggle_Diffusion.Enabled = True

        Toggle_Activation.Enabled = True

        Activation_PSI.Enabled = False

        Activation_DSI.Enabled = False

        Activation_SSI.Enabled = False

        Button_Mass.Enabled = True

        Mass.Enabled = True

        MassCoeff.Enabled = True

        Button_Thick.Enabled = True

        thick.Enabled = True

        thickcoeff.Enabled = True

        Button_Area.Enabled = True

        Area.Enabled = True

        areacoeff.Enabled = True
```

```
   Button_Time.Enabled = True

   Time.Enabled = True

   timeCoeff.Enabled = True

   Button_Pressure.Enabled = True

   PPD.Enabled = True

   ppdcoeff.Enabled = True

   Button_Energy.Enabled = False

   energy.Enabled = False

   EnergyCoeff.Enabled = False

   Button_MassPol.Enabled = False

   mass2.Enabled = False

   mass2coeff.Enabled = False

   Option_P.Enabled = False

   Option_D.Enabled = False

   Option_S.Enabled = False

   Button_masstranscalc.Enabled = True

   OLE_Perm.Enabled = True

   OLE_Sol.Enabled = False

   OLE_Diff.Enabled = False

   OLE_Act.Enabled = False

    [Forms]![Form]![Values].[Form]![entry].SetFocus

Case 2

   [Permeability SI].Enabled = False

   Toggle_Permeability.Enabled = True
```

```
[Solubility SI].Enabled = True

Toggle_Solubility.Enabled = True

[Diffusion SI].Enabled = False

Toggle_Diffusion.Enabled = True

Toggle_Activation.Enabled = True

Activation_PSI.Enabled = False

Activation_DSI.Enabled = False

Activation_SSI.Enabled = False

Button_Mass.Enabled = True

Mass.Enabled = True

MassCoeff.Enabled = True

Button_Thick.Enabled = False

thick.Enabled = False

thickcoeff.Enabled = False

Button_Area.Enabled = False

Area.Enabled = False

areacoeff.Enabled = False

Button_Time.Enabled = False

Time.Enabled = False

timeCoeff.Enabled = False

Button_Pressure.Enabled = True

PPD.Enabled = True

ppdcoeff.Enabled = True

Button_Energy.Enabled = False
```

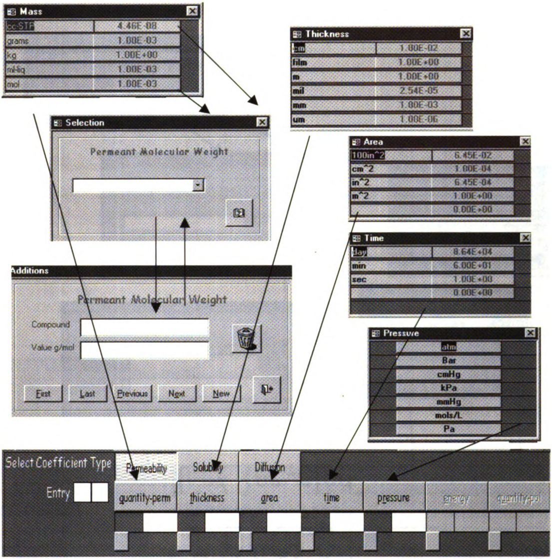
```
   energy.Enabled = False
   EnergyCoeff.Enabled = False
   Button_MassPol.Enabled = True
   mass2.Enabled = True
   mass2coeff.Enabled = True
   Option_P.Enabled = False
   Option_D.Enabled = False
   Option_S.Enabled = False
   Button_masstranscalc.Enabled = True
   OLE_Perm.Enabled = False
   OLE_Sol.Enabled = True
   OLE_Diff.Enabled = False
   OLE_Act.Enabled = False
    [Forms]![Form]![Values].[Form]![entry].SetFocus
Case 3
   [Permeability SI].Enabled = False
   Toggle_Permeability.Enabled = True
   [Solubility SI].Enabled = False
   Toggle_Solubility.Enabled = True
   [Diffusion SI].Enabled = True
   Toggle_Diffusion.Enabled = True
   Toggle_Activation.Enabled = True
   Activation_PSI.Enabled = False
   Activation_DSI.Enabled = False
```

```
Activation_SSI.Enabled = False
Button_Mass.Enabled = False
Mass.Enabled = False
MassCoeff.Enabled = False
Button_Thick.Enabled = False
thick.Enabled = False
thickcoeff.Enabled = False
Button_Area.Enabled = True
Area.Enabled = True
areacoeff.Enabled = True
Button_Time.Enabled = True
Time.Enabled = True
timeCoeff.Enabled = True
Button_Pressure.Enabled = False
PPD.Enabled = False
ppdcoeff.Enabled = False
Button_Energy.Enabled = False
energy.Enabled = False
EnergyCoeff.Enabled = False
Button_MassPol.Enabled = False
mass2.Enabled = False
mass2coeff.Enabled = False
Option_P.Enabled = False
Option_D.Enabled = False
```

```
    Option_S.Enabled = False
    Button_masstranscalc.Enabled = True
    OLE_Perm.Enabled = False
    OLE_Sol.Enabled = False
    OLE_Diff.Enabled = True
    OLE_Act.Enabled = False
     [Forms]![Form]![Values].[Form]![entry].SetFocus
Case 4
    [Permeability SI].Enabled = False
    Toggle_Permeability.Enabled = True
    [Solubility SI].Enabled = False
    Toggle_Solubility.Enabled = True
    [Diffusion SI].Enabled = False
    Toggle_Diffusion.Enabled = True
    Toggle_Activation.Enabled = True
    Activation_PSI.Enabled = True
    Activation_DSI.Enabled = True
    Activation_SSI.Enabled = True
    Button_Mass.Enabled = False
    Mass.Enabled = False
    MassCoeff.Enabled = False
    Button_Thick.Enabled = False
    thick.Enabled = False
    thickcoeff.Enabled = False
```

```
Button_Area.Enabled = False

Area.Enabled = False

areacoeff.Enabled = False

Button_Time.Enabled = False

Time.Enabled = False

timeCoeff.Enabled = False

Button_Pressure.Enabled = False

PPD.Enabled = False

ppdcoeff.Enabled = False

Button_Energy.Enabled = True

energy.Enabled = True

EnergyCoeff.Enabled = True

Button_MassPol.Enabled = True

mass2.Enabled = True

mass2coeff.Enabled = True

Option_P.Enabled = True

Option_D.Enabled = True

Option_S.Enabled = True

Button_masstranscalc.Enabled = False

OLE_Perm.Enabled = False

OLE_Sol.Enabled = False

OLE_Diff.Enabled = False

OLE_Act.Enabled = True

 [Forms]![Form]![Values].[Form]![entry].SetFocus
```

```
    Case 5
        Frame_MassTransfer = Null
        Frame_Activation = Null
        PolyMW.value = 1
        PermMW.value = 1
        PolyDensity.value = 1
        PermDensity.value = 1
        MsgBox   "Please   select   Permeability,   Diffusion,
Solubility or Activation button"
[Forms]![Form]![Values].[Form]![Frame_MassTransfer].SetFocu
s
   End Select
    Forms!Form!Values.Form!PermMW.Visible = False
    Forms!Form!Values.Form!Label_PermeantMW.Visible = False
    Forms!Form!Values.Form!PermDensity.Visible = False
    Forms!Form!Values.Form!Label_PermeantDensity.Visible   =
False
    Forms!Form!Values.Form!PolyDensity.Visible = False
    Forms!Form!Values.Form!Label_PolymerDensity.Visible    =
False
End Sub
```



Mass

cc-STP	4.46E-08
grams	1.00E-03
kg	1.00E+00
ml-liq	1.00E-03
mol	1.00E-03

Thickness

cm	1.00E-02
film	1.00E+00
m	1.00E+00
mil	2.54E-05
mm	1.00E-03
um	1.00E-06

Area

100in^2	6.45E-02
cm^2	1.00E-04
in^2	6.45E-04
m^2	1.00E+00
	0.00E+00

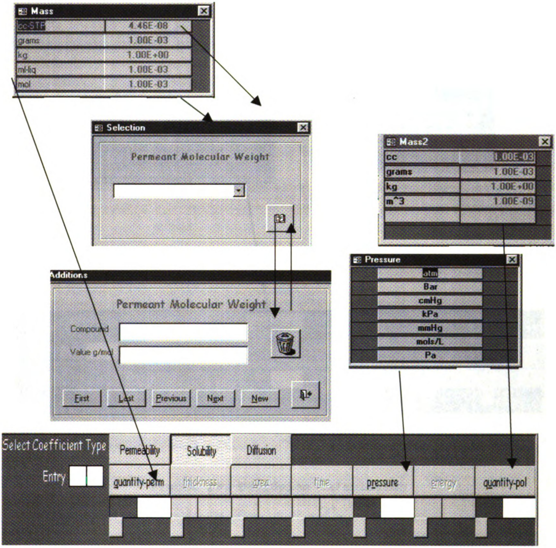
Time

day	8.64E+04
min	6.00E+01
sec	1.00E+00
	0.00E+00

Pressure

atm
Bar
cmHg
kPa
mmHg
mols/L
Pa

Figure 21. Permeability Calculation

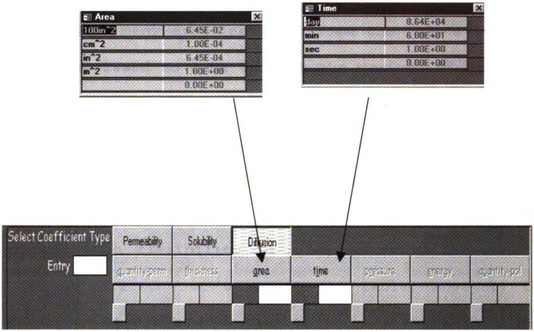


cc-STP	4.46E-08
grams	1.00E-03
kg	1.00E+00
ml-liq	1.00E-03
mol	1.00E-03

cc	1.00E-03
grams	1.00E-03
kg	1.00E+00
m^3	1.00E-09

- atm
- Bar
- cmHg
- kPa
- mmHg
- mols/L
- Pa

Figure 22. Solubility Calculation



Area

100in^2	6.45E-02
cm^2	1.00E-04
in^2	6.45E-04
m^2	1.00E+00
	0.00E+00

Time

day	8.64E+04
min	6.00E+01
sec	1.00E+00
	0.00E+00

Figure 23. Diffusion Calculation

It is important to understand that these three calculations for Permeability, Solubility, and Diffusion have been reported in many measurements; and, therefore, up until now, have been utterly impossible to effectively compare. While many articles taken from the 1950's to today have been reviewed to come up with the maximum of different possibilities for all variables in each equation, there may be new ones, or some which are missing. Additionally, new measurement techniques are being designed and implemented each day. It is for this reason that the database was programmed with flexibility in mind, enabling the user to add new calculations or units to the table. However, the final objective has always been to normalize the data into standard international units. Furthermore, every effort was made to automate the tedious process of data entry by programming a user-friendly interface whereby human data entry errors should be minimalized.

Input Reference Partial Pressure Gradient

The partial pressure gradient was designed using a substantial amount of visual basic for applications programming to keep the user from making errors and to speed up the calculation process. Table 4 lists the code used to "activate", "freeze", hide and show each of the functions seen in Figures 25-30. Table 5 is the partial pressure gradient calculation code.

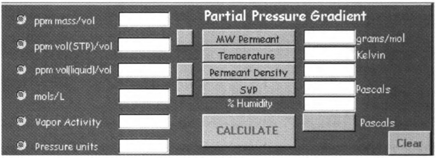


Figure 24. Partial Pressure Gradient

Table 4. VBA Partial Pressure Gradient code

```
Private Sub Frame_Gradient_AfterUpdate()
    Select Case Frame_Gradient.value
    Case 1
       ppm2.Enabled = True
       ppm1.Enabled = False
       ppm3.Enabled = False
       molsvol.Enabled = False
```

```
    VA1.Enabled = False

    VP1.Enabled = False

    [button_A_Saturation_VP].Enabled = True

    Mol1.Enabled = True

    [button_MWpermeant].Enabled = True

    [button_additionMWpermeant].Enabled = True

    TempCSI.Enabled = True

    [button_tempconvert].Enabled = True

    Pden1.Enabled = False

    [button_permeantdensity].Enabled = False

    [button_additionpermeantdensity].Enabled = False

    SVP1.Enabled = False

    [button_SVPconversion].Enabled = False

    [Calc_PPG].Enabled = True

    [Forms]![Form]![Values].[Form]![ppm2].SetFocus

Case 2

    ppm2.Enabled = False

    ppm1.Enabled = True

    ppm3.Enabled = False

    molsvol.Enabled = False

    VA1.Enabled = False

    VP1.Enabled = False

    [button_A_Saturation_VP].Enabled = False

    Mol1.Enabled = False
```

```
    [button_MWpermeant].Enabled = False
    [button_additionMWpermeant].Enabled = False
    TempCSI.Enabled = True
    [button_tempconvert].Enabled = True
    Pden1.Enabled = False
    [button_permeantdensity].Enabled = False
    [button_additionpermeantdensity].Enabled = False
    SVP1.Enabled = False
    [button_SVPconversion].Enabled = False
    [Calc_PPG].Enabled = True
    [Forms]![Form]![Values].[Form]![ppm1].SetFocus
Case 3
    ppm2.Enabled = False
    ppm1.Enabled = False
    ppm3.Enabled = False
    molsvol.Enabled = True
    VA1.Enabled = False
    VP1.Enabled = False
    [button_A_Saturation_VP].Enabled = False
    Mol1.Enabled = False
    [button_MWpermeant].Enabled = False
    [button_additionMWpermeant].Enabled = False
    TempCSI.Enabled = True
    [button_tempconvert].Enabled = True
```

```
    Pden1.Enabled = False
    [button_permeantdensity].Enabled = False
    [button_additionpermeantdensity].Enabled = False
    SVP1.Enabled = False
    [button_SVPconversion].Enabled = False
    [Calc_PPG].Enabled = True
    [Forms]![Form]![Values].[Form]![molsvol].SetFocus
Case 4
    ppm2.Enabled = False
    ppm1.Enabled = False
    ppm3.Enabled = False
    molsvol.Enabled = False
    VA1.Enabled = True
    VP1.Enabled = False
    [button_A_Saturation_VP].Enabled = True
    Mol1.Enabled = False
    [button_MWpermeant].Enabled = False
    [button_MWpermeant].Enabled = False
    TempCSI.Enabled = True
    [button_tempconvert].Enabled = True
    Pden1.Enabled = False
    [button_permeantdensity].Enabled = False
    [button_additionpermeantdensity].Enabled = False
    SVP1.Enabled = True
```

```
        [button_SVPconversion].Enabled = True
        [Calc_PPG].Enabled = True
        [Forms]![Form]![Values].[Form]![VA1].SetFocus
    Case 5
        ppm2.Enabled = False
        ppm1.Enabled = False
        ppm3.Enabled = False
        molsvol.Enabled = False
        VA1.Enabled = False
        VP1.Enabled = True
        [button_A_Saturation_VP].Enabled = False
        Mol1.Enabled = False
        [button_MWpermeant].Enabled = False
        [button_additionMWpermeant].Enabled = False
        TempCSI.Enabled = True
        [button_tempconvert].Enabled = True
        Pden1.Enabled = False
        [button_permeantdensity].Enabled = False
        [button_additionpermeantdensity].Enabled = False
        SVP1.Enabled = False
        [button_SVPconversion].Enabled = False
        [Calc_PPG].Enabled = True
        [Forms]![Form]![Values].[Form]![VP1].SetFocus
  Case 6
```

```
        ppm2.Enabled = False
        ppm1.Enabled = False
        ppm3.Enabled = True
        molsvol.Enabled = False
        VA1.Enabled = False
        VP1.Enabled = False
        [button_A_Saturation_VP].Enabled = False
        Mol1.Enabled = True
        [button_MWpermeant].Enabled = True
        [button_additionMWpermeant].Enabled = True
        TempCSI.Enabled = True
        [button_tempconvert].Enabled = True
        Pden1.Enabled = True
        [button_permeantdensity].Enabled = True
        [button_additionpermeantdensity].Enabled = True
        SVP1.Enabled = False
        [button_SVPconversion].Enabled = False
        [Calc_PPG].Enabled = True
        [Forms]![Form]![Values].[Form]![ppm3].SetFocus
    Case 7
        Frame_Gradient = Null
        ppm2.value = Null
        ppm1.value = Null
        ppm3.value = Null
```

```
        molsvol.value = Null

        VA1.value = Null

        VP1.value = Null

        Mol1.value = Null

        TempCSI.value = Null

        Pden1.value = Null

        SVP1.value = Null

        [%_Humidity].value = Null

        ConAnswer1.value = Null

        ConVP.value = Null

        End Select


End Sub
```

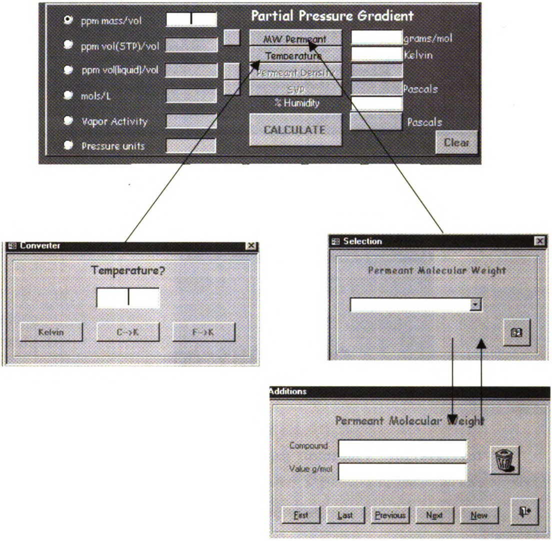


Figure 25. Partial Pressure Gradient: ppm mass/vol

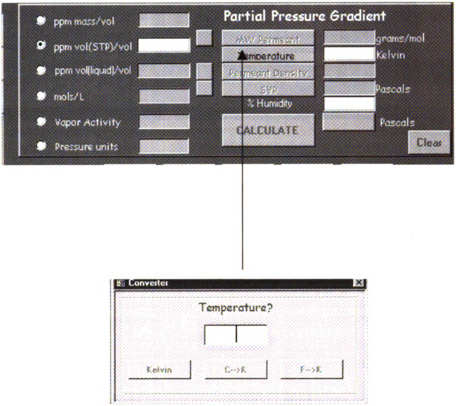


Figure 26. Partial Pressure Gradient: vol(STP)/vol

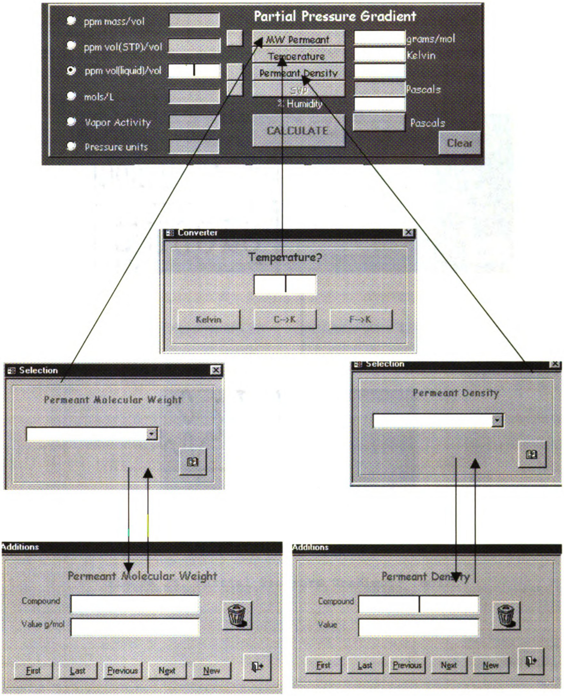


Figure 27. Partial Pressure Gradient: ppm vol(liquid)/vol

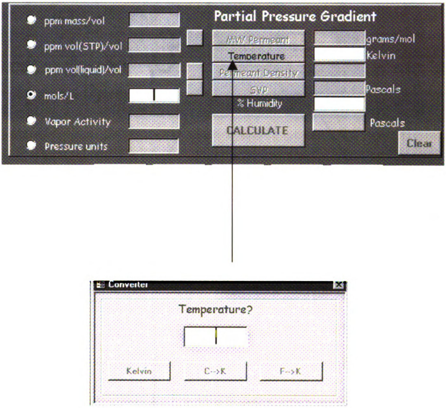


Figure 28. Partial Pressure Gradient: mol/L

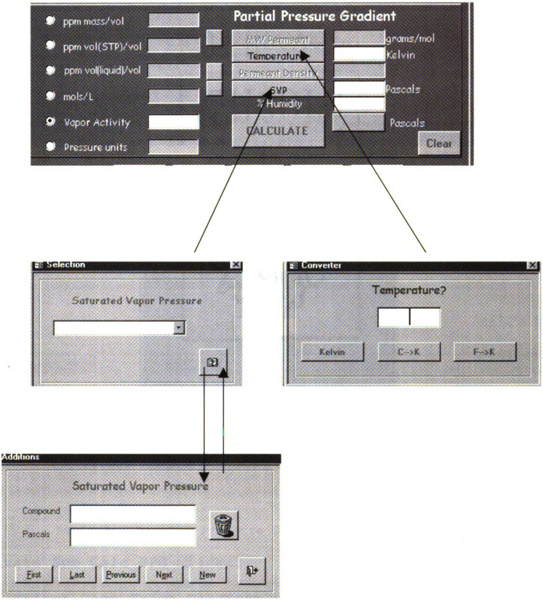


Figure 29. Partial Pressure Gradient: Vapor Activity

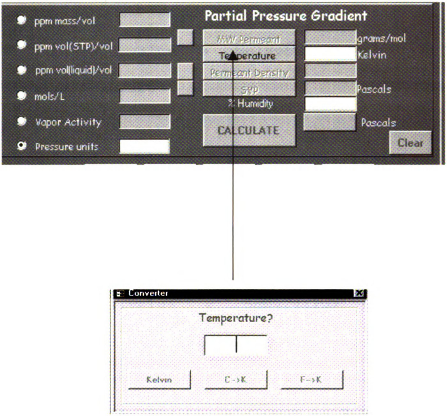


Figure 30. Partial Pressure Gradient: Pressure Units

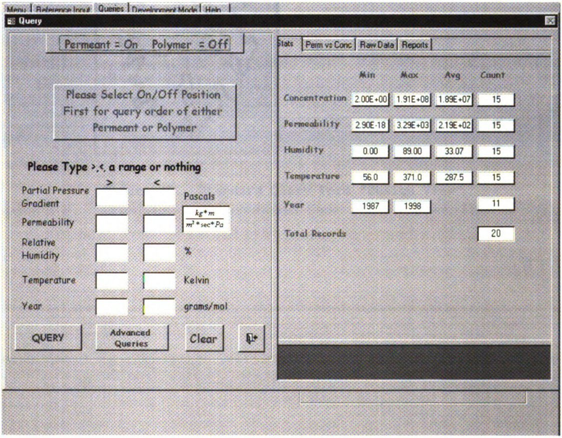
Table 5. Partial Pressure Gradient Calculation Code

```
Private Sub Calc_PPG_Click()

    Select Case Frame_Gradient.value

    Case 1

        ConAnswer1.value = ppm2.value * 0.000001 * 82.06 *

101325 * TempCSI.value / (Mol1.value)

    Case 2
```

```
        ConAnswer1.value = ppm1.value * 0.000001 *
TempCSI.value * 82.06 * 101325 / 22414
    Case 3
        ConAnswer1.value = molsvol.value * 0.08206 *
TempCSI.value * 101325
    Case 4
        ConAnswer1.value = VA1.value * SVP1.value
    Case 5
        DoCmd.RunMacro "Open.VP1"
    Case 6
        ConAnswer1.value = ppm3.value * 0.000001 *
TempCSI.value * 82.06 * 101325 * Pden1.value / Mol1.value
    Case Else
       Dim strMsg As String, strInput As String
        ' Initialize string.
        strMsg = "Please select a calculation type before"
    End Select
End Sub
```

Standard and Advanced Query

Polymer or Permeant may be selected to query first as shown in Figures 33 and 34. The advanced query form is available to see at Figure 35. The query and some of its table ties, and the "SQL design view" can be checked out in Figures 36 and 37. Figure 32 is the standard query form before selection of polymer or permeant. Table 6 is the standard query form visibility, requery and reset Visual Basic for Applications code.



Please Select On/Off Position First for query order of either Permeant or Polymer

Please Type >,<, a range or nothing

	Min	Max	Avg	Count
Concentration	2.00E+00	1.91E+08	1.89E+07	15
Permeability	2.90E-18	3.29E+03	2.19E+02	15
Humidity	0.00	89.00	33.07	15
Temperature	56.0	371.0	287.5	15
Year	1987	1998		11
Total Records				20

Figure 31. Standard Query Form

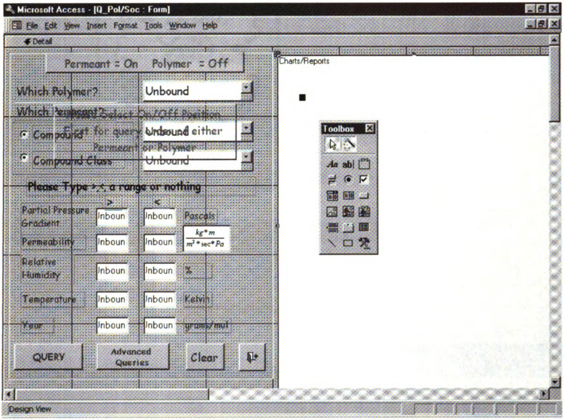
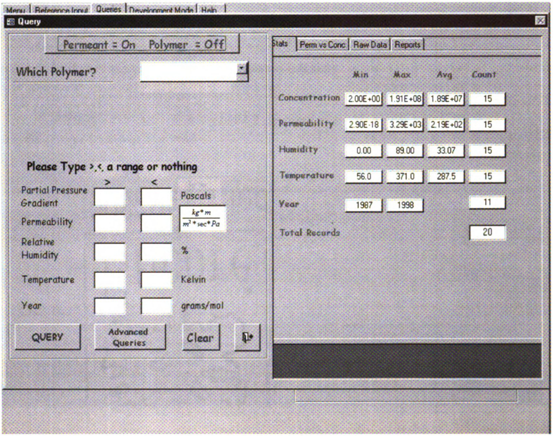
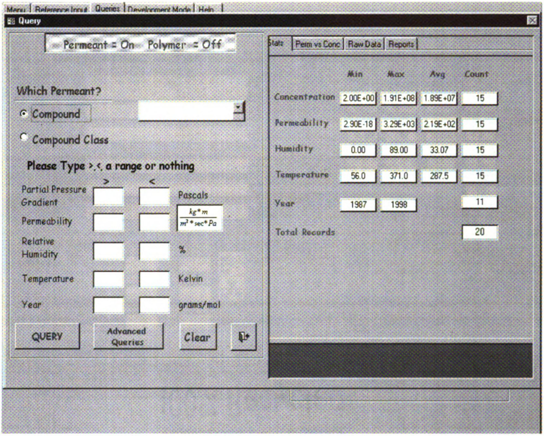


Figure 32. Standard Query Form "Design View"



	Min	Max	Avg	Count
Concentration	2.00E+00	1.91E+08	1.89E+07	15
Permeability	2.90E-18	3.29E+03	2.19E+02	15
Humidity	0.00	89.00	33.07	15
Temperature	56.0	371.0	287.5	15
Year	1987	1998		11
Total Records				20

Figure 33. Standard Query Form: Which Polymer?



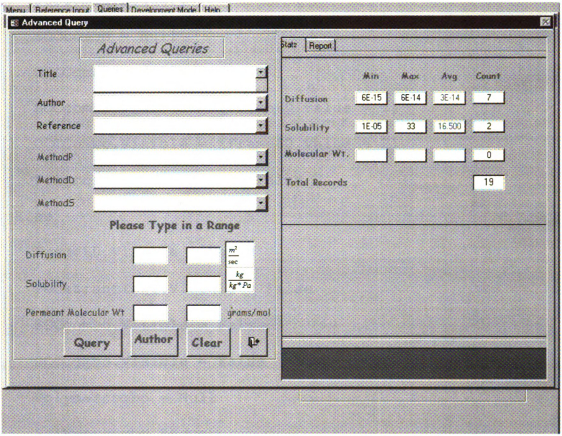
Permeant = On Polymer = Off

● Compound

○ Compound Class

	Min	Max	Avg	Count
Concentration	2.00E+00	1.91E+08	1.89E+07	15
Permeability	2.90E-18	3.29E+03	2.19E+02	15
Humidity	0.00	89.00	33.07	15
Temperature	56.0	371.0	287.5	15
Year	1987	1998		11
Total Records				20

Figure 34. Standard Query Form: Which Permeant?



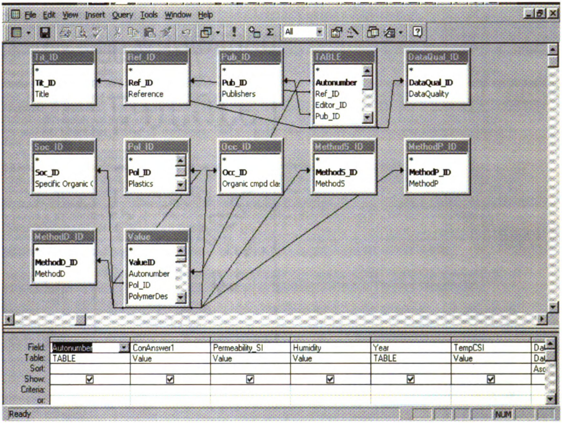
	Min	Max	Avg	Count
Diffusion	6E-15	6E-14	3E-14	7
Solubility	1E-05	33	16.500	2
Molecular Wt.				0
Total Records				19

Figure 35. Advanced Query Form

Table 6. Standard Query Form: visibility, requery and reset code

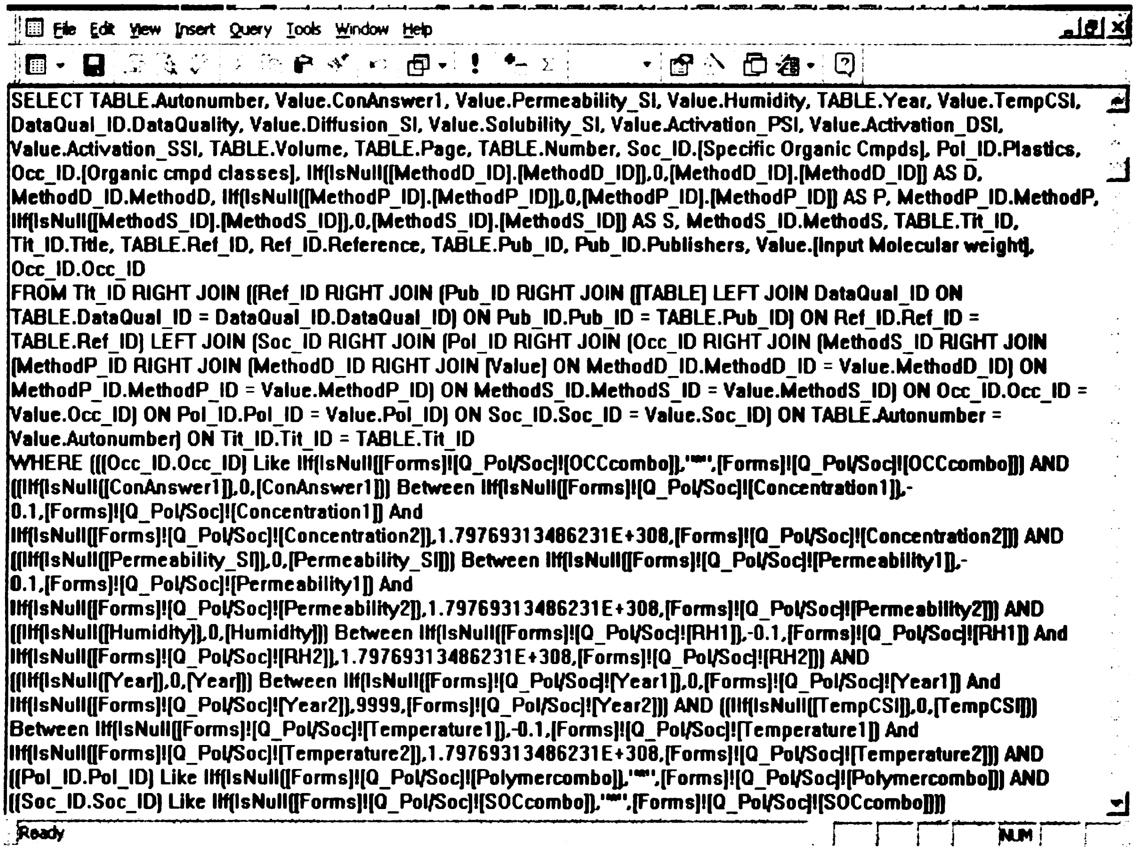
```
Private Sub DirectionToggle_AfterUpdate()

  Polymercombo.Requery

  OCCCombo.Requery

  SOCcombo.Requery

  If DirectionToggle Then   'selected

    Frame60.Visible = True

    PenetrantText.Visible = True
```

```
    SOCcombo.Requery
    OCCCombo.Requery
    SOCcombo = Null
    OCCCombo = Null
    SOCcombo.Visible = (Frame60.value = 1)
    OCCCombo.Visible = (Frame60.value = 2)
    Polymercombo.Visible = False
  Else
    Frame60.Visible = False
    PenetrantText.Visible = False
    SOCcombo.Visible = False
    OCCCombo.Visible = False
    Polymercombo = Null
    Polymercombo.Requery
    Polymercombo.Visible = True
    Plastics_Label.Visible = True
  End If
    Label_PolyPen.Visible = False
End Sub
```



Field:	Autonumber	ConAnswer1	Permeability_SI	Humidity	Year	TempCSI	Da
Table:	TABLE	Value	Value	Value	TABLE	Value	Da
Sort:							Asc
Show:	☑	☑	☑	☑	☑	☑	
Criteria:							
or:							

Figure 36. Standard Query "Design View"



```sql
SELECT TABLE.Autonumber, Value.ConAnswer1, Value.Permeability_SI, Value.Humidity, TABLE.Year, Value.TempCSI,
DataQual_ID.DataQuality, Value.Diffusion_SI, Value.Solubility_SI, Value.Activation_PSI, Value.Activation_DSI,
Value.Activation_SSI, TABLE.Volume, TABLE.Page, TABLE.Number, Soc_ID.[Specific Organic Cmpds], Pol_ID.Plastics,
Occ_ID.[Organic cmpd classes], IIf(IsNull([MethodD_ID].[MethodD_ID]),0,[MethodD_ID].[MethodD_ID]) AS D,
MethodD_ID.MethodD, IIf(IsNull([MethodP_ID].[MethodP_ID]),0,[MethodP_ID].[MethodP_ID]) AS P, MethodP_ID.MethodP,
IIf(IsNull([MethodS_ID].[MethodS_ID]),0,[MethodS_ID].[MethodS_ID]) AS S, MethodS_ID.MethodS, TABLE.Tit_ID,
Tit_ID.Title, TABLE.Ref_ID, Ref_ID.Reference, TABLE.Pub_ID, Pub_ID.Publishers, Value.[Input Molecular weight],
Occ_ID.Occ_ID
FROM Tit_ID RIGHT JOIN ((Ref_ID RIGHT JOIN (Pub_ID RIGHT JOIN ([TABLE] LEFT JOIN DataQual_ID ON
TABLE.DataQual_ID = DataQual_ID.DataQual_ID) ON Pub_ID.Pub_ID = TABLE.Pub_ID) ON Ref_ID.Ref_ID =
TABLE.Ref_ID) LEFT JOIN (Soc_ID RIGHT JOIN (Pol_ID RIGHT JOIN (Occ_ID RIGHT JOIN (MethodS_ID RIGHT JOIN
(MethodP_ID RIGHT JOIN (MethodD_ID RIGHT JOIN [Value] ON MethodD_ID.MethodD_ID = Value.MethodD_ID) ON
MethodP_ID.MethodP_ID = Value.MethodP_ID) ON MethodS_ID.MethodS_ID = Value.MethodS_ID) ON Occ_ID.Occ_ID =
Value.Occ_ID) ON Pol_ID.Pol_ID = Value.Pol_ID) ON Soc_ID.Soc_ID = Value.Soc_ID) ON TABLE.Autonumber =
Value.Autonumber) ON Tit_ID.Tit_ID = TABLE.Tit_ID
WHERE (((Occ_ID.Occ_ID) Like IIf(IsNull([Forms]![Q_Pol/Soc]![OCCcombo]),"*",[Forms]![Q_Pol/Soc]![OCCcombo])) AND
((IIf(IsNull([ConAnswer1]),0,[ConAnswer1])) Between IIf(IsNull([Forms]![Q_Pol/Soc]![Concentration1]),-
0.1,[Forms]![Q_Pol/Soc]![Concentration1]) And
IIf(IsNull([Forms]![Q_Pol/Soc]![Concentration2]),1.79769313486231E+308,[Forms]![Q_Pol/Soc]![Concentration2])) AND
((IIf(IsNull([Permeability_SI]),0,[Permeability_SI])) Between IIf(IsNull([Forms]![Q_Pol/Soc]![Permeability1]),-
0.1,[Forms]![Q_Pol/Soc]![Permeability1]) And
IIf(IsNull([Forms]![Q_Pol/Soc]![Permeability2]),1.79769313486231E+308,[Forms]![Q_Pol/Soc]![Permeability2])) AND
((IIf(IsNull([Humidity]),0,[Humidity])) Between IIf(IsNull([Forms]![Q_Pol/Soc]![RH1]),-0.1,[Forms]![Q_Pol/Soc]![RH1]) And
IIf(IsNull([Forms]![Q_Pol/Soc]![RH2]),1.79769313486231E+308,[Forms]![Q_Pol/Soc]![RH2])) AND
((IIf(IsNull([Year]),0,[Year])) Between IIf(IsNull([Forms]![Q_Pol/Soc]![Year1]),0,[Forms]![Q_Pol/Soc]![Year1]) And
IIf(IsNull([Forms]![Q_Pol/Soc]![Year2]),9999,[Forms]![Q_Pol/Soc]![Year2])) AND ((IIf(IsNull([TempCSI]),0,[TempCSI]))
Between IIf(IsNull([Forms]![Q_Pol/Soc]![Temperature1]),-0.1,[Forms]![Q_Pol/Soc]![Temperature1]) And
IIf(IsNull([Forms]![Q_Pol/Soc]![Temperature2]),1.79769313486231E+308,[Forms]![Q_Pol/Soc]![Temperature2])) AND
((Pol_ID.Pol_ID) Like IIf(IsNull([Forms]![Q_Pol/Soc]![Polymercombo]),"*",[Forms]![Q_Pol/Soc]![Polymercombo])) AND
((Soc_ID.Soc_ID) Like IIf(IsNull([Forms]![Q_Pol/Soc]![SOCcombo]),"*",[Forms]![Q_Pol/Soc]![SOCcombo])))
```

Figure 37. Standard Query "SQL View"

SUMMARY AND CONCLUSIONS

The beginning of this thesis includes a summary of the scientific investigations of Zobel, Gilbert, Delausses, Giacin and Hernandez. These four, modern, mass transfer, groups have been major contributors to published data in recent years.

A database was developed to calculate mass transfer (permeability, diffusion, and sorption coefficients), and their corresponding partial pressure gradient values. Through it information has been made readily accessible to technical and product/packaging professionals. For effective comparison purposes, all mass transfer and partial pressure gradient values were converted into standard international units. It includes the values with their respective literature reference.

The database can be separated into three major sections. The main table is divided into appropriate fields which store all normalized data as standard international units. This table cannot be seen by the user, and can be accessed for change and additions only by an administrator.

The input reference section consists of mass transfer, partial pressure gradient, polymer, penetrant, organic compound class, test methods, and literature references. This one page input reference form is the "conversion calculator" of the database, and can be accessed only by the administrator. All results of the input reference are converted into standard international units before being transferred into the main table for later query.

The query section performs sorting of the main table's data fields. It is divided into standard and advanced query levels. For each numerical query, the user can choose to enter a range, a minimum or maximum value, or nothing in both levels of querying. The choice of polymer or permeant, either specific or compound class, is required to start a standard query. Partial pressure gradient, permeability, relative humidity, temperature, or year are included in the possible numerical limitations. The advanced query empowers the user to sort by title, author, reference, testing method for permeability, diffusion, and solubility. It also permits the user to numerically limit the data by diffusion, solubility, or permeant molecular weight.

In conclusion, this database provides the normalization of units and compilation of data into one place. By accomplishing this milestone it now becomes more readily feasible to both compare data, and pin point the knowledge gaps in mass transfer research.

RECOMMENDATIONS

Based on the completion of this database, a number of recommendations can be made for future additions. As described in the summary, the database is divided into three major parts: main table, input reference, and queries. The query or sorting section is the area which can be expanded and automated according to the specific needs of the user and future advancement in software. Because the database was developed in Microsoft Access 97 format, it will be possible to export query results readily to any of the Microsoft family of applications. It would be possible to develop a web-based program to query results of the database on an Intranet. The open architecture allows for this possibility. Specifically, inside the database standard and advanced query page, it would be possible to add additional "tabs" to the already existing lineup of output possibilities. This might include automatic graphs, or Access reports. A customized package of Microsoft Word documents might be developed in which database query results would be transferred onto pre-made specialized Word documents. Essentially, further database improvement is only limited by the user's knowledge of the science of mass transfer, and computer programming skills.

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BIBLIOGRAPHY

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