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Part 2

THEORETICAL INVESTIGATION

OF THE MECHANISM OF TRANSFER

OF MATERIALS THROUGH POLYETHYLENE

Dr. Henry A. Bent
University of Connecticut
and
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Plax Corporation

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WRIGHT AIR DEVELOPMENT CENTER

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FOREWORD

This report was prepared by the Plax Corporation under USAF Contract No. AF 33(616)-112. The contract was initiated under Research and Development Order No. 618-11. "Improvement of Packaging Procedures", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. M. E. Bowman acting as project engineer.

ABSTRACT

The temperature variation of the P-factor has been found to be accurately represented by the two parameter equation

$$P = P_o e^{-Ep/RT}$$

in which Ep and P_o are constants for the particular permeant polymer system. These parameters are calculated from carefully constructed log vs. 1/T plots.

The size, shape, and polarity of the penetrant molecule are factors influencing E_p and for substances no more polar than acetone the expression

$$E_p = 0.0348V + 0.75 \ V/L + 2.4 \ \triangle \triangle H$$

reproduces the data to within about 0.5 kcal/mol. where polyethylene is the permeable film.

It is established that for four homologous series that

$$\log P_o = mEp + b$$

where m and b are constants peculiar to each series.

Master plots for interpolating homologous materials and extrapolating for temperature changes are included.

PUBLICATION REVIEW
This report has been reviewed and is approved

FOR THE COMMANDER

M. E. Sorte
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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TABLES

FIGURES

LIST OF SYMBOLS

P	Permeability weight/unit time/unit thickness/unit area
D	Diffusion weight/unit time/unit thickness/unit area
S	Solubility weight/unit weight plastic
P_o	Constant for given system
D_o	" " " "
S_o	" " " "
E_p	" " " "
E_d	" " " "
E_s	" " " "
R	Universal Gas Constant - 1.987 calories/°Kelvin/mole
T	Absolute Temperature °Kelvin
$\Delta\Delta H$	Measure of Polarity--Table 4
$\Delta\Delta H'$	"
ΔH	Heat of Vaporization--kcal/mole
V	Molar Volume c.cs. room temperature-gram.mol.wt./density
Ω	Absorption-gms. penetrant/gram polyethylene
ϕi	Volume fraction (i = 2 the penetrant or P the polymer)
D_p	Density of Polymer
D_2	Density of Penetrant
χ	Flory Huggins Polymer Interaction Parameter

LIST OF SYMBOLS

S_{th} Entropy (thermal)

S_{cf} Entropy of Configuration

F Free Energy

H Enthalpy

B Empirical constant (Van Laar Const.)

m "

b "   (see table 20)

v_2^o Molecular Volume pure penetrant

v_c^o Molecular Volume polymer

L Thickness Swollen Polymer

L^o Original Thickness of Polymer

λ Swelling Index

m_2 Weight of Penetrant Swelling Polymer

ΔS^* Entropy of Activation for diffusion

ΔF^* Free Energy of activation for diffusion

permeability usually expressed as grams/24 hrs./0.001 ins./ 100 in^2 at °F

Introduction

Permeability has been found by various investigations to be dependent upon several factors of which solubility, diffusion, and temperature are important factors and for a constant temperature is frequently expressed as

$$(1 - 1a) \qquad P = DS/d \qquad\qquad d = x \text{ thickness}$$

$$(1 - 1b) \qquad P = DS \qquad\qquad \text{where } d = 1$$

It is an experimental fact that the coefficient of permeability as well as those of diffusion and solubility are often well represented by the following equations

$$(1 - 2a) \qquad P = P_o e^{-E_p/RT}$$

$$(1 - 2b) \qquad D = D_o e^{-E_d/RT}$$

$$(1 - 2c) \qquad S = S_o e^{-E_s/RT}$$

to express their dependence on temperature. P, D and S are permeability, diffusion, and solubility expressed in grams/24 hours/0.001in. /100 in.^{2} of polyethylene unless otherwise stated. P_o, D_o, S_o, E_p, E_d, and E_s are constants for a given substance. R is the universal gas constant equal to 1.987 calories/degree Kelvin/mole and T the absolute temperature in degrees Kelvin.

In this study P ranged all the way from immeasurably small values (less than 0.02) for several of the hydrogen bonded compounds at 32°F to almost immeasurably large values for many of the hydrocarbons at 165°F (more than 21,000 for chlorobenzene at this latter temperature !): altogether, over a million-fold variation in the P-factor.

To check the exponential dependence of P upon the inverse of the absolute temperature and to evaluate the parameters P_o and E_p, equation 1-2a is rewritten as

$$(1-3) \qquad \log P = -(E_p/2.3R)(1/T) + \log P_o$$

showing that a plot of the common logarithm of P against the reciprocal of the absolute temperature should be a straight line with a slope of $-(E_p/2.3R)$ and an intercept at $1/T = 0$ of $\log P_o$. This has been done and the plot appears as Figure I.

The first step then in the reduction of the data is the construction of logP vs. 1/T plots as shown in Figure I. From these the parameters
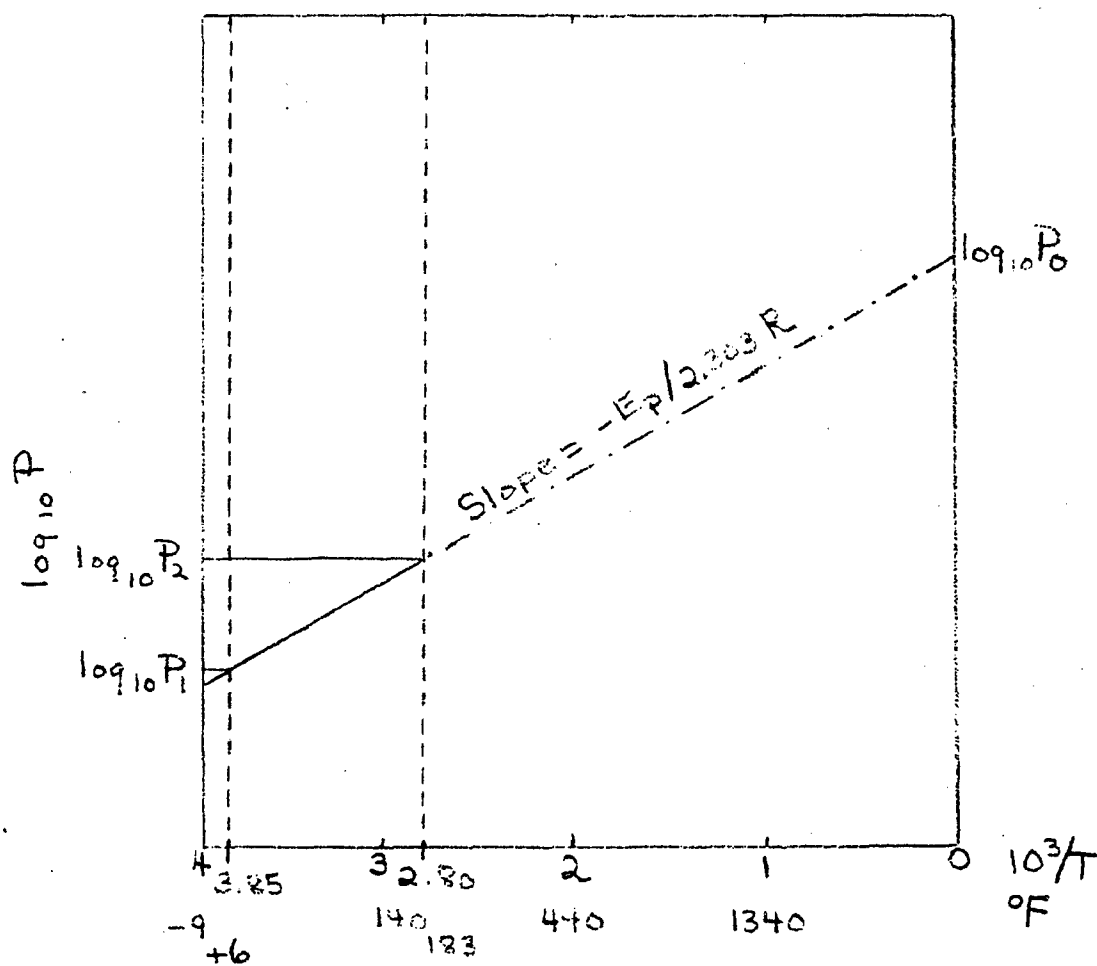
Fig. 1.   The Dependence of $\log_{10}P$ upon $1/T$.

P_o and E_p are determined and compared. Particular attention is given E_p since it is this so-called "activation energy" which determines the temperature variation of the P-Factor. Furthermore, knowing E_p it is possible sometimes to estimate good values for $\log P_o$ and hence for the P-Factor itself.

Thus the accuracy of the $\log P$ vs. $1/T$ plots is of paramount importance in this study, for the reliability of all subsequent calculations rests squarely upon the validity of these plots and the slopes and intercepts obtained therefrom.

2. The Master Data: Some Selected P-Factors at 32, 70, 100, 130, and 165°F

     As a liquid diffuses out of a bottle initially filled to the neck, the observed P-Factor, which is always a composite of the liquid and vapor transmission rates, will generally decrease with time, for that part of the air gap in contact with the bottle can never be completely saturated with vapor if the outside of the bottle is "dry". Hence the vapor-phase transmission rate will generally be somewhat less than the liquid-phase transmission rate, and the former becomes increasingly important as the bottle tends toward emptiness, causing the observed, instantaneous P-Factor to decrease with time. (Although when collapse occurs, this "tailing off" effect which must necessarily set in sometime may be delayed until the bottle is almost completely "empty".)

     For example, a bottle initially filled with 100 grams of ethyl acetate and kept for nearly two weeks at 165°F behaved as shown in Figure 2.

Weight Loss
(in grams)

Time (in days)
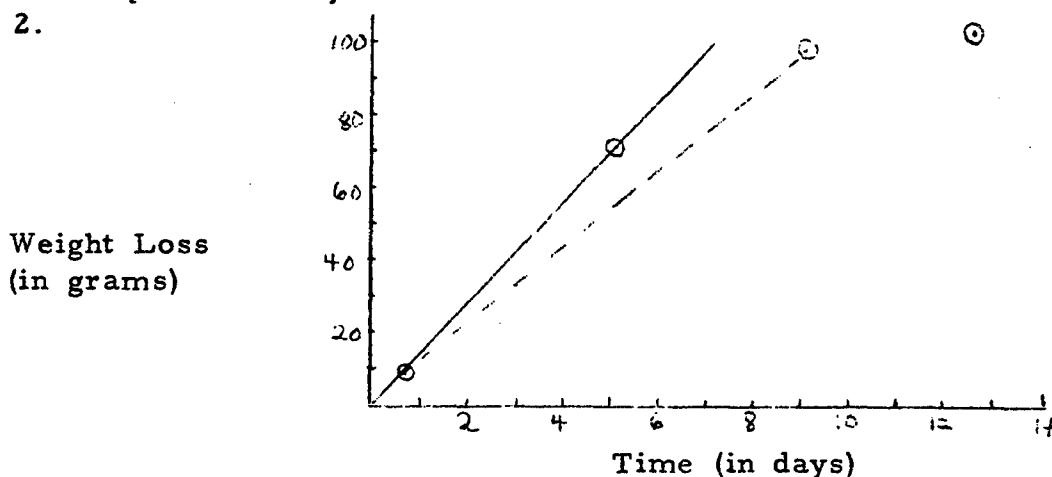
Fig. 2. The Diffusion of Ethyl Acetate at 165°F
(Initial Net Contents: 100 grams.)

     The slope of the solid line in Fig. 2 represents a P-Factor of 1990, that of the dotted line 1700. It is the former, which represents the initial P-Factor after steady-state has been established, that is of interest in this report. With this in mind, the following P-Factors in Table V - Part I have been revised somewhat (generally upwards):

> Ethylene glycol monobutyl ether at 165°F; ethyl acetate at 165°F; amyl acetate at 165°F; allyl alcohol at 70°F, sec.-butyl alcohol at 100°F, 130°F, and 165°F; dibutyl ether at 100°F and 165°F; butyraldehyde at 100°F and 130°F; aniline at 165°F; nitroethane at 130°F; heptane at 100°F; tetradecane at 70°F and 100°F; lubricating oil at 130°F and 165°F;

benzene at 32°F; ortho-xylene at 70°, 100°, and
130°F; para-xylene at 32°, 70°, 100° and 130°F;
cyclohexane at 70° and 100°F; chlorobenzene at 32°,
70° and 130°F; para-chlorotoluene at 32°, 70° and
130°F.

These revisions resulted in a general improvement in the overall
appearance of the data when the logarithms of the observed P-Factors
were plotted against 1/T. It should perhaps be noted, however, that such
revisions as have been made do not improve one's ability to predict
yearly losses--at least not at this point. In fact, as already observed,
in the case of ethyl acetate at 165°F, the bottles are essentially empty
after 14 days. The yearly loss in this case is the same as the 14 day
loss.

Finally, with regard to this reduction of the data, it remains to
be mentioned that at 32°F especially, most of the slow (and hygroscopic)
solvents exhibited either initial increases in weight or else relatively small
P-Factors at the start. Probably this is all just a matter of the degree
to which the moisture in the air permeates inward at the start. The effect
is most pronounced in the case of the 93% sulfuric acid.

Table 1

The Permeability of Polyethylene to Forty Substances at 32°, 70°, 100°, 130° and 165°F.

Gms/24 hours/0.001"/100"² / Temp.

Substance	32°F	70°F	100°F	130°F	165°F
Formic Acid	0.251	0.666	2.790	12.0	51.6
Acetic Acid	0.351	3.080	13.55	66.0	304.0
n-Butyric Acid	0.193	4.79	29.6	-----	579.0
Benzoic Acid	-----	0.067	0.570	5.67	35.9
Methyl Alcohol	0.253	1.22	5.35	27.8	-----
n-Propyl Alcohol	0.072	0.495	2.89	22.4	168.0
Allyl Alcohol	0.161	0.65	4.06	23.0	137.8
n-Butyl Alcohol	-----	0.462	3.12	20.4	164.
sec-Butyl Alcohol	-----	0.619	5.24	37.9	280.
tert.-Butyl Alcohol	-----	0.260	2.44	27.5	236.5
n-Octyl Alcohol	-----	0.498	3.31	25.6	188.5
Phenol	-----	0.484	3.28	24.0	119.0
Ethylene Glycol Butyl Ether		0.666	4.40	34.9	231.
Ethyl Acetate	1.903	16.55	83.3	378.	1990.
Amyl Acetate	0.566	8.70	37.7	269.	1300.
Dibutyl Phthalate	-----	-----	0.81	5.7	27.75
Diethyl Ether	48.0	313.0	-----	-----	-----
Dibutyl Ether	-----	-----	407.	1480.	4890.
Butyraldehyde	0.890	10.13	66.1	339.	-----
Benzaldehyde	0.369	6.80	32.85	206.5	1060.
Acetone	1.38	6.75	32.45	184.	-----
Methyl Ethyl Ketone	3.67	12.6	60.0	326.5	1401.
Diacetone Alcohol	-----	0.308	1.96	15.0	92.5
Acetic Anhydride	-----	0.809	4.145	29.65	150.
Nitroethane	0.968	2.71	11.4	61.3	290.
n-Pentane	96.9	526.0	-----	-----	-----
iso-Pentane	47.8	270.0	-----	-----	-----
Pentene-2	180.	695.0	-----	-----	-----
n-Heptane	48.6	269.5	929.	2650.	8160.
Decane	9.49	71.2	297.	1220.	4120.
Tetradecane	1.74	15.6	89.6	404.	-----
Benzene	50.5	440.	1585.	4480.	13670.
Ortho-Xylene	36.1	284.0	1167.	4270.	16600.
Para-Xylene	87.3	505.	1760.	4760.	16320.
Cyclohexane	31.6	281.	1223.	3730.	-----
Chlorobenzene	76.4	500.	1630.	5980.	21150.
para-Chlorotoluene	37.0	332.	1357.	4670.	18520.
Dipentene	15.0	128.	501.	2030.	8110.
Monochloroacetic Acid	-----	0.31	1.82	15.	59.9
Water	-----	0.279	0.835	3.94	18.4

3. The Master Plot and Its Uses

On a separate sheet the data of Table 1 have been plotted on semi-log paper as indicated by equation (1-3). This plot is of considerable value in the following respects. The Master Plot may be found on page 71.

a. It may be used to check on the over-all consistency of the data since in a vast majority of the cases the points do fall very nearly on perfectly straight lines as indicated except in those cases where several substances have nearly identical P-Factors. In this respect one observes that

i. On the whole, the data show up extremely well; indeed, very much better than expected, for as indicated later, certain aspects of the permeation process almost lead one to expect departures from linearity. But

ii. Only aniline seems to show signs of consistent curvature. However,

iii. More often than not the 100°F point lies a bit to the right of the best straight line through the data. Also,

iv. The 32°F point for methyl ethyl ketone seems too high by more than a factor of two. Finally,

v. As indicated earlier, the initial-slope correction for tailing off effects almost invariably brought otherwise seemingly erratic data into good straight-line agreement.

b. Thus, in view of the well established fact that the data do tend to fall almost exactly on straight lines, these plots may be used to "smooth" data that may happen to exhibit slight departures from linearity. Perhaps more important though,

c. With these plots one can easily extrapolate results obtained in the neighborhood of room temperature into experimentally difficult-to-measure regions. For example, for the alcohols and similar substances which showed weight increases and/or erratic behavior at 32°F, one can determine what the P-Factors probably would have been if the relative humidity had been zero both in the 32°F "oven" and during weighing by extrapolating down from higher temperatures where hygroscopic effects were negligible. Or, one can state with confidence that the P-Factor for n-heptane at -40°F and zero relative humidity is 0.73. This is not immediately obvious from the data of Table 2 alone. Furthermore,

d. One can accurately interpolate with these plots. Thus the P-Factor for n-heptane at 85°F is 500. Also,

e.   One can interpolate with respect to members of a homologous series. For example, the P-Factor for n-octane at 130°F is undoubtably within a few percent of 2000.   With this master plot one can probably reliably estimate P-Factors for hundreds, perhaps even thousands of similar compounds.   It is important though to classify a compound according to its dominant functional group.   Thus diacetone alcohol, $CH_3COCH_2COH(CH_3)_2$, belongs with the alcohols rather than the ketones as would be the case if the hydroxyl group, which takes precedence over all others studied, were absent.

Likewise, it should be noted that chlorine has no drastic effect upon P-Factors, behaving in this respect very much like a methyl group.   This is somewhat of an oversimplification, but observe that chlorobenzene has permeability characteristics similar to benzene itself, para-chlorotoluene to para-xylene, and chloroacetic acid to acetic acid.

As a further example of the importance of properly assessing the effects of functional groups, the following (with editorial remarks in parentheses) is quoted from an article "Polyethylene Packaging Problems" by Wight, Tomlinson and Kirmeier, Drug and Cosmetic Industry, 72, 767 (1953).

"Resinous and crystalline materials familiar to the trade as heavy, persistent, and of low volatility are not lost in appreciable amounts.   Alcohols are superior to the corresponding acetates by a factor ranging from two to ten, and, likewise, but to a smaller degree, are less permeable than the respective aldehydes; (Superior means smaller P-Factor.) dimethyl acetals are unexpectedly poorer than the parent aldehydes (that is, they have larger P-Factors). Terpenes and terpenic oils, low hydro-carbons and low ketones and esters are phenomenally bad while hydroxycitronellal (we repeat, hydroxycitronellal) is practically non-permeable.   Others skip around in a most unpredictable manner, eugenol diffusing quite slowly, anethole very rapidly."

Insofar as these observations overlap those of the present study, the order is the same; namely (in order of increasing P-Factor):

> Alcohols
> Acids
> Nitroderivatives
> Aldehydes
> Ketones
> Esters
> Ethers
> Hydrocarbons

(This is shown in Table 2.)

Table 2

ORDER OF P-FACTOR IN RELATION TO FUNCTIONAL GROUP

(From Table V Part I of This Report)

Group	Specific Material	P-Factor $gms/24\ hr./$ $0.001"/100"^2$ at 70°F
Alcohols -C-OH	Methyl alcohol	1.22
	n Propyl alcohol	0.49
Acids - C>O O H	Acetic acid	3.08
	Butyric acid	4.79
Nitro derivatives	Nitroethane	2.71
-C-NO2	Nitrobenzene	4.93
Aldehydes-H$_C$=O	Acetaldehyde	6.05
Ketones C = O	Acetone	6.75
	Methyl ethyl ketone	12.60
Esters -C=O-O-R	Ethyl acetate	16.55
	Amyl acetate	8.75
Ethers -C-O-C	Ethyl ether	313.
	Butyl ether	85.
Hydrocarbons	n-Pentane	526.
	Benzene	440.

The reason why acetals permeate more rapidly than the corresponding aldehydes is that the exposed oxygen of an aldehyde becomes an ether linkage in the corresponding acetal, and, as noted above, ethers permeate more rapidly than aldehydes. The increase, however, will not be as great as one might expect from this factor alone since the acetals are bulkier than the original aldehydes. (The effect of bulkiness upon P-Factors will be demonstrated when we compare the slopes of the curves LogP vs. 1/T for ter-butyl alcohol and n-butyl alcohol, ortho-xylene and para-xylene, and cyclohexane and pentane or heptane.)

As for hydroxycitronellal, anytime you have a hydroxyl group present you can to a first approximation just about forget about the rest of the molecule. The permeability through polyethylene will be low. This then explains eugenol and anethole. The former is essentially an alcohol, the latter an ether (Figure 3-1).
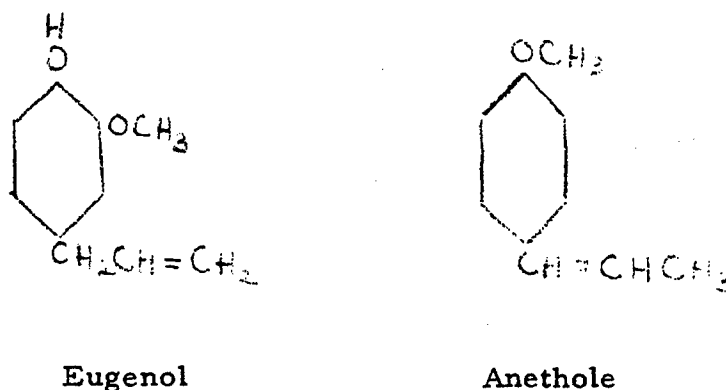
Eugenol   Anethole

Fig. 3.   The Structures of Eugenol and Anethole.

4.   Determination of the Parameters E_p and P_o.

E_p values were calculated from the slopes of curves similar to those presented in the Master Plot using either the $1/T = 2.80$ and $1/T = 3.85$ intercepts (Method I) or, for the slower permeators, the $1/T = 2.80$ and $1/T = 3.40$ intercepts (Method II):

(4-1a) $E_p^I = 4,360 \left[\log P(1/T = 2.80) - \log P(1/T = 3.85) \right]$, or

(4-1b) $E_p^{II} = 7,626 \left[\log P(1/T = 2.80) - \log P(1/T = 3.40) \right]$

calories per mole.

In all cases P_o was calculated from

(4-2) $\log P_o = \log P(1/T = 2.80) + 0.6119(E_p/1000)$

using the E_p value obtained from either method I or II above.

The intercept data and results of the calculations are tabulated in Table 3.

In every case P_2 refers to the $1/T \approx 2.80$ intercept and P_1 to the $1/T = 3.85$ or $1/T = 3.40$ intercept depending upon which method--equation (4-1a) or (4-1b) respectively--was used. This is indicated in the second column.

The E_p values were calculated to five significant figures and then rounded off to four although they are at best reliable to only three significant figures. The P_o values have been rounded off to three significant figures, again undoubtably one more than is actually warranted. In the case of the pentanes the calculations are based upon only two points.

Table 3

The Parameters E_p and P_o in the Equation $P = P_o e^{-E_p/RT}$
(Listed in order of decreasing E_p)

Substance	Method	P_2*	P_1	E_p kcal/mol	$\log P_o$	$P_o \cdot 10^{-12}$
ter-Butyl Alcohol	II	710	0.260	26.21	18.886	7,690,000
sec-Butyl Alcohol	II	650	0.619	23.04	16.911	81,500
Butyl Carbitol	II	620	0.680	22.57	16.604	40,200
n-Octyl Alcohol	II	445	0.500	22.49	16.411	25,800
n-Butyl Alcohol	II	395	0.462	22.36	16.278	19,000
iso-Propyl Amine	I	33,900	0.260	22.30	18.177	1,500,000
n-Propyl Alcohol	II	381	0.48	22.11	16.112	12,900
Diacetone Alcohol	II	357	0.308	21.91	15.769	5,870
Benzoic Acid	II	83	0.12	21.66	15.171	1,480
Phenol	II	293	0.484	21.22	15.449	2,810
Acetic Anhydride	II	357	0.809	20.17	14.894	783
Allyl Alcohol	II	304	0.680	20.21	14.851	709
Dibutyl Phthalate	II	66	0.153	20.09	14.114	130
Monochloroacetic Acid	II	155	0.39	19.82	14.318	208
Amyl Acetate	I	2,820	0.100	19.40	15.323	2,100
Benzaldehyde	II	2,360	6.80	19.37	15.227	1,690
Butyraldehyde	I	3,400	0.145	19.05	15.191	1,550
Acetone	II	1,700	6.30	18.54	14.724	530
Water	II	39.4	0.150	18.45	12.886	7.69
n-Butyric Acid	II	1,290	5.10	18.32	14.324	211
Methyl Ethyl Ketone	I	2,830	0.207	18.03	14.486	306
Tetradecane	I	3,800	0.284	17.99	14.588	388
Nitroethane	II	357	0.809	17.88	13.721	52.6
Acetic Acid	II	644	3.00	17.78	13.690	48.9
Methyl Alcohol	II	241	1.16	17.67	13.197	15.7
Ethyl Acetate	II	3,670	17.4	17.72	14.408	256
Formic Acid	II	100	0.65	16.68	12.206	1.61
Cyclohexane	I	32,200	6.3	16.17	14.402	252
Dipentene	I	15,700	3.35	16.00	13.989	95.7
Dibutyl Ether	I	10,900	2.41	15.94	13.789	61.6
p-Chlorotoluene	I	35,000	8.15	15.84	14.236	172
o-Xylene	I	30,300	8.00	15.60	14.028	106
n-Decane	I	7,650	2.06	15.56	13.407	25.6
Chlorobenzene	I	35,500	19.8	14.18	13.230	17.0
p-Xylene	I	28,300	24.3	13.37	12.632	4.29
Benzene	I	23,800	21.5	13.27	12.498	3.15
n-Heptane	I	14,000	13.0	13.22	12.235	1.72
iso-Pentane	I	14,000	13.4	13.16	12.200	1.58
n-Pentane	I	25,000	29.0	12.80	12.230	1.70

*P_o, P_1 and P_2 have the same units as P-Factor - gms/24 hrs/0.001"/100 in^2

5. The Physical Significance of the Activation Energy for Permeation, E_p.

It has been argued in considerable detail that insofar as diffusion in polyethylene is Fickian,

$$(5\text{-}1) \qquad E_p = E_d + E_s$$

where E_s is essentially the heat of solution of the permeant in polyethylene and E_d is the energy of activation for diffusion.

It has been established that

$$(5\text{-}2) \qquad P = DS$$

where D is the diffusion constant. From the comparison of propanol and decane it seems probable that E_s is proportional to

$$(5\text{-}3) \qquad \Delta\Delta H \cong \Delta H_{\substack{\text{vaporization} \\ \text{of permeant}}} - \Delta H_{\substack{\text{vaporization of a hydro-} \\ \text{carbon of similar size.}}}$$

This quantity $\Delta\Delta H$ will be zero for hydrocarbons such as decane which are non-polar. Therefore E_s will be small, S large, and the P-Factor, P large in such cases.

For polar compounds, however, we anticipate that $\Delta\Delta H$ will be inherently positive. Thus, using the group contributions to the cohesive energy of organic liquids as given in Table 4, we calculate that for propanol

$$\Delta\Delta H = \Delta H^{vap.}_{CH_3CH_2CH_2OH} - \Delta H^{vap.}_{CH_3CH_2CH_3} \cong (1.8 + 2 \times 1.0 + 7.3) - (2 \times 1.8 + 1.0)$$

or 6.5 kcal/mole. And this presumably is just about an upper limit to E_s. (Indeed, the absorption tests' data to be discussed later suggest that the heat of solution of propanol in polyethylene is around 4.7-4.8 kcal/mole.) Since E_p itself is 22.1 kcal/mole, this means that for propanol E_d is at least $22.1 - 6.5 = 15.6$ which is several times greater than E_s. Furthermore, insofar as $E_s \cong O$ for the hydrocarbons, $E_d \cong E_p$ which is greater than 12 kcal/mole in all cases investigated in this project.

Table 4

GROUP CONTRIBUTIONS TO THE COHESION ENERGY

OF ORGANIC LIQUIDS *

Group	Cohesion in kcal/mole	Group	Cohesion in kcal/mole
$-CH_2-$	1.0	$=CO$	4.3
$=CH-$	1.0	$-CHO$	4.7
$-O-$	1.6	$-COOCH_3$	5.6
$=CH_2$	1.8	$-COOC_2H_5$	6.2
$-CH_3$	1.8	$-NO_2$	7.2
$-F$	2.1	$-OH$	7.3
$-Cl$	3.4	$-COOH$	9.0
$-Br$	4.3	$-CONH_2$	13.2
$-I$	5.0	$-CONH-$	16.2

* Data from Dunkel (Z. physik. Chem. A 138,42 (1928)

In fact, the argument that led to the introduction of quantity $\Delta\Delta H$ compels one to ascribe such variations as there are in the E_p values for the hydrocarbons primarily to E_d. And these variations are not insignificant, E_p ranging all the way from 12.8 for n-pentane to 18.0 for tetradecane.

This all seems to say that D rather than S is the governing factor in the product DS. In a sense this is correct. Our earlier conclusions regarding the dependence of P upon S and hence upon $\Delta\Delta H$ are, however, still valid provided we supplement them with the following observations.

a. As one might expect, size and shape play an important role in the permeation process. They affect E_p primarily through their influence upon E_d, the kinetic part of E_p, having relatively little to do with E_s, the static or equilibrium part of E_p. Thus whereas the solubilities of the two xylenes, ortho and para, are nearly identical, their activation energies for permeation are significantly different: 15.6 and 13.4 respectively. This difference we ascribe to the bulkiness of the ortho molecule, for both isomers have essentially the same molar volume.

Or take the case of ter- and n-butyl alcohol, again rather two differ-ently shaped isomers with nearly the same molar volumes. Their E_p values are 26.2 and 22.4 respectively, yet the absorption tests indicate that their heats of solution differ by less than 0.1 kcal/mole. The remaining differ-ence must be due to the bulkiness of the tertiary construction as seen during diffusion. Finally, when we consider the normal aliphatic hydrocarbons, we find that their solubilities are, relatively speaking, all just about the same, yet there is a steady increase in E_p in going from pentane through heptane and decane to tetradecane. In this case the molecules are all the same general shape but of rather different sizes, and in general the larger the molecule the more difficult its motion during diffusion from one equilibrium position to the next. Here again the effect upon E_p is largely through E_d rather than E_s.

b. Nevertheless, other things being the same--namely size and shape--polarity as measured by $\Delta\Delta H$ (which depends upon $\Delta H_{vaporization}$) is the determining and distinguishing factor, and in the case of the more polar compounds it easily dominates factors of size and shape. Thus the addition of 9 CH_2 groups to pentane increases E_p by only 5.2 kcal/mole whereas the replacement of one hydrogen atom by a single OH group increases E_p by more than 8 kcal/mole!

c. However, and this is where we modify our earlier conclusions somewhat, the full effect of polarity upon E_p may not be felt at the E_s stage owing to

    i. an appreciable interaction of polyethylene with polar substances and

    ii. solvent association effects in the polymer systems. Evidence supporting these conclusions will be presented in later sections when we examine in detail the structure of E_p, the relation between E_p and P_o, and the temper-ature independent part of the polymer interaction parameter as revealed by the absorption tests.

d. Nevertheless, that part of $\Delta\Delta H$ which fails to appear in E_s owing to polymer interaction and solvent association shows up eventually in E_p through the E_d term except in extreme cases of polarity as in the hydrogen bonded alcohols and acids where it now seems probable that a dimer rather than the monomer is the diffusing entity.

e. To summarize then,

    i. E_p (and therefore P) is very structure sensitive, de-pending upon the size, shape, and polarity of the permeant molecule.

    ii. But whereas E_s and E_p both increase with increasing polarity as measured by $\Delta\Delta H$,

iii. Only E_d is markedly dependent upon the size and shape factors.

iv. However, when it exists, the polarity factor may greatly outweigh all others in its influence upon E_p.

v. Therefore S may be used as a qualitative guide to P, although it is perhaps important to note that

vi. The variations in S with $\Delta\Delta H$ will not be as great as those in P itself since D also varies with $\Delta\Delta H$. Also,

vii. E_s (and therefore S) will not properly reflect the effect of variations in size and shape upon E_p (or P).

So much for the general structure of E_p. We turn next to a consideration of special cases.

Now it would be nice if we could by a consideration of special cases establish in a general way the dependence of both E_s and E_d individually upon each of the factors: size, shape, and polarity. Then by synthesizing the two, we would have an elegant derivation of a general expression for E_p. This procedure presupposes that we have some method for determining either E_s or E_d in each case, and it was hoped initially that perhaps the temperature variation of the solubility would permit a determination of one of these, namely E_s. E_d could then be obtained by difference and the two studied separately. Unfortunately the solubility behavior in a number of crucial instances appears anomolous from the point of view of present polymeric theory. Probably the partial crystallinity of polyethylene is responsible for the observed departures from theory. In any event, a reliable decomposition of E_p into two terms, one associated with solubility and the other with diffusion, has probably not been effected. Experimentally there still remains the possibility of independently determining E_d from time dependent absorption and desorption studies. However, lacking such information, we turn now to E_p itself.

6. <u>The Qualitative Dependence of E_p Upon Size, Shape, and Polarity.</u>

Water and tetradecane form an interesting comparison. Molecule for molecule, tetradecane is more than 140 times larger than water, yet the activation energy for permeation of the hydrocarbon, $CH_3CH_2CH_2CH_2CH_2$ $CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, is 18.0 kcal/mole whereas that for H_2O is 18.4 kcal/mole !

Comparisons such as this are presented in a more systematic manner in Table 5.

Table 5

E_p and Size, Shape, and Polarity.

Substance	Molar Volume	$\Delta \Delta H$ kcal/mol	E_p kcal/mol
Pentane	115	0.0	12.8
Decane	194	0.0	15.6
Tetradecane	259	0.0	18.0
Ethyl Acetate	98	2.9	17.7
Amyl Acetate	148	2.5	19.4
p-Xylene	124	0.4	13.4
o-Xylene	121	0.6	15.6
n-Pentane	115	0.0	12.8
Cyclohexane	108	0.5	16.2
n-Butyl Alcohol	94	5.4	22.4
ter-Butyl Alcohol	92	4.8	26.2
Benzene	89	0.6	12.5
Butyraldehyde	88	2.4	15.2
Phenol	88	5.2	21.2
Heptane	146	0.0	13.2
Amyl Acetate	148	2.5	19.4
Acetone	74	3.0	18.5
n-Propyl Alcohol	75	6.3	22.1

In the pentane-decane-tetradecane series the shape and polarity factors are constant so that one is observing here the effect upon E_p of size alone. This is also nearly true of the two acetates.

On the other hand the shape factor differs for the two xylenes. Their size and polarity factors are nearly identical. Likewise, the principle difference between n-pentane and cyclohexane or n-butyl and ter-butyl alcohol is one of shape.

In the remaining examples of Table 5 the polarity factor varies, the size and shape within each set being essentially constant (with the exception of butyraldehyde). Observe that unless the molecules differ widely in geometry, the previously mentioned order of decreasing E_p (alcohol, aldehyde, ketone, ester, and hydrocarbon) seems to be preserved.

The problem before us then, is one of reducing these features of Table 5 to some sort of analytical statement that could be used to calculate reasonably reliable E_p values for substances of unknown permeability from readily available data. Such data for the substances under consideration in this report are assembled in Table 6.

Column three gives the vapor pressures at $25^\circ C$ estimated from Dreisbach's "P-V-T Relationships of Organic Compounds" which has been chosen as a convenient source of thermochemical data. Column four lists approximate heats of vaporization, uncorrected for non-ideal gas behavior, as estimated from Dreisbach. Then follows $\Delta\Delta H$ defined in equation (5-3) and evaluated from Dreisbach's heats of vaporization; $\Delta\Delta H$ evaluated using Table 4 (listed under $\Delta\Delta H'$); the molar volume in cc at room temperature; and L, the length in centimeters of the Taylor-Hirschfelder-Fisher molecular models.

Table 6

Supplementary Data Sheet: Size, Shape, and Polarity Factors

Substance	B.P. °C	V.P. mm/Hg	ΔH_{vap} k/cal/mol	$\Delta\Delta H$	$\Delta\Delta H'$	Volume cms^3/mol	L cms*	Vol/L
ter-Butyl Alcohol	82.8	45.	10.5	4.8	7.3	94.0	5.9	15.9
sec-Butyl Alcohol	100.	20.	11.1	5.4	7.3	91.7	7.7	11.9
n-Octyl Alcohol	195.	0.2	14.3	4.8	7.3	158.0	14.6	10.8
n-Butyl Alcohol	117.7	6.4	11.7	6.0	7.3	91.6	9.1	10.0
iso-Propyl Amine	34.0	550.	6.7	2.1	---	91.0	6.7	13.6
n-Propyl Alcohol	97.2	20.1	11.0	6.3	7.3	74.8	7.8	9.6
Diacetone Alcohol	165.	1.0	13.3	4.7	---	125.0	9.1	13.8
Phenol	182.	0.7	12.7	5.2	7.3	87.7	8.5	10.3
Allyl Alcohol	96.	25.	10.9	6.1	7.3	67.8	7.7	8.8
Chloroacetic Acid	189.	0.3	14.1	9.4	10.6	59.7	7.3	8.2
Amyl Acetate	148.*	5.	10.9	2.5	2.4	148.0	13.2	11.2
Benzaldehyde	179.5	1.5	10.9	2.5	---	101.	9.0	11.2
Butyraldehyde	75.7	100.	8.1	2.4	3.6	88.2	8.5	10.4
Acetone	56.5	230.	7.7	3.0	3.3	73.8	6.5	11.3
Water	100.	23.5	10.5	---	---	18.0	3.7	5.2
nButyric Acid	164.	1.	13.1	7.4	9.0	92.0	10.6	8.7
Methyl Ethyl Ketone	79.6	105.	8.5	2.8	3.3	89.5	7.9	11.3
Tetradecane	252.5	0.0	14.4	0.0	0.0	259.0	21.6	12.0
Nitroethane	114.8	20.	9.5	6.	6.	71.3	6.0	11.9
Acetic Acid	118.1	17.	10.0	6.1	9.0	57.3	6.3	9.1
Methyl Alcohol	64.6	100.	9.9	7.1	7.3	39.5	4.7	9.1
Ethyl Acetate	77.2	100.	8.5	2.8	2.4	97.9	9.2	10.6
Formic Acid	100.7	46.	8.7	6.	9.	37.5	5.6	6.7
Cyclohexane	81.4	100.	8.1	0.6	0.	81.4	6.9	15.6
Dipentene	177.	2.	11.5	0.0	0.	162.	10.7	15.1
Dibutyl Ether	142.	7.	10.3	0.8	0.6	169.5	15.1	11.3
p-Chlorotoluene	162.	3.	10.8	1.6	1.6	118.	9.5	12.4
o-Xylene	144.	17.	10.1	0.6	0.	121.	8.7	13.9
p-Xylene	138.5	26.	9.9	0.4	---	---	9.7	12.7
n-Decane	174.	1.5	11.4	0.0	0.0	194.	16.2	12.0
Chlorobenzene	132.	12.5	9.8	1.4	1.6	101.5	8.6	11.8
Benzene	80.0	100.	8.1	0.6	0.	88.9	7.0	11.7
n-Heptane	95.5	50.	8.4	0.0	0.0	146.5	12.2	12.0
n-Pentane	36.2	500.	6.6	0.0	0.0	115.2	9.5	12.1

In constructing this table, the following values have been used for the heats of vaporization of the normal aliphatic hydrocarbons: ethane, approx. 3.8; propane, approx. 4.7; butane, 5.7; pentane, 6.6; hexane, 7.6; heptane, 8.6; octane, 9.6; nonane, 10.6; decane, 11.6; undecane, 12.6; dodecane, 13.6; tridecane, 14.6 except that tetradecane was taken as determined from Dreisbach.

* at 737 millimeters of mercury.

The substances in Table 6 have been listed as in Table 3 according to decreasing E_p. Observe that the progressive diminuition of E_p does not seem to be reflected by any pronounced trend in either the boiling points (given in degrees centigrade). the vapor pressures (approximate values in mm). the heats of vaporization (approximate values in kcal/mole), the molar volumes (expressed in cm^3). the lengths L of the Fisher-Taylor-Hirschfelder molecular models (measured in cm). or the ratios of the molar volumes to L. If there is any significant correlation at all it is with $\Delta\Delta H$, illustrating as mentioned many times previously that polarity plays a prominent role in permeability behavior. It is for this reason that equilibrium solubility studies, which reflect polarity more than any other single factor, furnish considerable information about P-Factors.

In the next section we begin a quantitative study of the dependence of E_p upon size, shape, and polarity.

7. The Dependence of E_p Upon Size.

The strategy here is essentially that indicated by Table 5: to study the variations in E_p for a series of compounds differing as much as possible in size but as little as possible in shape or polarity. The series n-pentane, n-heptane n-decane. n-tetradecane fits these specifications almost exactly. A plot of E_p against the molar volume V for these substances is almost linear (n-heptane falls slightly below the straight line that passes through the points for n-pentane, n-decane, and n-tetradecane) with a slope of 0.0348 kcal/mole/cc. That is to say, an increase of 1 cc in the molar volume that leaves the overall shape and polarity unchanged increases E_p by 0.0348kcal/ mole; correspondingly. a change of 100 cc in V will alter E_p by 3.48 kcal/ mole. This information may also be expressed as follows:

$$(\partial E_p / \partial size)_{shape. \ polarity} = 0.0348 \ kcal/mole/cc$$

or, since we shall use V as a measure of size, V/L as a measure of shape and $\Delta\Delta H$ as a measure of polarity.

(7-1) $$(\partial E_p / \partial V)_{V/L. \ \Delta\Delta H} = 0.0348 \ kcal/mole/cc.$$

With this information, we are now in a position to investigate the effect of polarity upon E_p.

8. The Dependence of E_p Upon Polarity.

The strategy this time is to consider a series of compounds that have essentially the same shape but which differ in polarity. They may also differ in size, in which case we "correct" the observed E_p's for differences in molar volume using equation (7-1). Thus we could, for example, choose among the linear molecules say dibutyl ether as a reference for size

(V = 170 cc) and say that relative to this molecule the E_p for say ethyl acetate (V = 97.9) should be <u>smaller</u> by an amount (170 - 98) (0.0348) = 2.5 kcal/mole if there were no differences in shape or polarity between the two. But, although the shape factor V/L is not too greatly different, there are, however, significant differences in polarity, the $\Delta\Delta H$ index for ethyl acetate being 2.4 whereas that for the ether is only 0.8.

This difference in polarity tends to increase the E_p value for ethyl acetate relative to that for dibutyl ether. In fact, the ester's E_p value is <u>greater</u> than that of the ether by 17.7 - 15.9 = 1.8 kcal/mole. We say therefore that a change of 2.4 - 0.8 = 1.6 in the polarity factor increases E_p by 2.5 + 1.8 = 4.3 kcal/mole, or E_p increases by 4.3/1.6 = 2.7 kcal/mole per unit change in $\Delta\Delta H$ (also measured in kcal/mole).

Actually, in reducing the data for the straight-chain hydrocarbons, dibutyl ether, the two acetates, and methyl ethyl ketone for volume differences, it is easier to calculate $(E_p^{observed} - 0.0348V)$ for each case. This has been done and the values plotted against $\Delta\Delta H$, the polarity factor. The slope of the best straight line through the points which scatter a bit but not as much as expected is 2.5. This factor was then used along with that of the previous section to make a tentative estimate of the shape factor V/L as illustrated in the following section. Using this estimate of V/L, one can then go back and partially at least correct the $(E_p^{obs} - 0.0348V)$ values used above for slight differences in the shape factor, obtaining thereby a better value than 2.5 for the polarity factor which can then be used to redetermine V/L. etc. Thus, by the method of successive approximations we obtain finally the value 2.4 for the rate of change of E_p with respect to $\Delta\Delta H$, or more concisely,

$$(8-1) \qquad (\partial E_p / \partial \Delta\Delta H)_{V,V/L} = 2.4$$

Since from Table 6 we observe that variations of 3-4 kcal/mole in $\Delta\Delta H$ are not unusual, E_p may frequently vary from 7.2 - 9.6 kcal/mole because of the polarity factor alone. From equation (7-1) one estimates that it takes a change in molar volume of from 7.2/0.0348 = 206 to 9.6/0.0348 = 276 cc to cause such a change in E_p. **Such changes in size are unusual** (Table 6), the majority of the molar volumes fluctuating by one-half to one-third this amount, demonstrating again that the polarity factor is generally two or three times as important as the size factor.

Now, as already indicated in this section, we are prepared to estimate the importance of shape, other things being equal.

9. The Dependence of E_p Upon Shape.

The consideration of this variable has been left to last because, first of all, the size factor could be obtained immediately from the straight chain paraffins without any quantitative information whatsoever concerning either

the shape or polarity factors, and secondly because prior information and preliminary calculations definitely indicated that of the remaining two polarity was in most instances the dominating factor. Thus, whereas small variations in the shape factor threw off the initial $\Delta\Delta H$ calculation somewhat, even seemingly minor variations in $\Delta\Delta H$ would make it virtually impossible to draw reliable quantitative conclusions regarding the shape factor. That is to say the method of successive approximations converges most rapidly if we start with the polarity factor and then proceed to the shape factor as follows.

First, however, it would perhaps be in order at this point to explain why V/L was chosen as quantitative measure of the effect of molecular shape upon E_p.

Up to now the molecules that have been considered--those of sections 7 and 8--have all been essentially rodlike in character. No mention has been made of the more compact molecules such as ter-butyl alcohol, cyclohexane, or ortho-xylene which in every case (Table 3) have a larger E_p than the corresponding rod-like molecules.

This is to be expected, for it seems likely that the increase in E_p for cyclohexane over that for n-hexane arises from the fact that in permitting a molecule to diffuse from one equilibrium lattice site to another the polymer must open up a bigger hole for cyclohexane than for n-hexane. This is reflected in E_p. That is, n-hexane can squeeze through a smaller hole than cyclohexane. For this reason, an attempt has been made in the past to correlate E_p values (actually the E_d part of E_p) with the dimensions of the smallest hole through which the molecules can pass ("The Diffusion of Some Halo-Methanes in Polystyrene" by G. S. Park, Trans. Far. Soc. 46, 684 (1950)). Although it served to account for some of the experimental facts, this smallest-hole theory was not entirely successful in reducing the data to a common denominator even though relatively few compounds were studied perhaps in part because polar effects which we have found to be so important were not considered. It seems likely, therefore, that the smallest-hole theory really hasn't been given a fair test. Nevertheless, we reject it in favor of the V/L index for the following reasons.

First of all, it is often difficult to clearly determine a "smallest hole" for a molecule using molecular models, for by twisting the model around a bit it can be made to slip through a hole in a piece of plywood or cardboard which very often is significantly smaller than the smallest tube through which the model will pass. That is, the effect of the diameter of your "smallest hole" depends upon just how thick your hole is, and it isn't at all obvious what this thickness should be. Off hand one might guess possibly the length of two methyl groups (about 4-5 cm using the Fisher-Taylor-Hirschfelder models), but this could only be checked by constructing a whole set of holes of varying thicknesses and diameters which could then be used to obtain several sets of "smallest hole" dimensions to try on the data. All in all a fairly lengthy project. Furthermore, insofar as the following observations are correct, it isn't exactly the dimension of the "smallest hole" we want anyway.

For consider several of the isomers of decane. According to the smallest-hole theory 2,2-dimethyl octane and 2,2,3,3-tetramethyl hexane will have the same energy of activation, for they will pass through the same "smallest hole" (and they have essentially the same molar volumes). Still one just sort of feels that the tetramethyl isomer is bulkier than the dimethyl octane and should experience greater difficulty in getting through polyethylene. The reason for this seems to be that since polyethylene is a linear polymer, one naturally expects that random thermal motion of the polymer segments will open up rod shaped holes more often than spherically shaped ones of equal volume. There are perhaps more elegant ways of putting this. Thus, in comparing n-decane, 2,2-dimethyl octane, and 2,2,3,3-tetramethyl hexane, we could say that the standard free energy of formation in polyethylene of banana-shaped holes is less than that for pear-shaped holes which in turn is less than that for small watermel on-shaped holes, the volume of the holes being the same in each case, namely $194/6 \times 10^{23}$ cm^3 (Table 6).

In any event, whether we use every-day language or that of the Absolute Reaction Rate Theory, all we are suggesting at this point is that polyethylene will in fact distinguish between the two isomers of n-decane mentioned above. Since the smallest-hole theory does not predict this, we reject it for the V/L parameter which does. Furthermore, L is easily determined by simple measurement although here too there is ambiguity in some cases. Generally what has been done is to stretch the model out straight and take the longest linear dimension for L. (We shall encounter an interesting refinement upon this, however, whan we consider para-derivatives of benzene.)

We might summarize the argument leading up to the choice of V/L by saying that this parameter gives us a better measure of over-all bulkiness, the significant factor, than does the diameter of the smallest hole through which the molecule can pass.

For the straight chain hydrocarbons V/L is constant at about 12. The presence of an oxygen atom in an essentially linear molecule decreases the parameter by about a unit or so. Table 6 shows that the value of V/L most often falls between 9 and 12 with water and formic acid (5.2 and 6.7 respectively) and ter-butyl alcohol, cyclohexane, and ortho-xylene (15.9, 15.6, and 13.9 respectively) at the extremes.

To show the essence of the method used to determine the dependence of E_p upon V/L, we compare in Table 7 the parameters for ethyl acetate and cyclohexane as given in Tables 3 and 6.

Table 7

A Comparison of Ethyl Acetate and Cyclohexane.

Substance	V_{cc}	$\Delta\Delta H$	V/L cc/cm	0.0348V cc	2.4$\Delta\Delta H$ kcal/mol	E_p kcal/mol
Ethyl Acetate	97.9	2.4	10.6	3.4	5.8	17.7
Cyclohexane	81.4	0.6	15.6	2.8	1.4	16.2

Since the ethyl acetate molecule is both larger (column 2) and more polar (column 3) than the cyclohexane molecule, we expect that (equations 7-1 and 8-1) owing to these factors its activation energy will be greater by $(3.4+5.8)-(2.8+1.4)=5.0$ kcal/mole (columns 5 and 6) whereas in fact (last column) the difference is only $17.7-16.2=1.5$ kcal/mole in this direction. We say then that the E_p for cyclohexane has been raised relative to that for the acetate ester by $5.0-1.5=3.5$ kcal/mole because it is bulkier (column 4) by $15.6-10.6=5.0$ units. That is, in this case the rate of change of E_p with respect to V/L is $3.5/5=0.70$.

A number of substances (ethyl acetate, methyl ethyl ketone, dibutyl ether, acetone, the paraffins, and cyclohexane) have been compared in essentially this manner by plotting $(E_p-0.0348V-2.4\Delta\Delta H)$ against V/L. The best straight line through the points has a slope of 0.75, so that we have finally to go along with equations (7-1) and (8-1) the following value for the shape factor:

$$(9-1) \qquad (\partial E_p/\partial V/L)_{V,\Delta\Delta H} = 0.75$$

As already observed, the parameter V/L generally falls between 9 and 12. Hence the contribution the shape factor makes to E_p may often by expected to vary by about $3(0.75)=2.2$ kcal/mole though seldom by twice this amount. Comparing this with the results of the previous sections, we conclude, therefore, that generally speaking the polarity factor is most important followed by size and then shape. These three factors are synthesized into a single expression in the following section.

10. The Quantitative Dependence of E_p Upon Size, Shape, and Polarity.

To summarize the argument up to this point concerning the structure of E_p, it was suggested in section 6 that the observed activation energy for permeation should depend upon three factors relating to the properties of the permeant molecule, namely its size, shape, and polarity. In principle then variations in the observed E_p values are decomposable into three parts as indicated below.

$$(10-1a) \quad dE_p = (\partial E_p/\partial size)_{shape,\ polarity}\ d(size) + (\partial E_p/\partial shape)_{size,\ polarity}\ d(shape)$$

$$+ (\partial E_p/\partial polarity)_{size,\ shape}\ d(polarity).$$

If we take the molar volume V (the gram molecular weight divided by the density) as a measure of size, the parameter V/L (L = the length of the stretched-out Fisher-Taylor-Hirschfelder molecular models) as an indication of over-all shape, and $\Delta\Delta H$ (defined in equation 5-3) as an index of polarity, equation (10-1a) becomes

$$(10\text{-}1b) \qquad dE_p = (\partial E_p/\partial V)_{V/L,\Delta\Delta H}dV + (\partial E_p/\partial V/L)_{V,\Delta\Delta H}d(V/L)$$
$$+ (\partial E_p/\partial\Delta\Delta H)_{V,V/L}d(\Delta\Delta H).$$

In the preceding sections (7, 8, and 9), it was shown how the data of this project could be manipulated to yield values for the differential coefficients appearing in equation (10-1b). Using these results (equations 7-1, 8-1, and 9-1), we obtain finally

$$(10\text{-}1c) \qquad dE_p = 0.0348dV + 0.75d(V/L) + 2.4d(\Delta\Delta H).$$

The problem now is to integrate this equation. Proceeding directly as indicated, we get

$$(10\text{-}2a) \qquad E_p = 0.0348V + 0.75(V/L) + 2.4(\Delta\Delta H) + \text{constant}$$

where the constant of integration remains to be evaluated. Note, however, that this can not be done simply by arguing that $E_p \to 0$ as $V \to 0$ since V/L and $\Delta\Delta H$ do not necessarily approach zero with V even if E_p should, and, in fact, the evidence is against even this too.

One could, of course, proceed empirically at this point, substituting into (10-2a) from Tables 3 and 6. If concordant results were obtained, this procedure would not only yield a reliable value for the integration constant, but also, it would seem, should serve as a check on the assumption inherent in the derivation of (10-2a) that the differential coefficients in (10-1b) are independent of the values for V, V/L, and $\Delta\Delta H$. Actually, this seems unlikely. Thus, for example, one expects that the rate of increase in the energy required to form a hole with respect to increasing V or V/L should itself increase with increasing $\Delta\Delta H$. That is to say, one suspects that actually the differential coefficients $(\partial E_p/\partial V)_{V/L,\Delta\Delta H}$ and $(\partial E_p/\partial V/L)_{V,\Delta\Delta H}$ are increasing functions of $\Delta\Delta H$ rather than constants with the values 0.0348 and 0.75 respectively. This does not look too good for the theory. Fortunately there is a rather elegant way out of all this.

First we observe that although E_p increases with say V, E_p is not proportional to V as can be seen from the fact that E_p increases from 12.8 to only 15.6 in going from pentane to decane; that is, $E_p(2V,V/L,\Delta\Delta H) \neq 2E_p(V,V/L,\Delta\Delta H)$. If, however, at the same time V is doubled V/L and $\Delta\Delta H$ are also doubled, and if then E_p doubles, or, more generally, if

$$(10\text{-}2b) \qquad E_p(\lambda V,\lambda V/L,\lambda\Delta\Delta H) = \lambda E_p(V,V/L,\Delta\Delta H)$$

where λ is any arbitrary positive number, it follows immediately from Euler's theorem for homogeneous functions that

$$(10\text{-}2c) \qquad E_p = (\partial E_p/\partial V)_{V/L,\Delta\Delta H}V + (\partial E_p/\partial V/L)_{V,\Delta\Delta H}(V/L)$$
$$+ (\partial E_p/\partial\Delta\Delta H)_{V,V/L}(\Delta\Delta H).$$

The discussion leading to equation (10-2c) does not require that the differential coefficients be constant over the whole range of possible V, V/L, and $\Delta\Delta H$ values. Nevertheless, within the range of experimental interest the coefficients do indeed appear to be nearly constant in value as indicated by equations (7-1), (8-1) and (9-1). Substituting from these into (10-2c), we obtain finally

(10-2e) $E_p = 0.0348V + 0.75V/L + 2.4\Delta\Delta H$

where the integration constant of equation (10-2a) appears with a "theoretically" assigned value of 0. In the following section we begin a comparison of equation (10-2e) with experiment.

11. The Calculation of E_p Values for the Aliphatic Hydrocarbons, Ethers, Esters, and Ketones.

Using equation (10-2e) and the data of Table 6, E_p values for straight-chain compounds with polarities ranging from 0.0 to 3.0 are calculated and compared with experiment as shown in Table 8.

Table 8

Theory and Experiment Compared for Straight-Chain Compounds
With Polarities Between 0 and 3.

Substance	0.0348V cc	0.75V/L cc/cm	2.4$\Delta\Delta H$ kcal/mole	E_p calc. kcal/mol	E_p exp. kcal/mol	Diff. kcal/mol
n-Pentane	4.0	9.0	0.0	13.0	12.8	+0.2
n-Heptane	5.0	9.0	0.0	14.0	13.2	+0.8
n-Decane	6.7	9.0	0.0	15.7	15.6	+0.1
n-Tetradecane	9.0	9.0	0.0	18.0	18.0	+0.0
Dibutyl ether	5.9	8.5	1.9	16.3	16.0	+0.3
Cyclohexane	3.7	11.7	1.4	16.8	16.2	+0.6
Ethyl Acetate	3.4	8.0	6.7	18.1	17.7	+0.4
ME Ketone	3.1	8.5	6.7	18.3	18.0	+0.3
Acetone	2.6	8.5	7.2	18.3	18.7	-0.4
Amyl Acetate	5.1	8.4	6.0	19.5	19.4	+0.1

There are several things of interest in Table 8. First of all,

a. The hypothesis of a value zero for the integration constant of equation (10-2a) is confirmed. In fact, since as recorded in the last column the calculated value is usually slightly greater than the observed value,

b. The overall fit of the data by equation (10-2e) could undoubtedly be improved a bit by a slight readjustment in the three parameters 0.0348,

0.75, and 2.5. Nevertheless,

      c. The three parameter equation generally reproduces the ten observed values to within 2-3%. Hence it is felt that

      d. Equation (10-2e) can certainly reliably predict the order of magnitude of activation energies for the aliphatic hydrocarbons, ethers, esters, and ketones. By the order of magnitude of E_p we mean that the corresponding P values (equation 1-1) will not be in error by more than a factor of ten. From equation (1-2) it follows that at room temperature this amount of leeway requires that E_p be correct to within 1.4 kcal/mole. For an accuracy within a factor of two, the E_p calculation must not be in error by more than 0.4 kcal/mole. At higher temperatures less accuracy is required. Also, the method for estimating P_o values (to be presented later) automatically compensates in part for errors in E_p. Thus agreement between theory and experiment better than that suggested above would not be surprising. Finally,

      e. The structure of E_p is nicely revealed by the first three columns of figures. For example, the Master Plot shows that tetradecane and ME ketone exhibit similar permeability behavior but, as Table 8 shows, for rather different reasons: the size and polarity factors, operating in opposite directions, tend to cancel.

12. <u>The Calculation of E_p Values for the Aromatic Hydrocarbons, the Substituted Aromatic Hydrocarbons, and Dipentene.</u>

In this section we consider to what extent our formula for E_p is applicable to the aromatic compounds and the cyclic compound dipentene.

The values listed for E_p as E_p^{calc} in column 3 of Table 9 are calculated using equation (10-2e) and the data of Table 6. These are followed by the experimental values in column 4 and then a column headed E_p^{corr} to be explained later.

<div align="center">

Table 9

Theoretical and Experimental E_p Values for Some
Aromatic Compounds

</div>

Compound	Ref. Cpd. for $\Delta\Delta H$ Calc.	E_p^{calc}	E_p^{exp}	E_p^{corr}	$E_p^{corr} - E_p^{exp}$
Benzene	Hexane	13.1	13.3	13.1	-0.2
o-Xylene	Octane	16.0	15.6	16.0	+0.4
p-Xylene	Octane	14.7	13.4	13.7	+0.3
Chlorobenzene	Heptane	15.6	14.2	14.3	+0.1
p-Chlorotoluene	Octane	17.2	15.8	15.4	-0.4

The calculated value for benzene is probably within experimental error, that for o-xylene a bit high, and p-xylene is considerably off (1.3 kcal/mole). Chlorobenzene and p-chlorotoluene are also each too high by 1.4 kcal/mole.

These discrepancies may merely reflect second order structural effects that are inadequately accounted for by a single shape factor such as V/L. The structures of these molecules are shown below in Figure 4.

| Benzene | o-Xylene | p-Xylene | Chlorobenzene | p-Chlorotoluene |
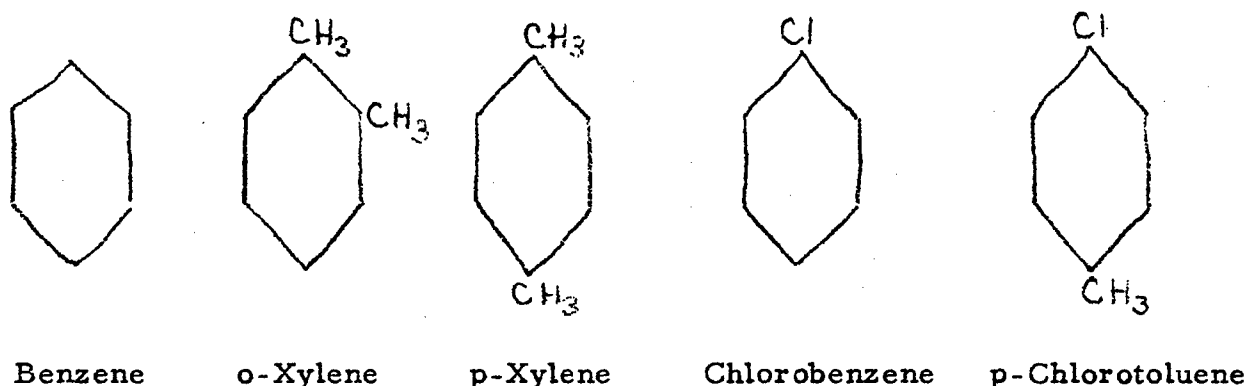
Fig. 4 Structures of Aromatic Compounds

Now presumably once a hole has been opened up large enough to accomodate a diffusing benzene molecule, it makes little difference if we then attach methyl groups fore and aft as in p-xylene since this is probably "dead air space" anyway; p-xylene is so to speak "streamlined".

Similarly, the chlorine atom which tags along with the benzene nucleus in chlorobenzene probably is acting in a partial vacuum so far as its polarity effects are concerned.

If we apply a correction of 0.5 kcal/mole for each methyl group in p-xylene and 1.3 kcal/mole for the chlorine atom in chlorobenzene, we obtain so-called corrected values as listed in the fifth column of Table 9. Applying both of these corrections to the last molecule, p-chlorotoluene also brings its calculated value into reasonable agreement with experiment.

With respect to these calculations, we observe that

     a. Although they are undoubtably based upon an over-simplified model, and

     b. Although they are highly empirical,

     c. It is nevertheless a fact that whereas the first two values in Table 9 agree about as usual with experiment, the last three are off by more than two or three times the usual amount.

d. Furthermore, it might be mentioned that the correction suggested by the p-xylene - benzene comparison did not at first seem to account for results obtained on chlorobenzene and p-chlorotoluene. A check of all the calculations involved finally revealed an error in the 1 mm column of **Chart 1 on page 16 of Dreisbach.**

e. Finally, this "streamlined" effect also seems to be operative in the case of the dipentene molecule pictured below in Figure 5.
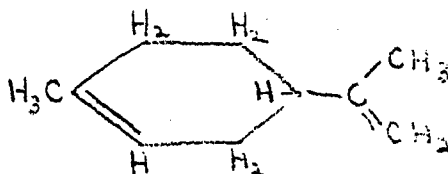
Fig. 5. Structure of Dipentene

Treating this compound as a hydrocarbon ($\Delta\Delta H = 0$), we calculate that $E_p = 0.0348(162) + 0.75(15.1) = 16.9$ kcal/mole as compared to the observed value of 16.0 kcal/mole.

In general, then, we expect that para-substituted compounds will have E_p values about 1 kcal/mole less than that calculated using equation (10-2e).

The following section gives some calculations on the more highly polar, strongly hydrogen-bonded alcohols and acids whose $\Delta\Delta H$ values are greater than 3.0.

13. Calculated and Experimental E_p Values for the Alcohols and Acids.

Table 10

Substance	0.0348V cc	0.75V/L cc/cm	2.4$\Delta\Delta H$ k/cal/mol	E_p^{calc} k/cal/mol	E_p^{exp} k/cal/mol	Difference
n-Propanol	2.6	7.2	14.9	24.7	22.1	+2.6
n-Butanol	3.2	7.5	14.0	24.7	22.4	+2.3
sec-Butanol	3.2	8.9	12.9	25.0	23.0	+2.0
ter-Butanol	3.3	11.9	11.5	26.7	26.2	+0.5
n-Octanol	5.5	8.1	12.2	25.8	22.5	+3.3
Phenol	3.0	7.7	12.5	23.2	21.2	+2.0
Acetic Acid	2.0	6.8	14.6	23.4	17.8	+5.6
Butyric Acid	3.2	6.5	17.7	27.4	18.3	+9.1

The explanation for the relatively large discrepancies between the calculated (equation 10-2e) and experimental values is probably this.

Suppose these substances dissolve in polyethylene as dimers rather than single monomeric molecules. (Additional evidence for believing this will be presented later.) Then when it comes to diffusing from one equilibrium position to another there exist at least two possibilities:

(1) The dimer splits apart as the transition state for diffusion is approached, or

(2) The dimer as a whole diffuses from one equilibrium position to another.

Now presumably all polar substances are to some extent associated (dimerized) in polyethylene which so to speak is a poorly ionizing--or, better, poorly dissociating--solvent; i.e., it has no great tendency to solvate (dissolve) the solute. Thus solute-solute contacts as pictured in Fig. 6 are energetically favored over solute-solvent (polyethylene) contacts, and at absolute zero (no random thermal motion) dimerization would be complete. (In fact, at this temperature even the dimers, which undoubtably still exhibit a slight residual polarity, would tend to dimerize, etc. until eventually a pure phase begins to separate out, merely another way of saying that at T=0 the solubility is zero.)
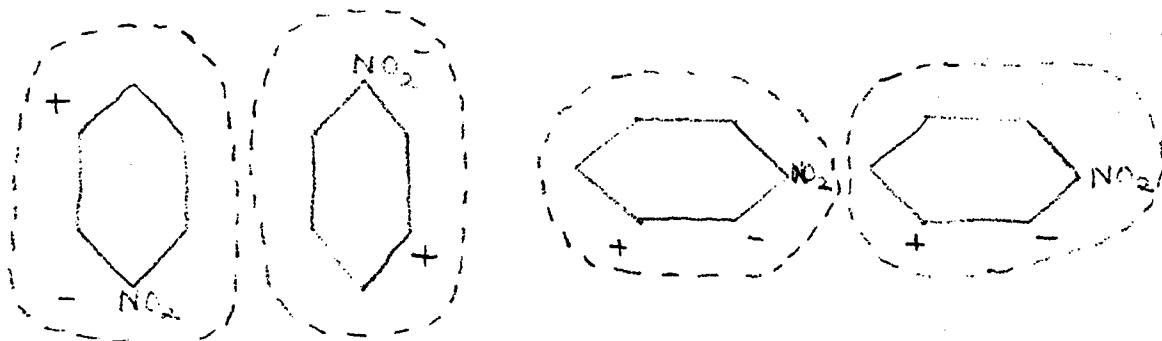
Figure 6

Mutual Attraction of Dipoles in Nitrobenzene

(G. Briegleb, Zwischenmolekulare Kraftz and Molekulstruktur Pg. 55)

But at any finite temperature random thermal motion (the entropy effect) will tend to break up the dimers until the free energy (E-TS) is a minimum. For the slightly polar ethers this thermal breakdown is probably nearly 100% complete at room temperature. There is no reason in this case for suspecting that the diffusing species is anything other than the simple monomeric molecule.

With a slightly more polar substance such as acetone, however, there may be some association, both in the pure liquid and in the liquid dissolved

in polyethylene. On the other hand, the gas in this case is not associated so that the full polarity of acetone shows up in $\Lambda\Delta H$ as it will too in E_p if it is the monomer that diffuses rather than the dimer; that is, if it is thermo-dynamically easier to break the not-too-strong intermolecular bonds between two acetone molecules and push through a single molecule of acetone rather than conserve at the first point by leaving such dimers as there are alone and then trying to push through this bulkier unit later on. In cases such as this the reasoning leading up to the introduction of the polarity factor $\Delta\Delta H$ is valid and we expect equation (10-2e) to hold.

Still, there must eventually come a point where it is thermodynamically uneconomical to sever the dimer before diffusion. Tetradecane, for example, undoubtably diffuses as just that: a 14 carbon hydrocarbon, rather than as two "heptane" fragments. This, of course, is an extreme case. Indeed, the "intermolecular force" between two seven carbon tetradecane fragments is essentially a strong, localized, honest-to-goodness 100% chemical bond. This bond (along with all the other bonds in the molecule) is so strong that even the possibility of great randomness in the gaseous state fails to cause the molecule to dissociate upon vaporization. Whatever "polarity" we might wish to ascribe to a tetradecane fragment is thus completely hidden from us at all times. At no point is there ever any excuse for including the great "polarity" of any tetradecane fragment in the $\Delta\Delta H$ for this substance.

With the alcohols and the acids, however, this is not the case. The intermolecular bonds here are, relative to the hydrocarbons, ethers, esters, and ketones very strong, so strong, in fact, that they earn a special name: hydrogen bonds
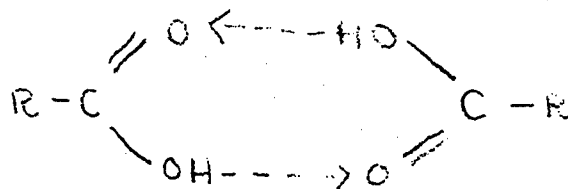

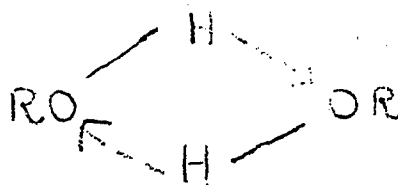Figure 7

Hydrogen Bond in Acids

Figure 8

Hydrogen Bond in Alcohols

But the hydrogen bonds in the alcohols and acids are not strong enough to maintain a degree of dimerization in the gaseous state anything like that in the liquid state. Hence pretty much the full polarity of these substances shows up in the heat of vaporization and, therefore, in $\Delta\Delta H$. When it comes to diffusing in the polymer, however, this $\Delta\Delta H$ factor is weighted rather heavily (the factor is 2.4), and in these alcohols and acids it is apparently thermodynamically easier to diffuse the dimer rather than the more polar although smaller monomer.

If we knew the shape of the dimer (Figure 6) and its residual polarity, it should be possible to calculate by equation (10-2e) a value for E_p which then could be compared with that for the simple molecule itself. Other things being equal (namely P_o), the observed E_p would be the lower of the two. Unfortunately neither the shape nor the polarity of the dimer are known.

With these remarks in mind, we turn back to a consideration of Table 10.

Among the alcohols the calculated value is on the average about 2.1 kcal/mole too large except in the case of ter-butanol which, owing to both its great bulkiness and reduced polarity, probably still diffuses as the dimer. The aromatic alcohol phenol behaves like the aliphatic alcohols in so far as E_p is concerned.

The two acids in Table 10 deviate from "ideal" behavior even more than the alcohols, reflecting, no doubt, the well established fact that hydrogen bonding in the carboxylic acids is stronger than in the corresponding alcohols (Table 4). Indeed, the hydrogen bonding in acetic acid is known to carry over to some extent to the gaseous state, hiding, therefore, some of its polarity as indicated by $\Delta\Delta H$. It might well be that a study of gas imperfections and the temperature variation of the second virial coefficient would reveal the reasons for the discrepancies between acetic and butyric acid recorded in the last column of Table 10.

Table 11

Comparison of Some Calculated and Observed E_p Values

Material	Calc. E_p k/cal/mol	Obs. E_p k/cal/mol
Diacetone Alcohol	26	21.9
Allyl Alcohol	23	20.2
Methyl Alcohol	26.7	17.7
Water	23.5	18.4
Formic Acid	20.2	16.7
Benzaldehyde	17.9	19.3
Butyraldehyde	16.7	19.0

In diacetone alcohol the difference (26.0-21.9=4.1) is larger than in the other alcohols because the ketone oxygen may be partially screened in the dimer; allyl alcohol is not far off from the other alcohols, and the great decrease (26.7-17.7=9.0) found for methyl alcohol is probably explained by the tendency of this relatively small molecule to trimerize, etc.* Water also probably tends to form higher polymers although there are no methyl groups to screen the oxygens in this case, and the decrease in E_p is only 5.1 kcal/mole. Formic acid continues the trend already observed with the other two acids. Finally, the calculated values for the relatively non-polar aldehydes are strangely too <u>low</u> by 1.3-1.4 kcal/mole.

14. The Calculation of E_p. A Summary.

From the above and earlier remarks, it is abundantly evident that the penetration of polyethylene by organic solvents is a very selective process, one which not infrequently is significantly dependent upon seemingly unimportant structural features. Nevertheless, it now seems possible to predict quite good activation energies for the aliphatic hydrocarbons, ethers, esters, and ketones with only a three parameter equation, and with the equation

$$(14-1) \qquad E_p = 0.0348V + 0.75V/L + 2.4\Delta\Delta H - C$$

reasonably reliable predictions can be made for the substituted aromatics, aldehydes, and the higher alcohols provided the following values are used for C.

Table 12

Values for the Parameter in Equation (14-1)

Class of Compounds	Value to Use for C
Straight Chain Hydrocarbons, sat'd	0
Branched Hydrocarbons, sat'd	0
Unsaturated Hydrocarbons	0
Cyclic Hydrocarbons	0
Ethers	0
Esters	0
Ketones	0
Aromatic Hydrocarbons	0
para-substituted Compounds	1
Alcohols	2.3
Aldehydes	-1.3

* Propanol may be doing this a bit too.

If information on one or two more acids were available equation (14-1) could probably be extended to this class of compounds, which has not been included in the table below.

Table 13

Comparison of Calculated and Observed E_p

Substance	E_p^{calc} kcal/mol	E_p^{exp} kcal/mol	$E_p^{calc} - E_p^{exp}$
n-Pentane	13.0	12.8	+ 0.2
n-Heptane	14.0	13.2	+ 0.8
n-Decane	15.7	15.6	+ 0.1
n-Tetradecane	18.0	18.0	0.0
Cyclohexane	16.8	16.2	+ 0.6
Dibutyl Ether	16.3	16.0	+ 0.3
Ethyl Acetate	18.1	17.7	+ 0.4
Amyl Acetate	19.5	19.4	+ 0.1
Acetone	18.3	18.7	- 0.4
Methyl Ethyl Ketone	18.3	18.0	+ 0.3
Benzene	13.3	13.1	+ 0.2
o-Xylene	16.0	15.6	+ 0.4
p-Xylene	13.6	13.4	+ 0.2
Chlorobenzene	14.3	14.1	+ 0.2
p-Chlorotoluene	16.2	15.8	+ 0.4
Dipentene	15.9	16.0	- 0.1
Butyraldehyde	19.0	19.0	0.0
Benzaldehyde	19.2	19.3	- 0.1
n-Propanol	22.4	22.1	+ 0.3
n-Butanol	22.4	22.4	0.0
sec-Butanol	22.7	23.0	- 0.3
ter-Butanol	26.7	26.2	+ 0.5
n-Octanol	23.5	22.5	+ 1.0
Phenol	20.9	21.2	- 0.3

The average error in the calculated value for the activation energies of the two dozen compounds listed in Table 13 is 0.2_6 kcal/mole although this value should not be taken too seriously inasmuch as the table was constructed with these compounds very much in mind. In practice it might not be too optimistic to expect that application of equation (14-1) to similar substances will yield E_p values reliable to within twice this average error or 0.5 kcal/mole on the average. As already mentioned, to know P itself within a factor of ten, it would be well to be off by not more than 1.4 kcal/mole on E_p.

15. Interlude.

The discussion up to now has been concerned almost entirely with the parameter E_p of equation (1-3);nothing yet has been said about P_o although from the last column of table 3 it appears that this parameter varies much more from compound to compound than does E_p. This observation, however, overlooks the exponential dependence of P upon E_p. As shown in equation (1-3) it is the logarithm of P_o rather than P_o itself that should be compared with E_p. Indeed, we have observed already that at room temperature a change of 1.4 kcal/mole in E_p alters P tenfold. A spread in E_p from 26.2 (ter-butyl alcohol) to 12.8 (n-pentane) represents, therefore, approximately a 10^{10} fold variation in the exponential factor of equation (1-1) whereas the factor P_o varies only somewhat less than 10^7 fold. (The variations of the two factors work in opposition so that P itself at room temperature shows a spread of about 0.26 (ter-butyl alcohol) to 526 (n-pentane); about a 2000 fold change.)

This then was one of the principle reasons for discussing E_p first. It is 1000 times more important than P_o. With information on E_p, furthermore, a single measurement of P at some convenient temperature will enable one to predict P-Factors from say -40°F to 212°F, for knowing P at some T and also E_p, one can solve either equation (1-2a) or (1-3) for P_o. Of course P_o if known along with one P-Factor would serve to determine E_p rather than vice-versa. But the factors that determine P_o are not as familiar nor as well understood as the effect of size, shape and polarity upon E_p.

In short, the problem of E_p is one of energetics. It resolves itself into concrete geometrical factors and familiar intermolecular interactions. The problem of P_o, on the other hand, is essentially one of entropy. It generally involves one in numerous difficulties about which unfortunately there is little concrete or familiar. To start the thermodynamical discussion of P_o, we begin by considering the absorption tests, which are also of interest from the point of view of the activation energy E_p.

16. The Master Solubility Data.

These data have already been reported by Plax as the grams of penetrant absorbed per gram of polyethylene, herein called Q. For the slightly soluble solvents Q is almost identical with the weight fraction of the pene-

trant in the (slightly) swollen polymer. What we require in all cases, however, is the volume fraction (ϕ). If we let p stand for the polymer and 2 for the penetrant, the two volume fractions are, respectively,

(16-1)
$$\phi_p = (n_p v_p^o)/(n_p v_p^o + n_2 v_2^o) \quad \text{and}$$

$$\phi_2 = (n_2 v_2^o)/(n_p v_p^o + n_2 v_2^o)$$

where the n's are the mole numbers (n. 6.10^{23} =number of particles) and the v^o's represent the molar volumes of the pure components. Naturally $\phi_p + \phi_2 = 1$.

The conversion from Q to say ϕ_p is given quite simply by

(16-2)
$$\phi_p = 1/(1 + D_p Q/D_2).$$

For the density D_p of polyethylene we have used the following values: 0.935, 0.922, 0.910, and 0.898 at 32°F, 70°F, 100°F, and 130°F respectively. The densities of the penetrants were calculated from data given in the International Critical Tables.

It might be observed at this point that equations (16-1) and (16-2) assume the volume of the swollen polymer can be calculated directly from the volumes of the pure starting materials. Experimental evidence bearing on this will be presented later.

In the table below the substances are listed approximately in order of increasing solubility in polyethylene at 70°F.

Table 14

Equilibrium Volume Fractions, ϕ_2, and χ Values for Some Organic Solvents in Polyethylene.

Solvent	32°F ϕ_2	32°F χ	70°F ϕ_2	70°F χ	100°F ϕ_2	100°F χ	130°F ϕ_2	130°F χ
Water			0.0009	6.0				
Methanol			0.0011	5.80				
Formic Acid	0.0012	5.75	0.0019	5.28	0.0027	4.90	0.0032	4.74
Ethylene Glycol	0.0020	5.23	0.0025	5.00	0.0037	4.60	0.0051	4.28
Acetic Anhydride	0.0025	5.02	0.0026	4.94	0.0034	4.68	0.0059	4.13
n-Propanol	0.0023	5.10	0.0037	4.60	0.0062	4.08	0.0099	3.70
Diacetone Alc.	0.0036	4.63	0.0050	4.30	0.0072	3.93	0.0118	3.52
Nitroethane	0.0036_5	4.62	0.0052	4.26	0.0067	4.00	0.0100	3.68
Glycerine	0.0050	4.30	0.0053	4.24	0.0064	4.08	0.0069	4.02
n-Butanol	0.0046	4.37	0.0066	4.03	0.0095	3.65	0.0141	3.37
Aniline	0.0064	4.05	0.0090	3.70	0.0128	3.45	0.0189	3.10
Butyl Cellosolve	0.0065	4.03	0.0097	3.67	0.0131	3.44	0.0209	2.98
Acetic Acid	0.0066	4.03	0.0092	3.66	0.0102	3.55	0.0166	3.23
Butyl Phthalate	0.0051	4.28	0.0109	3.60	0.0147	3.33	0.0227	2.95
sec-Butanol	0.0061	4.08	0.0115	3.55	0.0171	3.20	0.0283	2.75
ter-Butanol	0.0085	3.76	0.0130	3.44	0.0189	3.11	0.0310	2.67
Acetone	0.0108	3.62	0.0144	3.35	0.0183	3.13	0.0258	2.83
n-Octanol	0.0076	3.88	0.0148	3.33	0.0189	3.11	0.0317	2.65
Nitrobenzene	0.0129	3.45	0.0184	3.13				
Benzaldehyde	0.0158	3.27	0.0214	3.00	0.0288	2.74	0.0424	2.41
ME Ketone	0.0194	3.08	0.0252	2.84	0.0314	2.66	0.0447	2.37
Ethyl Acetate	0.0216	2.98	0.0272	2.77	0.0352	2.57	0.0464	2.33
Acetaldehyde	0.0224	2.95	0.0308	2.67				
n-Butyraldehyde	0.0246	2.87	0.0327	2.63	0.0456	2.35	0.0622	2.09
Amyl Acetate	0.0283	2.75	0.0384	2.48	0.0551	2.18	0.0867	1.83
Isopropyl Amine	0.0476	2.32	0.0627	2.08	0.0797	1.90		
Diethyl ether	0.0882	1.88	0.0933	1.77				
Tetradecane	0.0910	1.79	0.1030	1.70	0.1205	1.59	0.176	1.34
Dibutyl Ether	0.0800	1.90	0.0995	1.74	0.1337	1.53	0.1840	1.32
Decane	0.0964	1.75	0.117	1.62	0.157	1.42	0.213	1.23
n-Heptane	0.122	1.58	0.134	1.52	0.171	1.36	0.236	1.17
Iso-pentane	0.125	1.57	0.137	1.50				
Pentene-2	0.143	1.48	0.150	1.45				
n-Pentane	0.133	1.52	0.141	1.48				
Benzene	0.130	1.54	0.138	1.50	0.178	1.33	0.237	1.17
p-Chlorotoluene	0.128	1.55	0.146	1.47	0.188	1.30	0.302	1.02
Chlorobenzene	0.134	1.53	0.147	1.46	0.190	1.29	0.310	1.01
Ortho-Xylene	0.144	1.47	0.163	1.38	0.228	1.18	0.319	0.99
Para-Xylene	0.153	1.43	0.167	1.37	0.222	1.19	0.322	0.98
Cyclohexane	0.185	1.32	0.208	1.21	0.283	1.06	0.458	0.82

By definition, $\chi = \dfrac{-\log e\,(1-\phi_p) - \phi_p}{\phi_p^2}$, ϕ_p the equilibrium value.

17. Observations on the Master Solubility Data.

The volume fraction ϕ_2 recorded in Table 14 if not equal to is at least equivalent to the solubility coefficient S in the relation P = DS. It is not surprising, therefore, that the order of increasing ϕ_2 in Table 14 is essentially that already observed for P, namely: alcohols, acids, nitroderivatives, aldehydes, ketones, esters, ethers, and hydrocarbons. Such inversions as occur in the solubility order arise from systematic trends in solubility for members of any given homologous series, which naturally cause some overlaping unless corresponding members have widely different solubilities. The P values themselves overlap less than the solubilities because the diffusion factor D is also sensitive to polarity, which varies from functional group to functional group; in general D accentuates polar effects already discernable in S.

The trend in S within any homologous series pretty much follows the general solubility rule that "like dissolves like". As a polar functional group of a molecule is diluted with non-polar hydrocarbon fragments, the molecule as a whole approaches polyethylene in all of its properties, and the solubility increases. Table 15 illustrates this effect. The normal paraffins constitute an understandable exception to this rule. They are all pretty much like polyethylene to start with (There is from the solubility point of view no noticeable improvement in over-all polarity in tetradecane over say pentane.). But it seems reasonable to expect that once the polymer itself has set and partially crystallized--in this partially crystalline, partially amorphous state it is believed that each polymer molecule may pass alternately through several crystalline and amorphous areas so that in effect polyethylene is a cross-linked polymer at room temperature, the individual crystallites serving as tie points.--reorientation of the polymer segments is restricted. Therefore pentane is more easily accommodated than tetradecane, for penetration by the latter requires considerable rearrangement on the part of the polymer. Of the solvents studied, cyclohexane seems to be just about the best in this respect.

Table 15

The Trend in Solubility Within
a Homologous Series.

Substance	Solubility 70°F volume fraction
Water	0.0009
Methanol	0.0011
n-Propanol	0.0037
n-Butanol	0.0066
n-Octanol	0.0148
Formic Acid	0.0019
Acetic Acid	0.0097
Nitroethane	0.0052
Nitrobenzene	0.0184
Acetaldehyde	0.0308
n-Butyraldehyde	0.0327
Acetone	0.0144
ME Ketone	0.0252
Ethyl Acetate	0.0272
Amyl Acetate	0.0384
Diethyl Ether	0.0933
Dibutyl Ether	0.0995

An interesting and significant feature of the absorption tests shows up when comparing the order of increasing solubility with the order of increasing E_p. Since a large solubility suggests a large P whereas a large E_p implies a small P, one expects a large solubility to be associated with a correspondingly small E_p. With respect to the homologous series as a whole, this is by and large true. There is, of course, a certain amount of overlap to be expected between the large members of one series and the small members of the series above (on the E_p scale). Thus tetradecane overlaps ethyl acetate, but in general the hydrocarbons with the largest solubilities have the smallest E_p's and the alcohols with the smallest solubilities have the largest E_p's.

However, within any one homologous series just the reverse tends to be the case: large solubilities tend to be associated with large rather than

small activation energies; the order of increasing E_p for the straight chain alcohols is just the order of Table 15 and likewise for formic and acetic acid.

This seemingly anomolous behavior is more apparent than real when one realizes that diffusion is much more structure sensitive than solubility. (The E_p's for ortho- and para-xylene are 15.6 and 13.4 respectively, although their solubilities are nearly identical.) An increase in the length of the hydrocarbon chain attached to a polar functional group almost invariably seems to increase E_p (the 0.0348V term of equation 10-2e) and just as invariably increases the solubility in polyethylene too. The reason for the E_p increase with size has been discussed. The reason for the increase in the solubility of a polar molecule with increasing length of the hydrocarbon chain is due at least in part to the following effect.

A flexible hydrocarbon tail in a polar molecule can swing back and screen the polar group from interactions with similar groups on other molecules. In such instances the molecule will appear less polar than it might otherwise. The probability of such internal shielding acts therefore to increase the similarity between penetrant and polyethylene and consequently enhances the solubility.

It seems very likely that the solubility data indicate the operation of this internal shielding effect in the series water, methyl alcohol (no shielding at all possible in these two), n-propyl, n-butyl, and n-octyl alcohol. As one should expect, the degree of shielding increases with hydrocarbon length.

The molecular models also show that acetone is an excellent example of a molecule where no internal shielding is possible. This helps explain its position in the tables.

Shielding effects also help account for the relative behaviors of the three butyl alcohol isomers. The effect is least for n-butanol with its terminal hydroxyl group and greatest in ter-butanol where the polar hydroxyl group is embedded in a rather compact hydrocarbon matrix. These functional group structural features are reflected by both their polarity factors (n-butanol = 6.0, sec-butanol = 5.4, ter-butanol = 4.8) and their solubilities (0.0066, 0.0115, and 0.0130 respectively).

To summarize, then, as one goes from say pentane to an ester of essentially the same shape and size, the polarity of the molecule (its $\Delta\Delta H$) increases, the solubility decreases and E_p increases. If now one adds to the hydrocarbon portion of the ester, the overall size of the molecule increases of course, but its polarity decreases, and the solubility, which depends primarily upon polarity, now begins to increase; E_p, which depends upon both size and polarity, continues to increase although the two effects work in opposition here and seem nearly to cancel in the case of the straight-chain alcohols whose E_p values all hover pretty closely around 22.3 kcal/mole.

18. An Introductory, Thermodynamical Discussion of the Flory-Huggins Polymer Interaction Parameter χ.

The concept of molecular disorder of a system and its measure, the so-called entropy S has been considered. At absolute zero all systems strive to minimize their internal energy E (with a small term PV added to allow for pressure effects; i.e., actually it is E+PV $\stackrel{\cdot}{=}$ H, the enthalpy, that is minimized). The entropy of a perfectly ordered crystal at this temperature is zero. Observe, however, that although essentially all molecular motion ceases at absolute zero so that there is no thermal contribution to the over-all randomness or entropy of the system, supercooled liquids (i.e., glasses) do have a residual entropy at absolute zero relative to perfectly oriented crystals simply because of the random orientation of their molecular constituents.

We distinguish, therefore, two types of entropy: namely entropy arising from the random thermal vibrations and rotations of atoms, molecules, and polymer segments, symbol S_{th}, and entropy arising from randomness in position called entropy of configuration, symbol S_{cf}. The total entropy of any system is the sum of these two.

Now, at any temperature T above absolute zero all systems tend to adopt a certain amount of disorder: atoms begin to vibrate, molecules begin to rotate, and pure phases begin to dissolve in each other to form random mixtures. This all increases the entropy and, of course, the energy too, for it requires some of this to do all of these things. Clearly the energy is no longer a minimum under these conditions, nor is the entropy (i.e., the disorder) a maximum, for we could increase the haphazardness of the system by breaking down all molecules into atoms, and then these into free electrons, protons, and neutrons, etc. But at any reasonable temperature these later possibilities just seem energetically unlikely. This assessment of the situation is reduced by thermodynamics to the statement that at constant T and P all systems tend to strike a happy medium between maximizing their entropy (with a rise in internal energy) and minimizing their internal energy (with a decrease in entropy) by actually minimizing their so-called free energy, $F \stackrel{\cdot}{=} H - TS$.

From this statement about minimizing the total free energy of a system, it follows that the free energies of the components of a system at equilibrium must be the same throughout for otherwise in transfering a small amount of one component from one part of the system to another where its free energy is different the total free energy of the system would change; if the overall change were negative, the process would be a natural one since it is tending to decrease the free energy and should in time take place spontaneously, which is to say that the system was not initially in equilibrium. On the other hand, if the change should turn out to be positive, just the opposite transfer of matter would lead to a decrease in the total free energy as before.

We can perhaps see from this that the free energy of a substance is

essentially a measure of its stability. The greater the free energy (large H and/or small S), the more likely it is that the substance can possible revert to some form with a smaller free energy, i.e., the less its stability. This is sometimes put in another way: The greater the free energy of a substance, the greater its escaping tendency (as measured often by its vapor pressure), activity, or so-called fugacity. Thermodynamically these all mean essentially the same thing.

For a pure organic solvent in equilibrium with a strip of polyethylene, this discussion informs us that the escaping tendency (say the vapor pressure) of the solvent from the pure solvent phase must be equal to the escaping tendency of the solvent from the swollen polymer phase.

Thermodynamically this simply means that at equilibrium

$$(18-1) \qquad \bar{F}_2^{Liq} = \bar{F}_2^P$$

where as before 2 stands for the penetrating species and p for the polymer. The little superscript bars merely indicate that it is the actual contribution that species 2 makes to either the liquid or polymer phase that is important. Sometimes the combination $\bar{F}$ is replaced by the single symbol μ (mu). (Also, when using the $\bar{F}$ notation the escaping tendency is most often referred to as the "partial molal free energy" and, when using μ, as the "chemical potential"--all just names and symbols for the same thing however.)

Writing out the fundamental equality above in more detail, we get

$$(18-2) \qquad \bar{H}_2^L - T\bar{S}_2^L = \bar{H}_2^P - T\bar{S}_2^P$$

which upon rearranging becomes

$$(18-3) \qquad \bar{H}_2^P - \bar{H}_2^L = T(\bar{S}_2^P - \bar{S}_2^L), \text{ or}$$

$$(18-4) \qquad \Delta\bar{H}_2 = T\Delta\bar{S}_2$$

where in general $X \equiv$ (the X value for the polymer phase) - (the X value for the liquid phase).

These equations show that from the thermodynamic point of view the problem of absorption equilibrium is one of determining when the heat of solution of the solvent in the polymer, $\Delta\bar{H}_2$, is equal to the entropy of solution (multiplied by T), $T\Delta\bar{S}_2$.

According to Hildebrand (Hildebrand and Scott, "The Solubility of Non-Electrolytes", 3rd ed., p129), the heat of solution is essentially,

$$(18\text{-}5) \qquad \Delta \bar{H}_2 = \phi_p^2 \, v_2^0 \left[(\Delta E_2^{\text{vap.}} / v_2^0)^{1/2} - (\Delta E_p^{\text{vap.}} / v_p^0)^{1/2} \right]^2$$

where the terms in parentheses raised to the 1/2 power are the "solubility parameters" or "cohesive energy density".

Observe that $\Delta \bar{H}_2$ depends upon the polymer volume fraction ϕ_p squared. As this approaches zero (case of infinite swelling, i.e., complete solution of the polymer), so does $\Delta \bar{H}_2$ as we might expect, for this corresponds to mixing pure solvent with essentially pure solvent.

On the other hand, for the polar, rather insoluble solvents the polymer volume fraction, $(1 - \phi_2)$, is essentially unity even at the point of maximum swelling (Table 14). This means that it must be the $T\Delta \bar{S}_2$ term that varies as equilibrium is being established until finally equation (18-4) is satisfied.

At this point it is convenient to refer to our earlier discussion and decompose $\Delta \bar{S}_2$ into two parts;

$$(18\text{-}6) \qquad \Delta \bar{S}_2 = \Delta \bar{S}_2^{\text{th}} + \Delta \bar{S}_2^{\text{cf}}.$$

The first term represents the entropy changes that occur during mixing (solvent dissolves in polymer) owing to alterations in the random thermal motions (rotations and vibrations) of the atoms and molecules.

The second term represents always an increase in entropy that arises upon mixing owing to the increased number of configurational arrangements possible for the mixture over those available to the pure components. The now classical statistical calculation of this configurational entropy of mixing for the case of simple structureless systems dissolving in similar systems is given in Appendix A to this report. The problem becomes considerably more complex, however, when one of the components of the mixture is a polymer composed of long flexible molecules. For one must allow for the fact in computing the total number of possible geometrical arrangements that each polymer molecule may possibly be curled up, stretched out straight, bent in a zig-zag fashion, etc. although, of course, no two segments can occupy the same site (the so-called excluded volume effect). These possibilities all contribute to an entropy of mixing that is much greater than what one would obtain if the polymer molecules were treated as simple monomers. On the other hand, the entropy of mixing is less than what one would calculate if each segment of a polymer molecule were treated as an independent species. Using the simplest possible model, Flory and Huggins obtained the following now almost classical formula for $\Delta \bar{S}_2^{\text{cf}}$.

$$(18\text{-}7) \qquad \Delta \bar{S}_2^{\text{cf}} = -R \, \log_e (1 - \phi_p) + \phi_p \qquad \text{(For uncrosslinked, amorphous polymers)}$$

At this point the theory stops. There is not yet a reliable theoretical estimate of $\Delta \bar{S}_2^{\text{th}}$. For non-polar systems thermal randomness may be pretty much undisturbed by mixing, in which case $\Delta \bar{S}_2^{\text{th}} = 0$. But only by

chance would we expect $\Delta \bar{S}_2^{th}$ to be zero for polar solvents dissolving in polyethylene. Furthermore, equation (18-5) is theoretically valid only for relatively non-polar systems. In view of all this indeterminateness, the two terms $\Delta \bar{H}_2$ and $T\Delta \bar{S}_2^{th}$, which appear together always in the combination $\Delta \bar{H}_2 - T\Delta \bar{S}_2^{th}$, are lumped into a single parameter χ (chi) multiplied by ϕ_p^2 (since by (18-5) it is known that in some cases at least the first term, $\Delta \bar{H}_2$, varies in this way with composition).

(18-8)
$$\chi(RT\phi_p^2) = \Delta \bar{H}_2 - T\Delta \bar{S}_2^{th}, \text{ or}$$

(18-9)
$$\chi = \frac{\Delta \bar{H}_2}{RT\phi_p^2} - \frac{\Delta \bar{S}_2^{th}}{R\phi_p^2} \qquad (R = \text{gas constant})$$

If we use (18-5) with

(18-10)
$$B = v_2^o \left[(\Delta E_2^{vap}/v_2^o)^{1/2} - (\Delta E_p^{vap}/v_p^o)^{1/2} \right]^2$$

equation (18-9) becomes

(18-11)
$$\chi = \frac{B}{RT} - \frac{\Delta \bar{S}_2^{th}}{R\phi_p^2}$$

χ is formally known as the Flory-Huggins polymer interaction parameter.

Substituting now from (18-8), (18-7) and (18-6) into (18-4), we find that at equilibrium

(18-12)
$$\Delta \bar{H}_2 - T\Delta \bar{S}_2 = (\Delta \bar{H}_2 - T\Delta \bar{S}_2^{th}) - T\Delta \bar{S}_2^{cf} = (RT\phi_p^2) + RT \left[\log_e(1-\phi_p) + \phi_p \right] = 0.$$

which shows that the value of the interaction parameter for swollen systems can be obtained from solubility data.

19. The Evaluation of the Polymer Interaction Parameter From Equilibrium Swelling Measurements.

From equation (18-12) the value of the interaction parameter at equilibrium is

(19-1)
$$\chi = \frac{-\log_e(1-\phi_p) - \phi_p}{\phi_p^2}$$

where the volume fraction ϕ_p is assigned its equilibrium value.

Rather than substitute from Table 16-1 ($\phi_p = 1 - \phi_2$) directly into (19-1) to obtain χ values, the function on the right-hand side of equation (19-1) was plotted against the penetrant volume fraction ϕ_2 as shown schematically in Figure 9 and the values of χ at equilibrium read off from this using the calculated equilibrium volume fractions as tabulated in Table 14. The values so obtained have been included in Table 14.
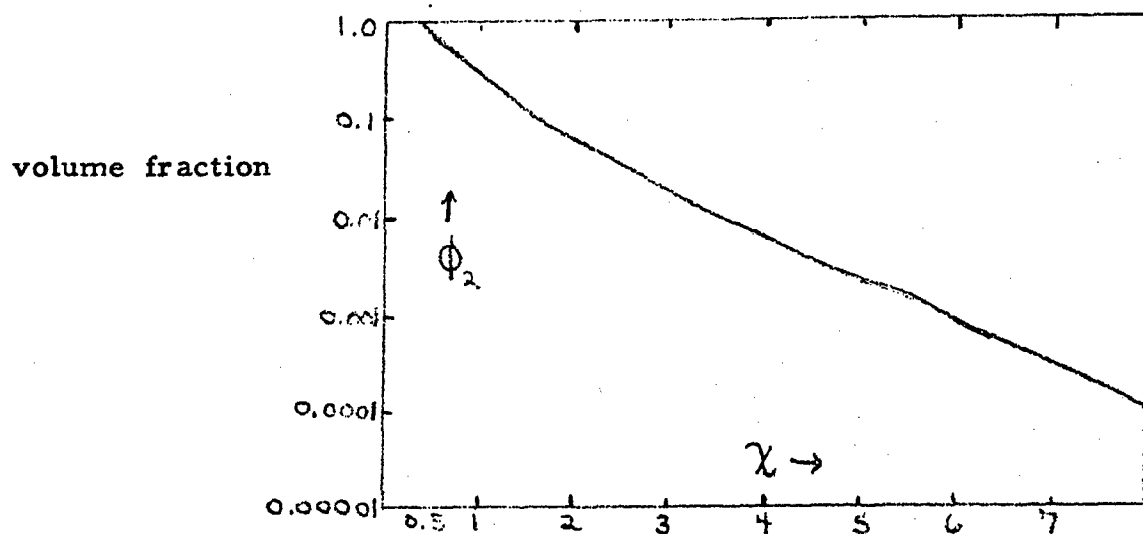

volume fraction

Fig. 9. Curve Used to Obtain χ at Equilibrium

20. χ Values for Organic Solvents and Polyethylene.

Although equilibrium swelling measurements have been used to obtain estimates of the magnitude of the interaction parameter (equation 19-1), it is perhaps more natural to think of χ as determining the degree to which swelling may occur. As figure 9 shows, there is a regular decrease in the equilibrium penetrant volume fraction as χ increases.

This decrease in swelling with increase in χ is not unexpected; equation (18-9) shows that χ depends directly upon the heat of solution, $\Delta \bar{H}_2$, of the penetrant in the polymer, and swelling should decrease as $\Delta \bar{H}_2$ increases; since the latter depends upon the polarity of the penetrant, the interaction parameter should show some correlation with our polarity index $\Delta\Delta H$ (Cf. Appendix B).

Comparison of Tables 6 and 14 reveals that in a general way the order of decreasing $\Delta\Delta H$ and decreasing χ is the same, namely: alcohols, the esters and ketones, the ethers, and, finally, the hydrocarbons. Indeed, Table 16 demonstrates that not only is the order of the functional groups preserved in passing from one parameter to the other, the trend within any homologous

series is preserved also. This is perhaps more than might be expected at first since (equation 18-9) the interaction parameter is a free energy term (actually the free energy of mixing exclusive of configurational effects divided by RT) whereas $\Delta\Delta H$ is strictly a heat term. As we shall see later, however, there is reason to believe often that the thermal part of the entropy change, $\Delta \bar{S}_2^{th}$, varies with the heat term, increasing as $\Delta \bar{H}_2$ increases and decreasing as ΔH_2 decreases. To the extent that this is so, χ will vary directly with $\Delta\Delta H$. Depending upon one's feelings about entropy, one may thus either consider the correlations of Table 16 to be "explained", or one may prefer to consider the data of the table as strong supporting evidence for the supposition that $\Delta \bar{S}_2^{th}$ varies with $\Delta \bar{H}_2$ (or else is essentially constant).

Table 16

The Dependence of the Interaction Parameter
Upon Polarity.

Substance	$\Delta\Delta H$ kcal/mol.	$\chi_{70^\circ F}$
Water (approx.)	9	6.00
Methyl Alcohol	7.1	5.80
n-Propyl Alcohol	6.3	4.60
n-Butyl Alcohol	6.0	4.03
sec-Butyl Alcohol	5.4	3.55
ter-Butyl Alcohol	4.8	3.44
n-Octyl Alcohol	4.8	3.33
Acetic Acid	6.1	3.66
Acetone	3.0	3.35
Methyl Ethyl Ketone	2.8	2.84
Benzaldehyde	2.5	3.00
n-Butyraldehyde	2.4	2.63
Ethyl Acetate	2.8	2.77
Amyl Acetate	2.5	2.48
Isopropyl Amine	2.1	2.08
Diethyl Ether	1.2	1.77
Dibutyl Ether	0.8	1.74
n-Decane	0.0	1.62

The following features of Table 16 are of special interest at this point. First of all,

     a. It was observed that ethyl acetate and methyl ethyl ketone have similar P-Factors at each of the temperatures studied; their solubilities in polyethylene are also nearly the same all along the line. Of the two, the acetate has the larger solubility and the smaller E_p. Both of these facts may reflect the possibility that exists for greater screening in the acetate of the ketone oxygen (the center of polarity in the molecule) by the ethyl group.

<div align="center">

Table 17

P-Factors and Solubilities of Ethyl Acetate and

Methyl Ethyl Ketone

(From Tables V and XXIV of Part 1)
</div>

| Temp $^\circ$F | Ethyl Acetate | | Methyl Ethyl Ketone | |
	P-Factor[1]	Solubility[2]	P-Factor[1]	Solubility[2]
32	1.9	0.0218	3.7	0.0175
70	16.5	0.0273	12.6	0.0225
100	83.3	0.0353	60.0	0.0282
130	378.	0.0466	326.6	--
165	1703.	--	1401.0	--

(1) gms/24 hrs/0.001 in./100 in.^{2}

(2) gms/gms polyethylene

     b. Two amines were studied in this project: aniline and isopropyl amine. The P-Factors for the former do not fall on a smooth curve on the Master Plot, so no E_p value has been calculated for it. And only two points are available for the other, which boils at 93°F. The E_p value calculated from these is 3 kcal/mole greater than that obtained using equation (10-2e). This all leaves the amine question an open one although there seems to be no compelling reason to expect them to deviate greatly from the norm established by the esters and ketones of similar polarity. In this respect, it seems not unusual to find the solubility (or χ value) of isopropyl amine in line with the other compounds listed near it in Table 16.

     c. The regularity of the $\Delta\Delta H - \chi$ correlation implies that the latter can be estimated from the former. Since one can estimate $\Delta\Delta H$ values from Dreisbach's tables knowing only boiling points, this $\Delta\Delta H - \chi$ correlation means that equilibrium up-take values can be predicted from readily available physical data. This assumes, of course, that the character of the polyethylene is the same. Even if it weren't, the order of Table 16 should be unaltered.

Observe that for substances with $\Delta\Delta H$ values between 2 and 3 the χ value at 70°F is just about numerically the same as $\Delta\Delta H$.

d. Finally, it is probably significant that the hydrogen-bonded substances (the alcohols and acids) exhibit χ values noticeably smaller than one would expect from their $\Delta\Delta H$ values. That is, with regard to solubility at least they don't look as polar as their heats of vaporization would suggest. Acetic acid, which is known to have strong dimerization tendencies, is especially anamolous, being slightly less soluble in polyethylene than acetone. Apparently association through hydrogen bond formation largely nullifies the inherent polarity of this substance, as seen upon vaporization, so far as the comparatively mild solution process is concerned. The substance dissolves as the relatively non-polar dimer rather than the highly polar monomer.

So much for Table 16 and χ values at 70°F. Next to be considered is the temperature variation of the interaction parameter. Under favorable conditions such information should in principle (equation 18-9) yield information on both $\Delta\bar{H}_2$ and $\Delta\bar{S}_2^{th}$.

21. **The Temperature Variation of the Polymer Interaction Parameter.**

The form of equation (18-11) suggests a plot of the interaction parameter against $1/T$ at constant ϕ_p. Unfortunately this is not possible since χ is only known for the swollen polymer systems at equilibrium, and the volume fraction at equilibrium naturally changes from one temperature to the next. Nevertheless, for the more polar substances the absolute values of ϕ_2 are small and hence, also, their variations; i.e., for the slightly soluble substances ϕ_p is always nearly unity.

Plotting χ values for the polar compounds against $1/T$, one finds that the 70, 100, and 130 degree points generally fall on or near a straight line but that the 32°F point almost invariably indicates an abnormally high solubility at this temperature. On the assumption that the hygroscopic nature of the penetrants was at least in part responsible for this anomolous behavior, the following data were obtained from the slopes and intercepts at $1/T = 0$ of the best straight lines through the 70, 100, and 130 degree points.

Table 18

Approximate Heats and Entropies of Solution in Polyethylene.

Substance	$\Delta \bar{H}_2$ kcal	$\Delta \bar{S}_2^{th}$ e.u.
n-Propanol	4.8	7.2
Dibutyl Phthalate	4.3	7.4
Ethylene Glycol	4.1	4.0
n-Octanol	4.0	6.9
n-Butanol	3.8	4.8
sec, ter-Butanol	3.9	6.1
Formic Acid	3.3	0.5
Acetic Acid	2.6	1.5
Acetone	3.0	3.5

The values of Table 18 are probably accurate to only one significant figure, if even that. The relative values scaled to acetone are presumably better, and it seems fairly certain that the process of solution for the carboxylic acids is somewhat unique considering the great contribution of the carboxyl group to the cohesive energy of organic liquids (Table IV). In view of the inherent large polarity of the carboxylic acids, the relatively small $\Delta \bar{H}_2$ and $\Delta \bar{S}_2$ (especially) indicate that in these cases the solute exists as a dimer in polyethylene.

Another way to express this argument would be to observe that $\Delta \bar{H}_2$ should be given by $\Delta\Delta H$, and indeed this is, perhaps somewhat fortuitously, exactly true for acetone. But for all the other substances listed in Table 18 $\Delta \bar{H}_2 < \Delta\Delta H$; the heat of solution is less than the polarity index would suggest. The reason for this is that our polarity index $\Delta\Delta H$ has been evaluated from data for the monomer species whereas it appears that it is the less polar dimer species that is, in fact, of interest here.

This same problem arose in the calculation of E_p for highly associatiated substances. If the dimer is the predominant diffusing species, then we should use $\Delta\Delta H_{dimer}$ rather than $\Delta\Delta H_{monomer}$ in the $2.4\Delta\Delta H$ term of equation (10-2e). Lacking information on $\Delta\Delta H_{dimer}$, we were unable to check this suggestion. But now it seems that we perhaps can in at least one instance.

The permeability data and the temperature variation of the permeability together with the solubility data and the temperature variation of the solubility data all strongly suggest that in the case of acetic acid and formic acid the dimer is the principle solute species in swollen polyethylene, even during diffusion. For these carboxylic acids, then, it is $\Delta\Delta H_{dimer}$ that we require in equation (10-2e). Moreover, it is just this quantity that is reflected by the

heat of solution, which we have. The chain of reasoning is thus this:

(21-1) $\quad\quad\quad\quad\quad \Delta\Delta H_{\text{for acetic acid}} = \Delta\Delta H_{\text{dimer}} = \Delta\bar{H}_2 = 2.6$ kcal/.mole
and polyethylene

rather than the value entered in Table 6, $6.1 = \Delta\Delta H_{\text{monomer}}$. Using this dimer value in equation (10-2e) and remembering that for a linear dimer the size factor is twice that for the monomer and the shape factor is essentially the same, we calculate for E_p a value of 17.1 as against the observed value of 17.8 and the monomer value of 23.4 kcal/mole. For formic acid the values are $(E_p^{\text{calc}})_{\text{monomer}} = 20.2$, $(E_p^{\text{calc}})_{\text{dimer}} = 15.9$, and $E_p^{\text{observed}} = 16.7$. In each case our improved calculation is low by about 0.7 to 0.9 kcal/mole. This is to be expected if a small part of the acid diffuses as the monomer.

There are several factors that make it difficult to extend this sort of calculation to the alcohols. The strength of the hydrogen bond is less than in the carboxylic acids and consequently the degree of dissociation upon diffusion will be greater. Also, the shape of the dimers may vary, and there may even be trimers, etc. in some cases.

When we come now to consider the solubility behavior of less polar, more soluble substances such as the hydrocarbons, a number of new complicating features enter the picture. Here for really the first time it appears that we must in some way explicitly allow for the structure of polyethylene itself.

22. The Solubility Behavior of the Hydrocarbons and the Structure of Polyethylene.

Perhaps the very first thing one observes regarding the interaction parameter - 1/T plots is their marked departure from linearity. Scarcely ever is it possible to fit even three of the points with a straight line whereas the $32°$, $70°$, $100°$ and $130°$F points all often lie on a smooth curve, the curve being such that the solubility seems to increase too rapidly with increasing temperature. This seemingly anomolous hydrocarbon solubility behavior is at first inspection most disconcerting but upon reflection rather revealing. At this writing the data have not been quantitatively accounted for. It seems very likely, though, that any satisfactory explanation of the hydrocarbon problem will be mainly a matter of giving quantitative expression to the following observations.

a. The reduction of equation (18-9) to (18-11) depended upon the fact that $\Delta\bar{H}_2$ is proportional to ϕ_p^2 (equation 18-5). And even if $\Delta\bar{H}_2$ isn't given precisely by (18-5) nor B by (18-10), the latter may still be nearly independent of the polymer volume fraction over a considerable range so that the form of (18-11) follows with B now a to-be-determined empirical constant.

The second term of (18-11) is, however, probably not independent of ϕ_p. ΔS_2^{th} must, of course, approach zero as the polymer becomes infinitely dilute, but it need not depend precisely upon the square of the polymer volume fraction to do this, and if the dependence upon ϕ_p is anything less than this, the whole term, $\Delta S_2^{th}/R\phi_p^2$, will increase as the polymer volume fraction decreases with increasing temperature, more will thus be subtracted from the positive B/RT term at high temperatures than at low, and curvature in the χ vs $1/T$ plot will tend to be as observed. In short, if the entropy term is not proportional to the square of the polymer volume fraction, the interaction parameter will be a function of the composition in addition to the temperature. This supposition is subject to direct experimental verification, (equilibrium absorption studies at different partial pressures).

b. Then there is the partial crystallinity of the polymer to consider. As the temperature is raised, the material becomes progressively less crystalline. This raises problems of a very fundamental sort. For suppose, as seems likely, that the penetrants penetrate only the amorphous regions; that is, we suppose that there are no solid solution effects. The crystalline material remains pure. Then of course our solubility data should be reported as grams absorbed per gram of amorphous polyethylene, which may be less than 50% of the total. This is the really fundamental quantity. Unfortunately it is not easily obtained either by theory or experiment. Of the usual experimental methods for determining percent polymer crystallinity, probably only the x-ray method would work here.

Nevertheless, it is easy enough to see in what direction our data should be altered. In every case of partial crystallinity the "actual" concentration of the penetrant is greater than we first thought. From figure 9 it is apparent that this means that all of the χ values in Table 14 should be lowered. (For the slightly soluble polar substances and 50% crystallinity, the correction is about -0.69 in χ. Thus the ΔH_2 values given in Table 18 will be unaffected, the full brunt of the correction falling on ΔS_2^{th}.) We have then that the interaction parameter is essentially infinite for crystalline polyethylene (no swelling) and less than the figures given in Table 14 for amorphous polyethylene (limited swelling). (Incidentally, figure 9 shows that swelling is infinite at χ equal to 0.5.)

Now we come to an important point. Of all the values listed for a given solvent in Table 14, the $32°$ values will have to be corrected the most and the $130°$ values (less crystallinity) the least. This may help explain the curvature in the apparent solubility curves: as the temperature is raised, the solubility does not actually increase as rapidly as the absorption tests suggest for the effective weight of the polymer (i.e., amount of amorphous material) is increasing. But if this is true of the hydrocarbons, why isn't it also true of the other solvents ?

Well, to some extent it is, and for this reason the data of Table 18 are only approximate as indicated. But for the slightly soluble substances the curvature in the χ vs. $1/T$ plots was much less than it was for the less polar

substance. This is perhaps not altogether surprising. Polyethylene completes its melting somewhere around 240°F. At 130°F there probably isn't too much melting going on in the pure polymer, and as the volume fraction figures in Table 14 show, polymer swollen to its maximum with say butyl alcohol or even acetone is still nearly pure polymer at all the temperatures studied. But this is far from the case for the more soluble hydrocarbons, especially at 130°F. At such high penetrant concentrations the properties of the swollen polymer are likely to be significantly different from the properties of the pure polymer at the same temperature.

c. In particular, the crystalline polymer - amorphous polymer equilibrium will be disturbed toward the amorphous polymer side. Another way of putting this is to say that the melting points of the crystalline regions are lowered as one dissolves "anti-freeze" in the amorphous regions.

In this respect ethylene glycol is a poor "anti-freeze" owing to its very limited solubility in amorphous polyethylene. On the other hand the hydrocarbons with their inherently large solubility in amorphous polyethylene are "good" anti-freezes and may well cause a significant amount of melting of the crystalline regions at 130°F.

With this discussion of polymer crystallinity, freezing point lowering effects, and $\Delta \bar{S}_2$ behind us, we are in a position to introduce an important although heretofore neglected feature of swelling equilibrium in polyethylene.

d. It may be introduced this way: Why doesn't polyethylene dissolve completely in a hydrocarbon such as decane? After all, decane is a non-polar substance ($\Delta\Delta H = 0$). Therefore its heat of solution, $\Delta \bar{H}_2$, in polyethylene should be small (zero according to our earlier discussions of this). This implies (equation 18-9) a small value for χ and therefore an infinite amount of swelling (Figure 9. Polymers dissolve in any solvent for which $\chi < 0.5$). Yet actually the swelling in decane is limited. This almost forces one to conclude that polyethylene is in effect cross-linked. (Figure 9 applies to only non-cross-linked polymers. For cross-linked polymers the swelling is always limited.) This notion has already been introduced in Section 17. It was pointed out there that each polymer molecule may pass alternately through several amorphous and crystalline regions. Thus no matter how much the amorphous regions may swell the polymer as a whole remains rigid so long as there are any appreciable number of crystalline tie points present.

It may at first seem strange that cross-linking should affect the interaction parameter primarily through the entropy term of equation (18-9) rather than the energy term, $\Delta \bar{H}_2$. But Flory and Rehner have shown that this is the case. The physical picture is simply this: as a cross-linked polymer is swollen by a penetrant the segments of the polymer molecules in the swollen regions are stretched out into unnatural elongated shapes. This decreases their configurational entropy. The theory suggests a simple correction of $(-Rv_2^0 \phi_p^{1/3}/v_c)$ to (18-7), the fundamental equation for non-cross-

linked polymers. Here as before v_2^o is the molar volume of the pure penetrant; v_c is the so-called molar volume of the polymer between cross-links. For a polymer in which there is no cross-linking v_c is infinite and the correction term above vanishes.

This all means that for cross-linked polyethylene (i.e., any crystalline polyethylene of average molecular weight) the term $\Delta \bar{S}_2^{th}$ we introduced as the purely thermal part of the entropy of mixing does in fact contain a configurational part, namely the entropy of elastic stretching of the polymer. Using the Flory-Rehner expression for this, we write

$$(22\text{-}1) \qquad \Delta \bar{S}_2^{th} = \Delta \bar{S}_2^{th'} - Rv_2^o \phi_p^{1/3}/v_c$$

where now, insofar as the theory has properly assessed configurational effects, $\Delta \bar{S}_2^{th'}$ is a purely thermal entropy term.

Equation (22-1) provides a quantitative explanation of the hydrocarbon non-vanishing χ values. Even if $\Delta \bar{H}_2 = \Delta \bar{S}_2^{th'} = 0$, one still has that

$$(22\text{-}2) \qquad \chi = \frac{v_2^o}{v_c \phi_p^{5/3}}$$

Equation (22-2) suggests several interesting "experiments" none of which has been tried.

For example, what values do the data on the various hydrocarbons give for v_c, and how does v_c vary with the temperature? Since v_c is a parameter characteristic of the polymer itself, its value should be the same in all penetrant-polymer systems of the same degree of crystallinity. And reliable information on the increase in v_c with temperature would tell us just how melting proceeds in these systems. The difficulty of course is that the melting information is required in order to obtain v_c in the first place.

Incidentally, equation (22-2) predicts the order of χ values for pentane, decane, and tetradecane actually observed. The smaller the molar volume of the penetrant, the smaller χ and ϕ_p must be if v_c is to be constant.

This essentially completes our discussion of the absorption tests. We conclude with a few remarks about the polarity index $\Delta\Delta H$ and its relation to the cohesive energy density, (C.E.D. $\equiv \frac{\Delta E^{vap}}{v^o}$) Also the thickness measurements will be briefly reviewed. Then we take up the last part of the P-Factor problem, the P_o factor of equation (1-2a).

23. The Polarity Index $\Delta\Delta H$ and its Relation to the Cohesive Energy Density.

According to equation (18-5) the heat of solution of a substance (component 2) in polyethylene (component p) is proportional to the square of the difference between the square roots of their respective cohesive energy densi-

ties, (the molar heat of vaporization divided by the molar volume). By slight rearrangement, we obtain

$$(23\text{-}1) \qquad \Delta\bar{H}_2 = \phi_p^2 \left[(\Delta E_2^{vap})^{1/2} - (\Delta E_p^{vap} v_2^o / v_p^o)^{1/2} \right]^2$$

which is to be compared to our $\Delta\Delta H$,

$$(23\text{-}2) \qquad \Delta\Delta H = \Delta E_2^{vap} - \Delta E_p^{vap} (v_2^o / v_p^o)$$

where the second term of (23-2) clearly corresponds to the second term of equation (5-3): "the heat of vaporization of a hydrocarbon of similar size."

Although the two equations look quite alike when ϕ_p is nearly one (the case for which $\Delta\Delta H$ was introduced), they yield rather different values. For example, if the two terms in (23-2) are 16 and 9 respectively, $\Delta\Delta H = 7$ whereas by (23-1) $\Delta\bar{H}_2 = 1$.

24. Swelling Index.

These data are reported as the thickness of the swollen polyethylene strips, L, minus their original thickness, L^o, divided by L^o. Let us call this quantity λ, '

$$(24\text{-}1) \qquad \lambda = (L - L^o)/L^o,$$

and let L_1, L_2, and L_3 be the final dimensions (those of the swollen strip) and L_1^o, L_2^o, and L_3^o the original dimensions (those of the unswollen polyethylene itself) of a strip. Then in general

$$(24\text{-}2) \qquad L_i = L_i^o(1+\lambda_i) \qquad i = 1, 2, 3.$$

If the strips are isotropic, $\lambda_1 = \lambda_2 = \lambda_3 = $ just λ say. This very possibly is not entirely true in the present instance, but we shall have to assume that it is. For then we can write that the volume V of the swollen polymer is

$$V = L_1 L_2 L_3 = L_1^o L_2^o L_3^o (1+\lambda)^3$$

where, of course, $L_1^o L_2^o L_3^o = V^o$, the volume of the pure polyethylene formerly symbolized as v_p^o. Expanding and rearranging, we find that

$$(24\text{-}3) \qquad (V - V^o)/V^o = 3\lambda(1 + \lambda + \lambda^2/3).$$

This expression is to be compared with our assumption earlier (Section 16) that the volume V of the swollen polymer is just the volume V^o of the pure polymer plus the volume m_2/D_2 of the pure penetrant. (Here $m_2 =$ weight of penetrant = increase in weight of the strip). The volume additivity

assumption implies therefore that

(24-4) $$(V-V^o)/V^o = (m_2/D_2)/(m_p/D_p) = Q(D_p/D_2)$$

where $Q = m_2/m_p = $ "grams absorbed per gram of polyethylene."

The two expressions, $3\lambda(1+ \lambda + \lambda^2/3)$ and $Q(D_p/D_2)$, have been compared at 32°, 70°, 100° and 130^oF for all substances as soluble as ethyl acetate; for substances less soluble than ethyl acetate the swelling was really almost too small to be determined accurately by direct linear measurement. In fact, the weight measurements generally seem to be approximately three times as precise (as judged by their reproducibility) as the linear measurements. Table 19 lists some representative values for these two expressions.

Table 19

A Comparison of the Absorption Tests and the Thickness Data. $\Delta V/V^o \equiv 3\lambda(1+\lambda+\lambda^2/3)$.

Substance	32° F	70° F	100° F	130° F
Ethyl Acetate				
$Q(D_p/D_2)$	0.0221	0.0280	0.0365	0.0486
$\Delta V/V^o$	0.01	0.014	.015-.034	.020-.048
Amyl Acetate				
$Q(D_p/D_2)$	0.0291	0.0400	0.0582	0.0950
$\Delta V/V^o$	.015-.024	.024-.039	.026-.043	.068-.093
Dibutyl Ether				
$Q(D_p/D_2)$	0.0869	0.1108	0.1556	0.225
$\Delta V/V^o$	.048-.058	.089-.102	.128-.139	.146-.148
n-Butyraldehyde				
$Q(D_p/D_2)$	0.0252	0.0339	0.0477	0.0663
$\Delta V/V^o$	.015-.024	.024-.034	.014-.024	0.038
n-Pentane				
$Q(D_p/D_2)$	0.154	0.164		
$\Delta V/V^o$	0.153	.169-.181		
n-Heptane				
$Q(D_p/D_2($	0.138	0.155	0.207	0.309
$\Delta V/V^o$	0.141	.141-.160	.182-.193	0.298
n-Decane				
$Q(D_p/D_2)$	0.107	0.133	0.186	0.271
$\Delta V/V^o$	.098-.085	.091-.098	.147-.151	0.232
n-Tetradecane				
$Q(D_p/D_2)$	0.100	0.116	0.137	0.212
$\Delta V/V^o$	.068-.088	.078-.086	.131-.149	.171-.206
Benzene				
$Q(D_p/D_2)$	0.150	0.160	0.217	0.312
$\Delta V/V^o$	.122-.138	.152-.172	.202-.211	.244-.33
o-Xylene				
$Q(D_p/D_2)$	0.168	0.195	0.295	0.586
$\Delta V/V^o$	.153-.171	.184-.212	.270-.292	0.50
p-Xylene				
$Q(D_p/D_2)$	0.180	0.200	0.284	0.473
$\Delta V/V^o$	.145-.188	.162-.193	.242-.278	.402-.422
p-Chlorotoluene				
$Q(D_p/D_2)$	0.148	0.171	0.231	0.433
$\Delta V/V^o$	.128-.148	.169-.199	.187-.240	.394-.413
Cyclohexane				
$Q(D_p/D_2)$	0.228	0.262	0.394	0.847
$\Delta V/V^o$	.187-.194	.266-.331	0.394	

It seems that about all one can safely conclude from these calculations is that the actual swelling as determined by the thickness measurements is generally equal to or less than the swelling that one calculates from the additivity assumption. That is, there may be a certain amount of filling in of voids in the polyethylene by the penetrants. If the voids are not equilibrium thermal ones, solution by this mechanism will increase the mass of the polymer phase but not its volume.

In principle measurements such as these might under favorable conditions yield valuable information on polymer-penetrant interactions. Unfortunately, from this point of view, the swelling of polyethylene is often scarcely detectable. On the other hand, in cases where the swelling is easily measurable the problem is complicated by the "anti-freeze" effect. So we leave these measurements now and turn finally to the problem of P_o.

25. An Empirical Treatment of the P_o Data.

Table 3 reveals that there is a general decrease in P_o with E_p. This suggests a plot of the logarithm of P_o (all logarithms from here on are to the base 10) against E_p (in kcal/mole) as shown in Figure 10. Not all the data of Table 3 appear in this figure. Only those homologous series are represented for which there are data on at least three members, namely the aliphatic hydrocarbons, the aromatic hydrocarbons, the aliphatic acids, and the aliphatic alcohols.

The extent to which the nineteen compounds plotted in Figure 10 group themselves according to homologous series membership is truly gratifying. Furthermore, the following compounds could have been added and still the overall picture would have been pretty consistent.

Cyclohexane (with the aromatic hydrocarbons),

Phenol (with the aliphatic alcohols), and

Dibutyl ether, Ethyl Acetate, ME Ketone, Acetone,
Amyl Acetate, Butyraldehyde, and Benzaldehyde
(all with the aliphatic hydrocarbons, although
several of these fall on a nice straight line of
their own).

Such a classification shows that the grouping in Figure 10 is to some extent determined by shape and, perhaps to a larger extent, by polarity. Thus non-polar but round-shaped cyclohexane falls in with the also relatively non-polar aromatic ring compounds, and the straight chain ethers, esters and ketones are grouped somewhat with the straight chain hydrocarbons. But highly polar phenol clearly belongs with the straight chain alcohols, and the straight chain acids fall in a class by themselves rather than with the paraffins.

FIGURE 10

$LOG_{10} P_0$ vs. E_p VALUES

$LOG_{10} P_0$

E_p kcal/mole

(1)

Legend:
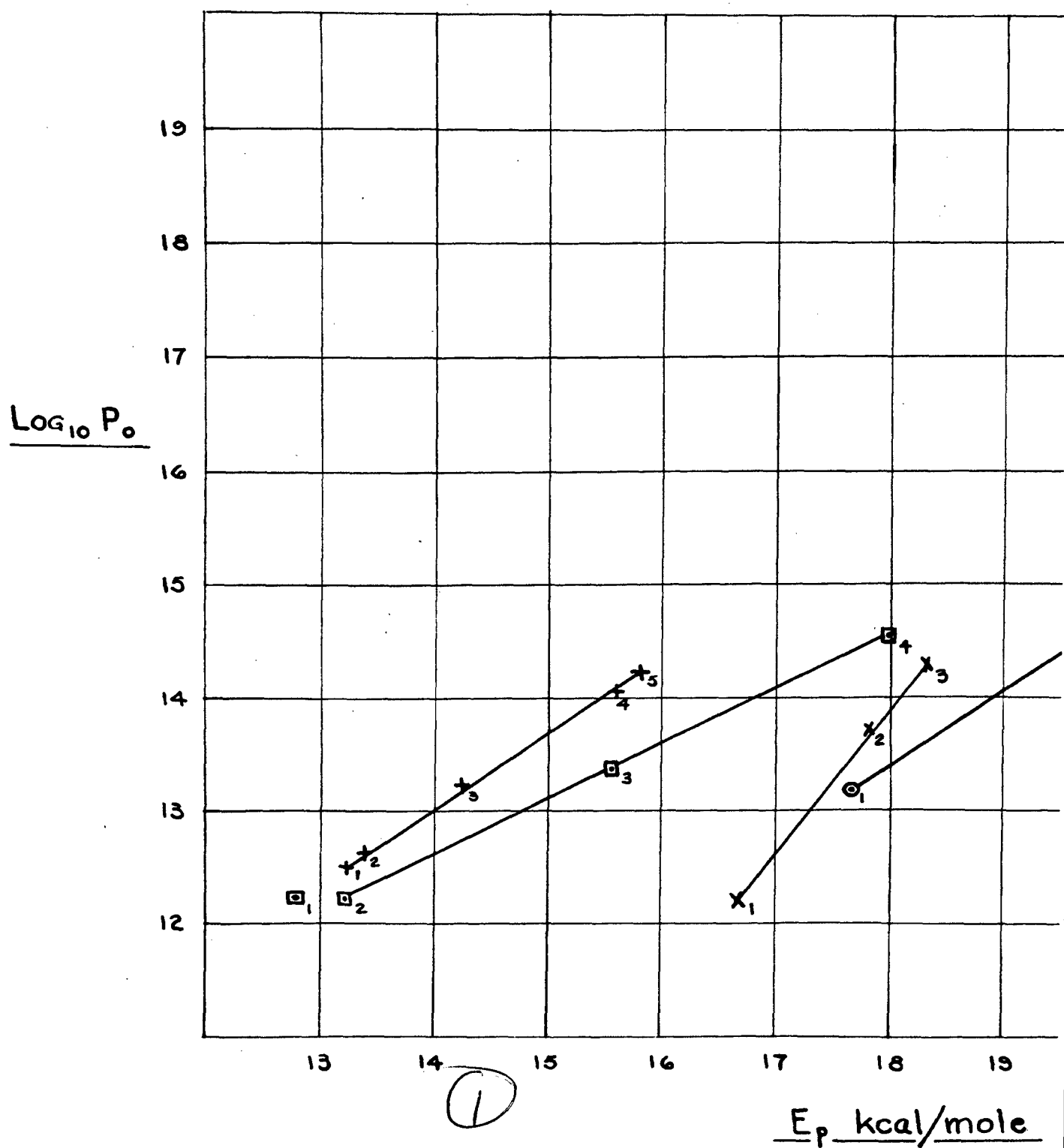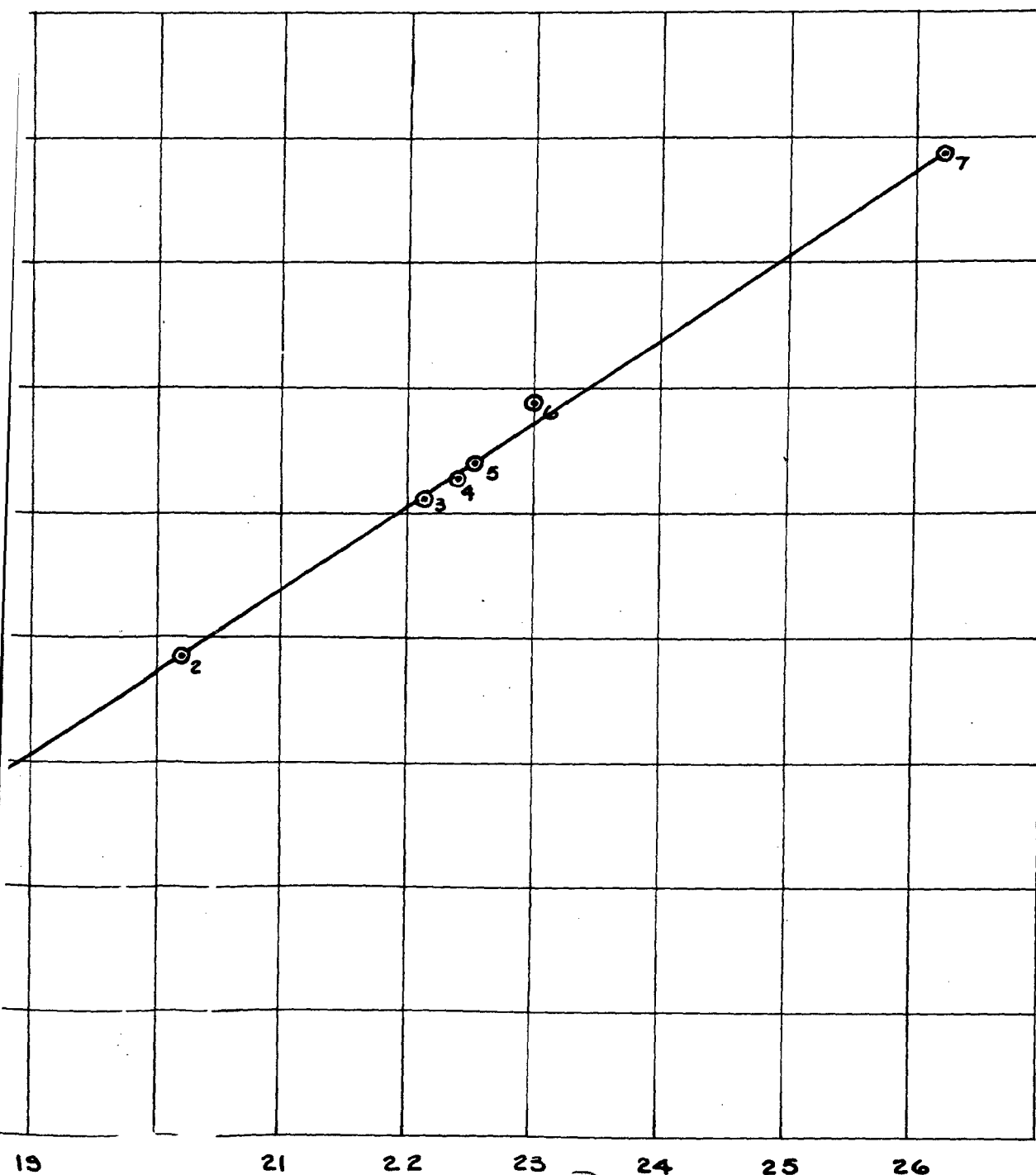
◻ ALIPHATIC HYDROCARB(

1. n - PENTANE
2. n - HEPTANE
3. n - DECANE
4. n - TETRADECA(

+ AROMATIC HYDROCARE

1. BENZENE
2. p - XYLENE
3. CHLOROBENZE
4. o - XYLENE
5. p - CHLOROTOLU(

X ALIPHATIC ACIDS

1. FORMIC ACID
2. ACETIC ACI(
3. n - BUTYRIC AC(

⊚ ALIPHATIC ALCOHO

1. METHYL ALC(
2. ALLYL ALCO(
3. n - PROPYL ALC(
4. n - BUTYL ALCO(
5. n - OCTYL ALCO(
6. sec - BUTYL ALC(
7. ter - BUTYL ALC(

x-axis: 19   21   22   23   24   25   26

26. The $\log P_O$ vs. E_p Plot and its Uses.

Figure 10 in conjunction with our earlier discussions may in some instances be as or even more useful than the Master P-Factor Plot itself. Its utility will be demonstrated by two rather different examples.

(1) In conjunction with equation (10-2 *e*) Figure 10 can be used to obtain absolute values for P-Factors. It *is only necessary* to have the usual vital statistics on the compound in question (i.e., density, molecular weight, model length, and heat of vaporization) and information regarding its family ties in Figure 10. For example, knowing that amyl acetate is more or less related to the straight chain hydrocarbons, we find, using the value 19.5 for E_p (Table 13), that $\log P_O = 15.2$ (compared to the observed value, Table 3, of 15.32). From these values for E_p and $\log P_O$ the P-Factor for amyl acetate at 70°F is calculated to be $5._0$. The observed value was 8.7 (Table 1).

It might perhaps be worth mentioning that a certain amount of interpolation is possible in Figure 10 just as it was in the Master Plot. Dipentene, for example, probably does not belong either with the aromatics or the aliphatic hydrocarbons, but rather some place in between (see structural formula in Section 12). Just where in between is determined by its calculated E_p value, 15.9, and guesstimate, say 13.9 to 14.0 for $\log P_O$.

(2) It may be, though, that for one reason or another a trustworthy value for E_p is not available: Possibly the heat of vaporization is in doubt. In this case a single P-Factor determination, say at room temperature, will suffice to determine the permeability behavior at all other temperatures provided the compound can be assigned to one of the families in the $\log P_O$ vs. E_p plot. We will illustrate the application of Figure 10 to such a problem with allyl alcohol.

Let us suppose that all we know about allyl alcohol is that it is an alcohol and that at room temperature (70°F) it has a P-Factor of 0.65. What is its P-Factor at 165°F?

If we only knew E_p, we could use the 70° P-Factor and equation (1-2a) to find P_O, and then with this and E_p, P could be calculated at 165°F. This sort of calculation has been mentioned before. Now this time, however, we are supposing that we do not know E_p. But we do know that whatever E_p and $\log P_O$ may be for allyl alcohol, they must be such that the point for it falls on the alcohol curve in Figure 10. Of course there are many sets of values for the pair that satisfy this condition, but only one set that will, when used in equation (1-2a), give the right value for P at 70°F. So in principle the problem is solved. In practice it is convenient to know the equation for the $\log P_O$ vs. E_p curve. From Figure 10 we find that the parameters m and b in the equation

(26-1) $$\log P_O = mE_p + b$$

have the following values.

Table 20

The Values of the Parameters in the Equation:
$$\log P_o = mE_p + b.$$

Family	m	b
Aliphatic Hydcb.	0.483	5.86
Aromatic "	0.661	3.74
Alcohol	0.664	1.40
Aliphatic Acid	1.28	-9.00

Essentially what we have then are two unknowns, E_p and $\log P_o$, and two relations between them:

$$\log P = -E_p/2.3RT + \log P_o, \text{ and}$$

$$\log P_o = mE_p + b.$$

Adding and solving for E_p, we obtain in general

(26-2) $$E_p = (b - \log P)/(1/2.3RT - m)$$

$$= (b - \log P)/(218.6/T - m)$$

and in particular for allyl alcohol at $70°F$,

$$E_p = (1.40 - \log 0.65)/(218.6/294.2 - 0.664)$$

$$= 20.1 \text{ kcal/mole}$$

compared to the observed value of 20.2 kcal/mole. From equation (26-1) (or Figure 10) it then follows that

$$\log P_o = 14.75$$

for allyl alcohol (the observed value is 14.85). Substituting in the logP equation with $T = 347°K$, we find finally a value of 123 for the P-Factor of allyl alcohol at $165°F$. The observed value is 138. This is remarkable agreement but then so is the linearity of the curves in Figure 10.

One of the advantages of this method is that if the E_p value used is too large, $\log P_o$ will also be too large, and the two errors will tend to cancel.

27. A Qualitative Theoretical Discussion of the P_o Factor.

As we mentioned previously, just as the P-Factors are of the form

$$P = P_o e^{-E_p/RT}$$

so too the solubility and diffusion coefficients in the relation $P = DS$ are of the form

$$D = D_o e^{-E_d/RT} \text{ and}$$

$$S = S_o e^{-E_s/RT}$$

where $E_p = E_d + E_s$ and $P_o = D_o S_o$.

Actually the absorption tests data reveal that the solubilities of organic liquids in polyethylene are not described as easily as the simple exponential form above would suggest. But for the slightly soluble substances the solubility behavior approximates this where E_s is essentially $\Delta \bar{H}_2$ and is small compared to E_d and where S_o is essentially $e^{\Delta \bar{S}_2^{th'}/R}$.

In the transition state theory (Glasstone, Laidler and Eyring, "The Theory of Rate Processes", p524) the diffusion constant receives a similar treatment. By considering the equilibrium between activated penetrant molecules (molecules just in the act of diffusing) and normal penetrant molecules (ones at rest in the polymer), one finds that E_d is the so-called "energy of activation for diffusion" and D_o is essentially $e^{-\Delta S*/R}$ where $\Delta S*$ is the entropy change that occurs within the system when a normal penetrant molecule is "activated." It is called the "entropy of activation".

Combining these statements, we have the following equivalence.

$$\log P_o = \log D_o + \log S_o$$

$$\sim \Delta S* + \Delta \bar{S}_2^{-th'}.$$

But we also have the relation (equation 26-1)

$$\log P_o = m E_p + b.$$

It is worth noting that in the language of the transition state theory E_p would be written $\Delta E*$. This suggests that

$$m E_p \sim \Delta S* \quad \text{and hence also that}$$

$$b \sim \Delta \bar{S}_2^{-th'}.$$

All we need to do is justify one of these and the other one follows. We shall attempt to argue the first one.

It says that the entropy of activation is roughly proportional to the energy of activation. That this might indeed be so can perhaps be seen from these considerations. There are many many ways a normal penetrant molecule might get activated. Of all of these, the most probable one is the one with the largest equilibrium constant K = (activated molecules)/(normal molecules). (The polymer immediately surrounding a molecule in the act of diffusion constitutes part of the so-called "activated complex". Likewise the polymer immediately surrounding a molecule at rest constitutes part of what we might call a "normal complex". In the equilibrium constant expression above "activated complex" and "normal complex" have simply been written 'activated molecules' and 'normal molecules' respectively.)

Now from classical thermodynamics

$$RT \log_e K(\text{normal molecules} = \text{activated molecules}) = -\Delta F^{0*}$$

where ΔF^{0*} is the standard free energy change for the reaction indicated above of normal molecules going to activated ones; i.e., it is the so-called "free energy of activation". Clearly K will be greatest when ΔF^{0*} is as small as possible. Now, again from classical thermodynamics,

$$\Delta F^{0*} = \Delta H^{0*} - T\Delta S^{0*}.$$

(The little superscript zeros on these terms merely indicate that configurational effects have been sorted out. For most purposes it really isn't necessary to show this for the ΔH term, but as we have seen configuration can have a large effect upon the entropy and hence, as the equation shows, upon the free energy too.)

In this equation the ΔF^{0*} term, for example, represents the difference between the free energy of an activated molecule and a normal one. Since we start with the latter, nothing can be done in the way of adjusting its free energy in order to minimize ΔF^{0*}. This leaves only the free energy of the activated molecules to examine. If we let $F_{\text{activated molecule}} \equiv F^*$, etc., this means that K will be as large as possible when

$$F^* = H^* - TS^*$$

is as small as possible.

At this point we encounter a fundamental aspect of nature. F^* is not minimized by making H^* as small as possible. Rather, it is minimized by striking some sort of compromise between a not too large H^* and a not too small S^*. This argument may sound a bit familiar, for we have used it before--several times. H^* could conceivably be large and S^* small, but this is (thermodynamically) unlikely, and the converse can never be true. So

there are good sound reasons why S* should follow H*, which is essentially equivalent to E_d. And since E_d is the major part of E_p, we have established what we wished to establish.

This correlation of

$$mE_p \sim \Delta S^* \quad \cdot \quad \Delta S_{activation} \qquad and$$

$$b \sim \Delta \bar{S}_2^{-th'} \quad \sim \quad \Delta S_{solution}$$

helps explain several interesting features of Table 20, namely the decrease in b and the increase in m in going from the aliphatic hydrocarbons to the aliphatic acids. It seems reasonable to expect that the entropy of solution will be small whenever there is a tendency toward dimerization. This accounts for the trend in b. The trend in m, although not at all surprising, is not rationalized so readily. A small entropy of solution of course leaves a lot to be gained during activation if the dimers, or even just a part of them, are split during diffusion. But this could come about without any increase in the m factor of the product mE_p since E_p will naturally be larger than it might otherwise be if there is dimer dissociation during diffusion.

Well, in any event there are trends, and a plot of m against b is best fitted by a straight line connecting the two extreme points (the aliphatic hydrocarbon and aliphatic acid points) and passing between the two intermediate ones which don't lie too far from it.

28. Summary.

Neither polyethylene nor the organic penetrants of this project should be considered, even by themselves, as simple substances, for there is not yet a satisfactory theoretical explanation for even the commonest physical properties of this polymer, nor is the liquid state entirely understood even for substances as simple as liquid argon. It is not surprising, therefore, that the interaction of polyethylene with an organic penetrant turns out to be a relatively complex problem in statistical thermodynamics and diffusion theory. Now no such problem has ever been worked out exactly even in the very simplest possible cases. This report shows, nevertheless, that it is possible to draw a number of interesting conclusions from the data supplied by Plax on the permeability of polyethylene to organic solvents. These conclusions are summarized below. Their theoretical justification and the exact conditions under which they may be expected to be valid, were established in the earlier sections of this report.

1. An inductive picture of the permeability of polyethylene to organic solvents is best based upon the relation: $P = DS$.

2. Of the two, S may be taken to be much more important than D.

3.   Very often the order of S from swelling measurements is also precisely the order of the observed P-Factors.

4.   The solubility coefficient S follows the general rule that "like dissolves like". Hence we may also say that

5.   "Like permeates through like."

6.   Since polyethylene is itself relatively non-polar, P-Factors invariably decrease as the polarity of the penetrant increases.

7.   There are several reliable ways of indicating the polarity of a penetrant.

8.   Qualitatively at least
      a.   Dunkel's group contributions to ΔH_{vap} and
      b.   the Cohesive Energy Density of the penetrant are
fairly reliable guides to polarity.

9.   Quantitatively it has been found that the so-called
      a.   Polarity Index $\Delta\Delta H$ as determined from experimental
           heats of vaporization and the so-called
      b.   Flory-Huggins Polymer Interaction Parameter
           as determined by swelling equilibrium
are better guides to polarity in polyethylene - organic solvent systems.

10.   A correlation was found between the Polarity Index $\Delta\Delta H$ and the temperature variation of the Flory-Huggins parameter.

11.   An oxygen atom may often be a seat of polarity in a molecule. It is, however, very important to distinguish the type of linkage.

12.   All of the indices mentioned in 8 and 9 agree in assigning the greatest polarity to the -OH or hydroxyl group, which can hydrogen bond with itself. the next greatest polarity for oxygen linkages to the $C = O$ or carbonyl group, and the least polarity to the C-O-C linkage. Thus

13.   The alcohols were the most polar and the least permeable of all the substances studied. The esters and ketones were always somewhat more permeable, and the ethers resembled the corresponding hydrocarbons.

14.   The carboxylic acids are more permeable than their polarity indexes would suggest. They are, in fact, effectively less polar than the corresponding alcohols.

15.   Considerable evidence points to the existence of carboxylic acid dimers in polethylene. This largely explains their seemingly anomolous behavior.

16. Dimerization tendencies also explain why the heat of solution of penetrant in polymer is generally significantly less than $\Delta\Delta H$.

17. In general, though, any hydrogen bonded substance will have a very low permeability factor.

18. With regard also to the polarity factor, there is evidence for internal shielding effects in the higher aliphatic compounds, which operates to increase S and P slightly.

19. This internal shielding effect also explains why the order of S is the reverse of E_p for members within a single homologous series, except in the extreme cases of the hydrocarbons and the alcohols, which can be explained.

20. The limited swelling that polyethylene undergoes in even the best solvents at room temperature resides in its partial crystallinity. Otherwise it would dissolve in most hydrocarbons.

21. The partial crystallinity of polyethylene, however, gives rise to an "anti-freeze effect" which seriously complicates the quantitative development of the theory of permeability.

22. It has been assumed that the penetrants do not penetrate the crystalline regions in polyethylene.

23. The solubility coefficient, however, is not the whole story.

    a.   Although S always increases with temperature, the P-Factor itself increases much more rapidly.
    b.   Indeed, E_p was in every instance greater than 12 whereas E_s was always less than 5.
    c.   Furthermore, S is not very much dependent upon molecular geometry, but P very definitely is.
    d.   Finally, the effect of polarity extends beyond S.

24. A quantitative picture of the permeability of polyethylene to organic solvents is best based upon the relation:

$$P = P_o e^{-E_p/RT}.$$

25. The Master logP vs. 1/T Plot can be used to

    a.   Determine the parameters E_p and P_o; to
    b.   Check the over-all consistency of the data; to
    c.   Smooth the experimental data; to
    d.   Extrapolate the experimental data; and to
    e.   Interpolate with the experimental data between
        i. two temperatures, same compound, or
        ii. two compounds, same temperature.

26. The size and shape of the penetrant affect P primarily through the kinetic factor D.

27. It has been proposed to use the molar volume as an index of size and the molar volume divided by the length of the corresponding Fisher-Hirschfelder-Taylor molecular model as an index of shape.

28. The diffusion coefficient is also significantly dependent upon the polarity index $\Delta\Delta H$.

29. Quantitatively, we can say that

    a. E_p increases 0.0348 Kcal/mole per cc of molar volume;

    b. E_p increases 0.75 Kcal/mole per unit increase in the shape factor V/L; and

    c. E_p increases 2.4 Kcal/mole per Kcal of polarity as measured by $\Delta\Delta H$; or altogether,

    d. $E_p = 0.0348V + 0.75V/L + 2.4\Delta\Delta H$.

30. In some cases it is necessary to correct 29d as follows:

    a.   Subtract 1 for para-substituted compounds.

    b.   Subtract 2 for all alcohols.

    c.   Add 1.3 for all aldehydes (This rule is based on data for only two compounds).

31. At the moment $\Delta\Delta H$ for the carboxylic acids must be determined from swelling measurements.

32. In general E_p is more important than P_o in determining relative P values at room temperature.

33. A rather remarkable correlation between E_p and $\log P_o$ has been found and partially explained.

34. Using this $\log P_o$ vs. E_p Plot,

    a.   A single P-Factor determination, say at room temperature, suffices to determine the permeability behavior at all other temperatures; also

    b.   an absolute value for the P-Factor can be calculated at any temperature given only E_p, which we can calculate.

That is to say, it is only necessary to have the usual vital statistics on the compound in question, namely its density, molecular weight, model length, and heat of vaporization, and one can calculate good values for its permeability factor.

The value of the equation:

$$P = P_o e^{-E_p/RT}$$

may be observed in Table 21 in which the P-factors calculated by the above equation are compared with observed values. In Table 21 are listed most of the substances examined in this report (actually all those given in Table 13). The agreement between the fourth and fifth columns is fairly impressive. As indicated by the last column, the calculated values are clearly of the right order of magnitude (off by less than a factor of 10), and, with one exception, better even than the hoped for factor of 2. Indeed, in 50% of the cases the calculated and observed values agree to within the limit of the probable experimental error.

Table 21

A FINAL COMPARISON BETWEEN THEORY AND EXPERIMENT:

The Prediction of Permeability Factors at 70°F for
the Diffusion of Organic Solvents through Polyethylene.

Substance	E_p^{calc} [a]	$logP_o$ [b]	$P_{70°F}^{calc}$ [c]	$P_{70°F}^{obs}$ [d]	$P_{70°F}^{calc}/P_{70°F}^{obs}$
n-Octanol	23.5	17.17	0.52	0.50	1.05
ter-Butanol	26.7	19.36	0.34	0.26	1.30
sec-Butanol	22.7	16.62	0.54	0.60	0.88
n-Butanol	22.4	16.40	0.57	0.46	1.25
n-Propanol	22.4	16.40	0.57	0.40	1.44
Phenol [e]	20.9	15.38	0.72	0.48	1.44
Butyraldehyde [e]	19.0	15.10	9.77	10.13	0.97
Benzaldehyde [e]	19.2	15.20	8.71	6.80	1.28
Acetone [e]	18.3	14.76	14.8	6.75	2.19
Methyl Ethyl Ketone [e]	18.3	14.76	14.8	12.6	1.16
Ethyl Acetate [e]	18.1	14.66	16.6	17.0	0.98
Amyl Acetate [e]	19.5	15.35	7.41	8.30	0.89
Dibutyl Ether [e]	16.3	13.80	49	88	0.55
Pentane	13.0	12.22	371	526	0.70
Heptane	14.0	12.68	190	270	0.70
Decane	15.7	13.50	69.2	71.2	0.97
Tetradecane	18.0	14.60	17.0	17.0	1.00
Benzene	13.3	12.52	436	440	0.99
o-Xylene	16.0	14.38	316	290	1.09
p-Xylene	13.6	12.73	427	500	0.85
Chlorobenzene	14.3	13.22	398	500	0.79
p-Chlorotoluene	16.2	14.51	302	300	1.01
Cyclohexane [e]	16.8	14.93	282	285	0.99
Dipentene [f]	15.9	13.95	138	128	1.08

E_p expressed as kcal/mol

P = grams/24 hrs/0.001 in./100 in.[2]

Notes for Table 21

a   Taken from Table 13.

b   Obtained using the E_p values in the second column and Figure 10.

c   Calculated using equations (1-2a) and (1-3).

d   Smoothed experimental values obtained from the Master Plot.

e   See section 25.

f   See section 26, point (1).

A few sample calculations of the P-factor using the Bent Equation and appearing in Table 21 are included.

n-Octanol

$$P = P_o e^{-Ep/RT} \quad \text{or}$$

$$\log P = -Ep/RT + \log P_o$$

$$= -23.5/(2.3 \times 1.987 \times 10^{-3} \times 294) + 17.17$$

$$= -23.5/(1.345) + 17.17$$

$$= -17.45 + 17.17$$

$$= -0.28 \quad \text{or} \quad 9.72 - 10$$

$$P = 0.52 \text{ gms}/24\text{hrs}/0.001\text{in}/100\text{in}^2$$

Tetradecane

$$\log P = -Ep/RT + \log P_o$$

$$= -18.0/(2.3 \times 1.987 \times 10^{-3} \times 294) + 14.60$$

$$= -18.0/(1.345) + 14.60$$

$$= -13.37 + 14.60$$

$$= 1.23$$

$$P = 17.0 \text{ gms}/24\text{hrs}/0.001\text{in}/100 \text{ in}^2$$

Benzene

$$\log P = -Ep/RT + \log P_o$$

$$= -13.3/(2.3 \times 1.987 \times 10^3 \times 294) + 12.52$$

$$= -13.3/(1.345) + 12.52$$

$$= -9.88 + 12.52$$

$$= 2.64$$

$$P = 436 \text{ gms}/24\text{hrs}/0.001 \text{ in}/100 \text{ in}^2$$

MASTER PLOT P vs $\frac{1}{T}$

p XYLENE
ter BUTANOL
BENZENE
AMYL ACETATE
DECANE
TETRADECANE
METHYL ETHYL KETONE
n OCTYL ALCOHOL
n BUTYRIC ACID
n PROPYL ALCOHOL
ACETONE
ACETIC ANHYDRIDE
BENZOIC ACID
DIACETONE ALCOHOL
NITROETHANE
ACETIC ACID
FORMIC ACID
WATER

n-PENTANE   +
p-XYLENE
 BENZENE
n-HEPTANE   ⊕
 CHLOROBENZENE O   0.1

p-CHLOROTOLUENE +
o-XYLENE
 CYCLOHEXANE

DECANE   ⊙   0.01

ACETONE   ▣
TETRADECANE   O   0.001
ETHYL ACETATE

| 4.3 | 4.2 | 4.1 | 4.0 | 3.9 | 3.8 | 3.7 | 3.6 | 3.5 | 3.4 | 3.3 |

−40. −31. −20. −9.4 +1.4 +14. +27. +41. +59. +70. +86.

③

											$\dfrac{10^3}{T°K}$
3.4	3.3	3.2	3.1	3.0	2.9	2.8	2.7	2.6	2.5	2.4	

+70. +86. +104. +122. +141. +162. +183. +207. +234. +261. +289.   °F

④

A Selected Bibliography

This is a 'selected' bibliography. It is not intended to be complete. It should nevertheless afford an easy entry to most of the pertinent literature on permeability, solubility, and diffusion in polymer systems.

I. ARTICLES.

A. Permeability in General.

Van Amerongen appears to be nearly the only investigator who has published work concerned primarily with the permeability factor itself. Two of his articles are listed below.

1. "The Permeability of Different Rubbers to Gases and Its Relation to Diffusivity and Solubility."
   G. J. Van Amerongen, J. App. Phys. 17, 972 (1946).

   A very pertinent article. Many of his conclusions are similar to those reached in this report.

2. "Solubility, Diffusion, and Permeation of Gases in Guttapercha."
   G. J. Van Amerongen, J. Poly. Sci. 2, 381 (1947).

   A typically readable Van Amerongen article.

B. Diffusion.

Although the literature on this subject does not include much on polyethylene, diffusion in polymers has received considerable attention, particularly by a group of investigators at ICI. Their work is generally published in the Transactions of the Faraday Society.

1. "The Diffusion of Some Organic Substances in Polystyrene."
   G. S. Park, Trans. Far. Soc. 47, 1007 (1951).

   An interesting paper. Attempts to describe quantitatively the effect of size and shape on the diffusion constant (The 'Smallest-Hole" Theory).

2. "The Diffusion of Some Halo-Methanes in Polystyrene."
   G. S. Park, Trans. Far. Soc., 46, 684 (1950).

B. <u>Diffusion</u> cont.

        The predecessor to the paper above. Considers only the molar volume of the penetrant. Also gives a brief discussion of the diffusion coefficient in terms of the transition state theory.

3.   "Diffusion in High Polymers: Some Anomalies and Their Significance."
J. Crank and G. S. Park, <u>Trans</u>. <u>Far</u>. <u>Soc</u>. 51, 10072 (1951).

        Anomalies are attributed to (a) variable surface concentration, (b) diffusion coefficient dependence on the history of the diffusion process, and (c) stresses exerted on one part of the polymer sheet by other parts.

4.   "Diffusion of Organic Vapors into Polyvinyl Acetate."
R. J. Kokes and F. A. Long, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>. 75, 6142 (1953).

        A report of some interesting recent work with many observations that are of significance for polyethylene. The influence of penetrant concentration, size, and polarity upon D is noted.

5.   "Theory of D_O for Atomic Diffusion in Metals."
Clarence Zener, <u>J</u>. <u>App</u>. <u>Phys</u>. 22, 372 (1951).

        Included here for its clarifying discussion of the relation of $S*$ to D_O.

C. <u>Solubility</u>.

    The theoretical work in the high polymer field of solubility was iniatiated essentially independently in 1942 by Flory and Huggins. E. A. Guggenheim has recently thoroughly reviewed the theory in a book, "Mixtures". These treatments are all quite mathematical. The emphasis in the references listed below is by contrast largely experimental.

1.   "Influence of Structure on Polymer-Liquid Interaction.
I.   Relative and Absolute Values of Swelling Equilibria."
G. Salomon and G. J. Van Amerongen, <u>J</u>. <u>Poly</u>. <u>Sci</u>. 2, 355 (1947).

        A good introductory discussion; possibly the most readable in the literature on this somewhat difficult subject.

C. <u>Solubility</u> cont.

2. "Influence of Structure on Polymer-Liquid Interaction.
   III. Swelling and Mechanical Properties of Some Partly
   Crystallized Polymers."
   G. Salomon, J. Poly. Sci. 3, 776 (1948).

   Continues along the lines of the previous reference.

3. "The Interaction Between Rubber and Liquids. VIII. A New
   Examination of the Thermodynamic Properties of the System Rubber
   + Benzene."
   Geoffrey Gee and W. J. C. Orr, <u>Trans. Far. Soc.</u> 42, 507 (1946).

   Suggests a number of experiments that might be tried on
   polyethylene.

4. "The Phase Equilibria Between A Crystalline Polymer and Solvents.
   I. The Effect of Polymer Chain Length on the Solubility and
       Swelling of Polythene.
   II. The Effect of Solvent Type on the Solubility and Swelling of
       Polythene."
   R. B. Richards, <u>Trans. Far. Soc.</u> 42, 10-28 (1946).

   Highly recommended reading for anyone interested in
   polyethylene. These articles contain a lot of information that
   might profitably be correlated with that of the present study.

5. "Swelling and Solubility in Mixed Liquids."
   Geoffrey Gee, <u>Trans. Far. Soc.</u> 40, 468 (1944).

   More good reading. Use is made of the cohesive energy
   density argument.

6. "Determination of Polymer-Liquid Interaction by Swelling measure-
   ments."
   Paul Doty and Helen S. Zable, <u>J. Poly. Sci.</u> 1, 90 (1946).

   A fairly detailed report on the swelling of a cross-
   linked polymer in a wide variety of liquids. Includes a relatively
   non-mathematical discussion of Flory-Huggins interaction parameter.

7. "Some Thermodynamic Properties of Slightly Cross-Linked Styrene-
   Divinylbenzene Gels."
   R. F. Boyer and R. S. Spencer, <u>J. Poly. Sci.</u> 3, 97 (1948).

C. Solubility cont.

Very similar in content to the previous reference. Quite complete so far as the experimental work goes with many references.

8. "Thermodynamics of High-Polymer Solutions. III. Swelling of Cross-Linked Rubber."
R. L. Scott and M. Magat, J. Poly. Sci. 4, 555 (1949).

A description of some absorption experiments that are very similar to those of the present project.

9. "Equilibrium Sorption of Several Organic Diluents in Polyvinyl Acetate."
R. J. Kokes, A. R. DiPietro and F. A. Long, J. Am. Chem. Soc. 75, 6319 (1953).

Another recent article by F. A. Long and co-workers. Includes an application of equation (18-9).

D. The Physical Properties of Polyethylene.

One of the distinguishing features of polyethylene is that it is a partially crystalline at room temperature. The evidence for this consists primarily of the pioneer work of the ICI research team on the heat capacity, heat of solution, density, and x-ray diffraction of polyethylene. More recently a group at Du Pont has made some contributions to this field.

1. "The Effect of Temperature on the Density of Polyethylene."
E. Hunter and W. G. Oakes, Trans. Far. Soc. 41, 49 (1945).

Perhaps the simplest way of following the change in crystallinity with temperature.

2. "The Heat Capacity, Heat of Solution, and Crystallinity of Polyethylene."
H. C. Raine, R. B. Richards and H. Ryder, Trans. Far. Soc. 41, 56 (1945).

Contains data relating to the "anti-freeze" effect.

3. "The Melting of Polythene."
R. B. Richards, Trans. Far. Soc. 41, 127 (1945).

A noteworthy attempt to give a theoretical explanation of

D. __The Physical Properties of Polyethylene.__ cont.

the phase relationships in pure polyethylene and swollen poly-
ethylene; is successful in only a semi-quantitative way. The dis-
cussion is sometimes a bit mathematical. (Supersedes Frith and
Tuckett's treatment, "The Melting of Crystalline Polymers",
Trans. Far. Soc. 40, 251 (1944))

4. "The Texture of Polythene."
   C. W. Bunn and T. C. Alcock, Trans. Far. Soc. 41, 317 (1945).

   Beautiful evidence for the crystallinity of polyethylene.

5. "The Molecular Structure of Polyethylene. I. Chain Branching in
   Polyethylene During Polymerization."
   M. J. Roedel, J. Am. Chem. Soc. 75, 6110 (1953).

   This is the first of a series of five articles by the
   Du Pont group that appear consecutively in the same issue of
   JACS. We mention them here primarily because they are of some
   interest and afford a very recent entry to the literature in this
   field. The titles of the remaining articles are given below.

II.	Determination of Short Chain Branching.
III.	Determination of Long Chain Branching.
IV.	Kinetic Calculations of the Effect of Branching on Molecular Weight Distribution.
V.	The Effect of Chain Branching and Molecular Weight on Physical Properties.

6. "The Mechanical Properties of High Polymers."
   H. Mark, Trans. Far. Soc. 43, 447 (1947).

   A lecture by Professor Mark which nicely surveys the
   polymer field.

II. BOOKS.

There are several books that have been found useful in this problem.
Listed in order of more or less decreasing interest, they are:

1. "Elastomers and Plastomers. I. General Theory."
   Edited by R. Houwink. Elsevier Publishing Co. (1950)

   The chapters "Molecular Constitution", "Physics and

Structure" (Section 5 is on Permeability), and "Polymer-Liquid Interaction" by Van Amerongen form an excellent introduction to the polyethylene permeability problem.

2. "The Solubility of Nonelectrolytes."
   J. H. Hildebrand and R. L. Scott. Reinhold. (1950)

   The new third edition of this classic contains a chapter on high polmer solutions with seventy-one references to the literature.

3. "Advances in Colloid Science." Vol. I I.
   Edited by H. Mark and G. S. Whitby. Interscience. (1946)

   Gee contributed a readable chapter to this volume on "The Thermodynamic Study of Rubber Solutions and Gels."

4. "Diffusion in and through Solids."
   R. M. Barrer. Cambridge University Press. (1951)

   This book which first appeared in 1941 contains much valuable data on diffusion.

Finally, mention should be made of the invaluable "Annual Reviews of Physical Chemistry" which was established in 1950. This review almost always contains something on polymers. Volume 4, for example, has a chapter on the "Physical Properties of High Polymers" with 310 citations to the literature, and volume 5 is also scheduled to have a chapter on polymers.

APPENDIX A

Derivation of the Ideal Solubility Equation: $\quad N = \exp(-\Delta H_{soln}/RT)$

According to classical thermodynamics, when a polymer is saturated with a solvent designated here as component 2,

$$\mu_2^P = \mu_2^L$$

where μ_2^P = the so-called chemical potential or the partial molal free energy of the solvent in the saturated polymer and μ_2^L = the chemical potential of the solvent in the pure solvent phase. Furthermore, we have that

$$\mu_2^P = H_2^P - TS_2^P \quad \text{and}$$

$$\mu_2^L = H_2^L - TS_2^L$$

where $\quad \Delta H \text{ solution} = H_2^P - H_2^L,$

$$S_2^L = k \ln W_2^L, \quad \text{and}$$

$$S_2^P = \frac{\partial S^P}{\partial n_2} ; \quad S^P = k \ln W^P$$

at this point it becomes necessary to make some assumptions regarding W^P

We shall assume that W^P can be written as

$$W^P = W_1^P W_2^P Wc$$

where

$$W_2^P = (W_2^L)^{n_2},$$

$$Wc = \frac{(n_{sites})!}{(n_{sites} - n_2)! \; n_2!},$$

and where W_1^P is independent of n_2 as is n_{sites}, the total number of positions in the polymer available to organic solvent molecules. The equations above

essentially define what we have called an ideal solution.

Now, since $S^P = k\ln W^P = k\left[\ln W_1^P + \ln W_2^P + \ln W_c\right]$ and since

$$\frac{\partial \ln W_2^P}{\partial n_2} = \ln W_2^L \; ,$$

$$\Delta H_{soln} = T(S_2^P - S_2^L) = T(k\ln W_2^L - k\ln W_2^L - k\frac{\partial \ln W_c}{n_2})N$$

$$= RT \ln \frac{n_{sites} - n_2}{n_2} \approx RT \ln \frac{n_{sites}}{n_2}$$

for dilute solutions where $n_2 \ll n_{sites}$

calling $n_2/n_{sites} = N$, this gives $N = e^{\frac{-\Delta H}{RT}soln}$

APPENDIX B

## The Heats of Solution of Liquids in Polyethylene.

Let us return to our earlier example and consider the mechanism by which a molecule of benzene dissolves in polyethylene.

First it is necessary to separate it from the pure liquid benzene phase by breaking the intermolecular bonds that it forms with neighboring benzene molecules. If we were to do this for a whole mole of molecules we would write

$$(17.1) \qquad \text{Benzene(liquid)} = \text{Benzene(gas)},$$
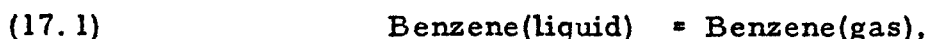
and the heat of this reaction is just the heat of vaporization of pure benzene. It is symbolized by $\Delta H_{vaporization}$ which stands for the difference $H_{benzene}$ as a gas $- H_{benzene \ as \ a \ liquid}$.

The second step in the solution process is then to place this free (gaseous) benzene molecule in the polymer,

$$(17.2) \qquad \text{Benzene (gas)} = \text{Benzene (polymer)}.$$
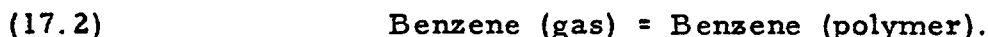
The sum of reactions (17.1) and (17.2) is reaction (13) which may be abbreviated as

$$(17.3) \qquad \text{Benzene(liquid)} = \text{Benzene(polymer)}.$$
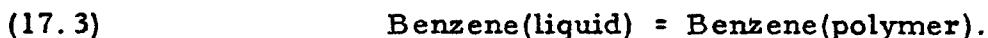
Calling the heat of the reaction (17.2) $\Delta H_{solution}^{gas}$, we have that the heat of the net reaction, equation (17.3), is just the sum of the heats of the two reactions (17.1) and (17.2). That is,

$$(18) \qquad \Delta H_{solution} = \Delta H_{vaporization} + \Delta H_{solution}^{gas}.$$

Thus we are led from the permeability P to the solubility S (P $=$ DS) to the heat of solution $\Delta H_{solution}$ ($N =^{(-\Delta H_{soln}/RT)}$) and finally to the heat of vaporization ΔH_{vap} and ΔH_{soln}^{gas} (equation (18)).

Of these latter two terms, ΔH_{vap} is of course always positive whereas $\Delta H_{solution}^{gas}$ has just the opposite sign principally because of the intermolecular attractive forces which play a relatively important role in condensed phases but are unable to exert their full effect in the comparatively dilute gaseous phase. Since it is to be expected that ΔH_{soln} will be positive, the absolute magnitude of ΔH_{soln}^{gas} must be less than that of ΔH_{vap}.

The interplay of these three quantities can perhaps best be discussed by considering two contrasting cases: propanol and decane.

It has been established that both the permeability and the solubility (in polyethylene) of decane,
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, are significantly greater than those of propanol, $CH_3CH_2CH_2OH$. From equation (15), $N = (-\Delta H_{soln}/RT)$, we conclude therefore that the heat of solution of decane in polyethylene is less than the heat of solution of propanol in polyethylene. Looking now at equation (18), we might be inclined initially to conclude that the heat of vaporization of decane is significantly less than the heat of vaporization of propanol, yet, in fact, they are nearly equal (we have already seen that the heat of vaporization of propanol is about 11.6 kcal/mole. Using table 4 it is estimated that the heat of vaporization of decane should be $8(1.0) + 2(1.8) = 11.6$ kcal/mole.).

The reason for this near equality and actually relatively high heat of vaporization is that in the case of decane although the intermolecular force field surrounding the molecule is at no point very intense it does operate over a large area and manages to accumulate to 11.6 kcal/mole; and in the case of the much smaller propanol molecule hydrogen bonds are largely responsible for this high heat of vaporization. Indeed, from Table 4 one -OH group is in this respect equivalent to roughly 7 -CH$_2$- groups.

Now when we come to consider the situation to be expected in the polymer, we see that a decane molecule experiences very much the same general dispersion forces that exist in pure decane, which implies that ΔH_{soln}^{gas} will in this case be comparable to ΔH_{vap}. However, for propanol the situation is quite different since polyethylene is a nonpolar, essentially neutral or non-specific solvent medium. Thus the OH$\rightarrow$O bonds that play such an important role in pure propanol are largely non-existent in the polyethylene system, causing ΔH_{soln}^{gas} to subtract off much less from ΔH_{vap} than in the case of decane (equation (18)). This then explains why the heat of solution of propanol in polyethylene can be expected to be significantly greater than that of decane even though both have essentially the same heat of vaporization.

More generally, since the -CH$_2$- groups in polyethylene have a relatively small polarizability (see C-H in Table V) and dipole moment (see HC- in Table III) so that London-type and dipole-dipole- type interactions with groups on other molecules will at most be quite non-specific and small and furthermore since -CH$_2$- groups do not form hydrogen bonds, it is to be expected that whenever these specific intermolecular interactions do exist in the pure solvent phase (as for so-called polar liquids), $\Delta H_{vaporization}$ will be large compared to ΔH_{soln}^{gas}, and, therefore $\Delta H_{solution}$ will in such instances be large when $\Delta H_{vaporization}$ itself is large.