INVESTIGATION OF THE SHELF LIFE
OF LIQUIDS IN POLYETHYLENE BOTTLES

Part 3, Sup. 1 — Theoretical Investigation of the Effects of
Molecular Weight, Side Chain Branching, and Irradiation on
The Mechanism of Transfer of Materials Through Polyethylene

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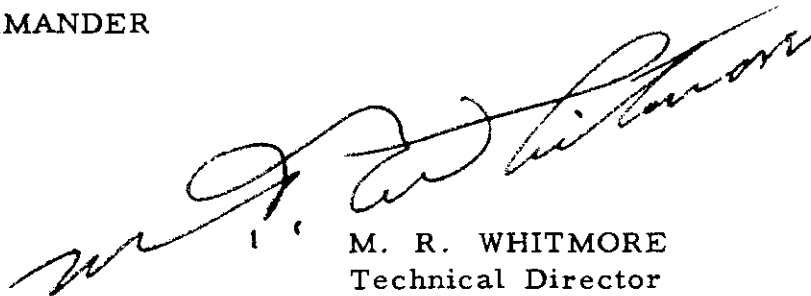
WADC TR 53-133 Part 3, Sup. 1

ABSTRACT

In this study P-Factors and absorption tests reported in Part 3 are analyzed and discussed, together with some data on aqueous solutions from Part 1. The theory of mass transfer through polyethylene is extended, particularly with regard to the $\log P_o$ vs E_p plot, and the results applied to recent data on carbon tetrachloride.

It is found that chain branching and irradiation increase swelling coefficients and diffusion constants at low temperatures, but decrease them at very high temperatures. The importance of placing room temperature P-Factors in this perspective is stressed. It is suggested that activated diffusion through polyethylene induces structural changes in the polymer not unlike local melting. Thermodynamical reasoning also indicates that frequency and P-Factors increase with increasing rigidity and mass of penetrant. In both respects carbon tetrachloride shows this increase with polyethylene.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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P	Permeability	weight/unit time/unit thickness/unit area
P_1		"　　"　"　　"　　"　　"　　"　　"
P_2		"　　"　"　　"　　"　　"　　"　　"
P_o	Constant for a given system - base permeability	
D	Diffusion	weight/unit time/unit thickness/unit area
S	Solubility	weight/unit weight plastic
E_p	Constant for a given system (permeability activation energy)	
E_d	"　　"　"　"　　" (diffusion activation energy)	
R	Universal Gas Constant = 1.987 calories/°Kelvin/mole	
T	Absolute Temperature °Kelvin	
$\Delta\Delta H$	Measure of Polarity	
m	Empirical Constant	
b	"　　　　"	
Q	Absorption - gms. penetrant/gram polyethylene	
ϕ_2	Volume fraction of the penetrant in swollen polymer at equilibrium	
χ	Flory Huggins Polymer Interaction Parameter	
$\Delta S*$	Entropy of Heat of Solubility	
$\Delta H*$	Entropy of Heat of Vaporization	
ΔH_f	Heat of Vaporization in Fusion	
ΔS_f	Heat of Solubility in Fusion	
v	Number of jumps a penetrant molecule makes per second when there are no others around to clog up naturally occurring defects in the polymer structure	
λ	Reciprocal of coordination number of the polymer structure	
Δ	The elementary jump distance	
k	Henry's Law Constant	
V.P.	Vapor Pressure	

THEORETICAL INVESTIGATION OF THE EFFECTS OF

MOLECULAR WEIGHT, SIDE CHAIN BRANCHING, AND IRRADIATION ON

THE MECHANISM OF TRANSFER OF MATERIALS THROUGH POLYETHYLENE.

Presentation of the Permeability Data

1. Introduction.

This report covers a continuation of the study reported on in WADC Technical Report 53-133, Part 2: "Theoretical Investigation of the Mechanism of Transfer of Materials Through Polyethylene".

The earlier study (Part 2) was based on experimental data obtained by the Plax Corporation on Bakelite's polyethylene DE-2400 and reported in Part 1: "Investigation of the Shelf Life of Liquids in Polyethylene Bottles". The permeability of Bakelite DE-2400 to approximately forty organic solvents was studied at five temperatures (32°, 70°, 100°, 130°, and $165^\circ F$) and the swelling of DE-2400, to the same solvents, at four temperatures (32°, 70°, 100°, and $130^\circ F$).

The present study, (Part 3), is based on experimental data obtained by the Plax Corporation on four different polyethylenes, Bakelite's DE-2450 and Du Pont's Alathon 10, Alathon S-1439, and Alathon S-1447, and reported in Part 3: "Investigation of the Effects of Molecular Weight, Chain Branching, and Irradiation on Polyethylene With Regard to Shelf Life in Bottles". The permeability of these polyethylenes, and also irradiated DE-2450, to approximately twenty solvents was studied at four temperatures (70°, 100°, 130°, and $165^\circ F$) and swelling, to four solvents, at two temperatures (70° and $130^\circ F$).

In this study, P-Factors and absorption tests reported in Part II are analyzed and discussed, together with some data on aqueous solutions, not previously considered, from Part 1; the theory of the mechanism of the transfer of materials through polyethylene is extended, particularly with regard to the $\log P_o$ vs E_p plot; and the results applied to recent data on carbon tetrachloride.

2. Characteristics of the Polyethylenes Considered in this Study.

Before presenting a summary of recently determined P-Factors and swelling indices, on which this report is largely based, we list below esti-

mated crystallinities and side-chain branching ratios for the five polyethylenes considered in this report (Table I, Part 3).

TABLE I

CHARACTERISTICS OF THE POLYETHYLENES CONSIDERED IN THIS STUDY

Polyethylene Powder	Melt Index (decigrams/min.)	% Crystallinity	Side Branching CH_3/100 C Ratio
Bakelite			
DE-2400	1.04	58	2.2
DE-2450	1.22	58	2.2
Du Pont			
Alathon 10	1.93	60	1.6
Alathon S-1439	1.36	60	1.6
Alathon S-1447	0.337	60	1.6

The irradiated polyethylene was Bakelite's DE-2450. Standard 4-ounce DE-2450 bottles were irradiated with a dosage of 26 megareps by electron bombardment at the High Voltage Corporation, Cambridge, Mass.

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

The data listed below in Table II are abstracted from Table I, Part 2, and Table VII, Part 3. The order is that of Table I, Part 2. Of the three Du Pont Alathon polyethylenes, values are given only for Alathon 10, since all three -- Alathon 10, S-1439, and S-1447 -- had nearly identical P-Factors for all substances at all temperatures. DE-2450-I represents irradiated Bakelite polyethylene 2450.

TABLE II

P-FACTORS FOR POLYETHYLENES DE-2400, DE-2450, DE-2450-I, AND ALATHON 10 AT FOUR TEMPERATURES

(In grams/24 hours/$0.001''$/$100''^2$)

Penetrant	Temp.	DE-2400	DE-2450	DE-2450-I	Alathon 10
Acetic Acid	70°F	3.08	3.24	3.95	2.05
	100°F	13.55	17.7	20.2	12.1
	130°F	66.0	66.4	70.9	44.4
	165°F	304.0	319.	344.	221.
Methyl Alcohol	70°F	1.22	1.10	1.24	1.03
	100°F	5.35	6.15	7.96	4.45
	130°F	27.8	26.5	28.4	18.5
n-Propyl Alcohol	70°F	0.49	0.52	0.92	0.25
	100°F	2.89	4.0_5	4.70	2.71
	130°F	22.4	22.4	24.5	14.7
	165°F	168.	171.	174.	114.
95% Phenol	70°F	0.48	0.49	0.565	0.32
	100°F	3.28	4.54	5.25	3.03
	130°F	24.0	22.4	25.2	15.0
	165°F	119.	151.	164.	107.
Water	70°F	0.28	0.14	0.13	0.11
	100°F	0.84	0.99	1.03	0.89
	130°F	3.94	3.80	3.91	2.89
	165°F	18.4	20.6	22.5	16.2
50% Sulfuric Acid	70°F	----	----	----	----
	100°F	0.24	0.29	0.34	0.30
	130°F	2.04	1.13	1.13	0.94
	165°F	6.03	6.95	6.90	5.68

TABLE II (Cont.)

P-FACTORS FOR POLYETHYLENES DE-2400, DE-2450, DE-2450-I, AND ALATHON 10 AT FOUR TEMPERATURES

Penetrant	Temp.	DE-2400	DE-2450	DE-2450-I	Alathon 10
Aniline	70°F	1.71	1.79	2.07	1.14
	100°F	9.93	12.8	15.3	9.63
	130°F	59.6	60.4	65.3	42.4
	165°F	294.	340.	340.	250.
Ethyl Acetate	70°F	16.55	23.9	28.9	15.1
	100°F	83.3	140.	154.	94.0
	130°F	378.	368.	486.	324.
	165°F	1990.	2990.	2990.	1910.
Amyl Acetate	70°F	8.70	9.67	12.8	5.64
	100°F	37.7	65.0	75.5	40.3
	130°F	269.	256.	285.	164.
	165°F	1300.	1630.	1630.	1120.
Dibutyl Phthalate	130°F	5.70	5.42	6.30	4.31
	165°F	27.8	49.3	52.2	37.6
Dibutyl Ether	70°F	----	94.5	115.	55.2
	100°F	407.	430.	579.	250.
	130°F	1480.	1405.	1400.	875.
	165°F	4890.	6300.	6040.	4470.
Benzaldehyde	70°F	6.80	7.03	8.54	4.35
	100°F	32.8	49.3	51.9	34.0
	130°F	206.	214.	236.	130.
	165°F	1060.	1150.	1210.	762.
Methyl Ethyl Ketone	70°F	12.6	12.8	14.9	8.17
	100°F	60.0	78.5	88.0	51.6
	130°F	326.	301.	289.	207.
	165°F	1401.	1790.	1890.	1250.

TABLE II (Cont.)

P-FACTORS FOR POLYETHYLENES DE-2400, DE-2450, DE-2450-I, AND ALATHON 10 AT FOUR TEMPERATURES

Penetrant	Temp.	DE-2400	DE-2450	DE-2450-I	Alathon 10
n-Heptane	70°F	269.	280.	305.	162.
	100°F	929.	955.	857.	589.
	130°F	2650.	3750.	2985.	2220.
	165°F	8160.	9820.	9130.	7530.
Benzene	70°F	440.	461.	528.	269.
	100°F	1585.	1730.	1770.	1195.
	130°F	4480.	6050.	5460.	4250.
	165°F	13670.	22800.	25200.	15600.
Ortho-Xylene	70°F	284.	294.	306.	168.
	100°F	1167.	1160.	1160.	824.
	130°F	4270.	4460.	3860.	2800.
	165°F	16600.	23400.	17800.	12400.

4. Observations on the Master Data.

Approximately ninety percent of the time, the order of the P-Factors listed, over the temperature interval studied, is

$$DE\text{-}2450\text{-}I \underset{(1)}{>} DE\text{-}2450 \underset{(2)}{>} DE\text{-}2400 \underset{(3)}{>} Alathon\ 10.$$

Excluding the case of 50% H_2SO_4, which permeates very slowly, there are, out of 70 comparisons, nine exceptions to inequality (2) between DE-2450 and DE-2400, five of them among slow, difficult-to-measure hydrogen-bonded permeators, with most of the inversions well within experimental error.

There are only six, out of 60, inversions of the third inequality (between DE-2400 and Alathon 10), all of them seemingly scattered at random, with again no apparent theoretical significance.

If we except the P-Factors at 130° and 165°F for the last three penetrants (heptane, benzene, and ortho-xylene), only two of the remaining 54 comparisons between DE-2450-I and DE-2450 (inequality 1) are inverted.

However, five of the six high temperature P-Factors for the rapid permeators heptane, benzene, and ortho-xylene are inverted.

We conclude from this that over the temperature interval studied a dose of 26 megareps increases the permeability of polyethylene to materials of high to medium polarity -- with, correspondingly, low to average P-Factors, but may decrease the permeability of polyethylene to relatively non-polar substances, like the aliphatic and aromatic hydrocarbons, which have large P-Factors. In all cases, however, the effect of 26 megareps on permeability is not very great.

5.   The Parameters E_p and P_o.

Logarithms of the P-Factors listed in Table II were plotted against the reciprocal of the absolute temperature. Where the data plotted up smoothly, slopes $(-E_p/2.3R)$ and intercepts $(logP_o)$ were determined following the methods developed in Part 2 (Section 4) (Page 10). The results are listed below in Table III in the order of the substances in Table II. (The data on DE-2400 are taken from the earlier study: Table III, Part 2.

TABLE III

THE PARAMETERS E_p AND P_o IN THE EQUATION $P = P_o e^{-E_p/RT}$

(Units on P, P_o, P_1, and P_2 are gms/24 hours/0.001 in/

100 in^2. E_p in kcal/mole.   R = 1.987 cal/deg/mole)

Penetrant and Polyethylene.	Method	P_2	P_1	E_p	$logP_o$
Acetic Acid					
DE-2400	II	644	3.00	17.78	13.69
DE-2450	II	640	3.35	17.40	13.45
DE-2450-I	II	640	4.50	16.42	12.85
Alathon 10	II	480	2.20	17.84	13.60
Methyl Alcohol					
DE-2400	II	241	1.16	17.67	13.20
DE-2450	II	258	1.10	18.08	13.47
DE-2450-I	II	300	1.44	17.68	13.30
Alathon 10	II	142	1.00	16.41	12.19

TABLE III (Cont.)

THE PARAMETERS E_p AND P_o IN THE EQUATION $P = P_o e^{-E_p/RT}$

Penetrant and Polyethylene	Method	P_2	P_1	E_p	$\log P_o$
n-Propyl Alcohol					
DE-2400	II	381	0.48	22.11	16.11
DE-2450	II	374	0.52	21.79	15.91
DE-2450-I	II	352	0.91	19.73	14.62
Alathon 10	II	330	0.24	23.80	17.08
Aniline					
DE-2400	II	690	1.70	19.89	15.01
DE-2450	II	800	1.86	20.08	15.19
DE-2450-I	II	830	2.40	19.36	14.77
Alathon 10	II	580	1.13	20.67	15.41
Ethyl Acetate					
DE-2400	II	3,670	17.4	17.72	14.41
DE-2450	II	6,600	23.5	18.67	15.24
DE-2450-I	II	6,200	29.0	17.77	14.66
Alathon 10	II	4,100	15.0	18.58	14.98
Amyl Acetate					
DE-2400	I	2,820	0.10	19.40	15.32
DE-2450	II	3,850	9.70	19.82	15.71
DE-2450-I	II	3,450	12.50	18.61	14.92
Alathon 10	II	2,450	6.00	19.91	15.57
Dibutyl Ether					
DE-2400	I	10,900	2.41	15.94	13.79
DE-2450	I	11,900	2.50	16.00	13.89
DE-2450-I	I	11,000	3.85	15.07	13.26
Alathon 10	I	8,100	1.36	16.46	13.98
Benzaldehyde					
DE-2400	II	2,360	6.80	19.37	15.23
DE-2450	II	2,600	7.70	19.28	15.21
DE-2450-I	II	2,650	8.5	19.02	15.06
Alathon 10	II	1,750	4.5	19.75	15.33

TABLE III (Cont.)

THE PARAMETERS E_p AND P_o IN THE EQUATION $P = P_o e^{-E_p/RT}$

Penetrant and Polyethylene	Method	P_2	P_1	E_p	$\log P_o$
Methyl Ethyl Ketone					
DE-2400	I	2,830	0.21	18.03	14.49
DE-2450	II	3,650	13.5	18.55	14.91
DE-2450-I	II	4,200	15.0	18.66	15.04
Alathon 10	II	2,710	9.0	18.90	15.00
n-Heptane					
DE-2400	I	14,000	13.0	13.22	12.24
DE-2450	I	17,600	12.4	13.74	12.65
DE-2450-I	I	15,700	16.4	13.00	12.15
Alathon 10	I	14,100	5.45	14.88	13.25
Benzene					
DE-2400	I	23,800	21.5	13.27	12.50
DE-2450	I	36,800	17.3	14.51	13.44
DE-2450-I	I	28,200	26.8	13.18	12.63
Alathon 10	I	28,000	8.0	15.45	13.90
ortho-Xylene					
DE-2400	I	30,300	8.0	15.60	14.03
DE-2450	I	36,000	7.8	16.00	14.34
DE-2450-I	I	25,300	12.5	14.42	13.23
Alathon 10	I	23,600	4.1	16.40	14.41

Inversion Temperatures

6. Observations on the Numerical Values of E_p and $\log P_o$.

As evident from the P-Factors themselves, mass transfer depends more on the penetrant than the polyethylene polymer. Thus E_p varies more from penetrant to penetrant, polymer constant, than it does from polymer to polymer, penetrant constant. For example, for any one of the polyethylenes, E_p changes by about 6 kcal when the penetrant is changed from benzene to aniline, but only about 1 - 2 kcal with the various polyethylenes for all penetrants except methyl alcohol.

In the previous report (Part 2), it was stressed that the frequency factor (essentially $\log P_o$) increases quite regularly with E_p for a given class

of penetrants (aromatic hydrocarbons, aliphatic alcohols, etc.). $LogP_o$ also increases regularly with E_p for a given class of polymers, namely the four polyethylenes considered in this study. Thus as one passes from DE-2450-I through DE-2400, DE-2450 and Alathon 10, E_p generally increases, and with it $logP_o$.

To repeat, for a given penetrant in the different polyethylenes, approximately eighty percent of the time the listed E_p's increase in the order

$$DE\text{-}2450\text{-}I \; < \; DE\text{-}2400 \; < \; DE\text{-}2450 \; < \; Alathon \; 10.$$

That is, generally the activation energies and frequency factors for a given penetrant are greatest in Alathon 10 and least in DE-2450-I. Of the seven odd exceptions to this sequence, three involve slow permeators (methanol, propanol, and acetic acid), which are difficult to measure accurately, and several of the others are very close to the right order. (It should perhaps be noted, however, that ethyl acetate and methyl ethyl ketone, which have previously been found to behave very similarly in polyethylene, figure in several of these inversions.)

7. A Note on Relative P-Factors at Different Temperatures.

Often in the earlier study (Part 2), large activation energies were found associated with small P-Factors: for example, the alcohols and acids compared to the hydrocarbons; or, better for our purposes, two substances from the same $logP_o$ vs. E_p class of compounds, say decane (E_p = 15.56, and $logP_o$ = 13.41) compared to pentane (E_p = 12.80, and $logP_o$ = 12.23), with P-Factors at 32°F of 9.5 and 97 respectively for DE-2400 (Part 2, Table I).

But note that whereas at 32°F, P (pentane) / P(decane) = 97/9.5 = 10.1, at 70°F, P(pentane) / P(decane) = 526/71.2 = 7.4, and at still higher temperatures the ratio would be even less; in fact, at a temperature

$$T \; (^oK) \; = \; \Delta E_p / R \Delta logP_o$$

the two P-Factors will just be equal, with their order reversed above this temperature.

The inversion temperature for the pentane - decane pair is quite high,

$$(15.56 - 12.80)1000/R(13.41 - 12.23) \; = \; 1170^oK,$$

which is well outside the experimental range. But for the benzene-ortho-xylene pair in polyethylene DE-2400, the inversion temperature is just slightly above 130°F (See Table II). Thus at 70°F their P-Factors are 440 and 284, with benzene the larger; but at 165°F it is ortho-xylene, 16,600 to 13,670.

This illustration shows how important it is to focus attention in a study such as this, not on the temperature dependent P-Factors themselves, which may reverse their order with increasing or decreasing temperature, but rather on the temperature independent parameters E_p and P_o, which have no inversion temperature.

8. An Analytical Discussion of Inversion Temperatures.

The inversion temperature has been defined as that temperature at which the P-Factors for a pair of substances are equal. If each P-Factor is of the form $P = P_o e^{-E_p/RT}$, then, as has been mentioned,

$$T(\text{inversion}) = \Delta E_p / R(\Delta \log P_o).$$

The existence of an inversion temperature depends on the fact that P_o increases as E_p increases. For at high temperatures (T approaching infinite values, with E_p/RT tending to zero and $e^{-E_p/RT}$ to unity) the ratio of two P-Factors approaches the ratio of their frequency factors; the penetrant with the largest frequency factor has the largest P-Factor when T is very large. But generally this is the penetrant with the largest activation energy too; that is, the one with the steepest temperature dependence and lowest P-Factor at low temperatures, where the exponential term takes over ($e^{-E_p/RT}$ smallest for that penetrant with the largest E_p).

When it is known for a series or family of compounds that $\log P_o$ increases linearly with E_p, $\log P_o = m E_p + b$, then, to this approximation,

$$T(\text{inversion}) = 500/m,$$

where, from Table XX of Part II, we find that T(inversion) is equal to

$$500/0.483 = 1040^{\circ}K \text{ for aliphatic hydrocarbons,}$$
$$500/0.661 = 756^{\circ}K \text{ for aromatic hydrocarbons,}$$
$$500/0.664 = 753^{\circ}K \text{ for alcohols, and}$$
$$500/1.28 = 391^{\circ}K \text{ for aliphatic acids.}$$

That is to say, all aliphatic hydrocarbons, for example, should have identical P-Factors at $1040^{\circ}K$. Such a P-Factor inversion temperature of a $\log P_o$ vs. E_p plot family is closely analogous to the so-called "infinite point" of a "Cox Chart Family". A Cox Chart Family is a group of compounds whose vapor pressures, plotted logarithmically against the reciprocal of the absolute temperature, extrapolate linearly to a common point, called the infinite point. R. R. Dreisbach ("Pressure-Volume-Temperature Relationships of Organic Compounds", page 294) gives rather detailed directions on how to determine the Cox Chart Family to which a compound belongs.* His assignments are probably transferable to penetrants in poly-

* Also see Lange "Hand-book of Chemistry" 8th Edition, page 1528 ff.

ethylene and our $\log P_o$ vs. E_p Plot Families, although this application of the Cox Chart Families has not been developed in the present study.

In practice, not all inversion temperatures are as high as those indicated above. The calculation for the aliphatic hydrocarbons checks rather nicely for the decane-pentane pair, but the value for the aromatic hydrocarbons is considerably above that actually observed for the particular pair benzene - o-xylene. Nevertheless, it is an experimental fact that few inversions have been observed over the temperature interval 32° - 165^oF, with one exception: non-polar penetrants in DE-2450 and irradiated DE-2450 (designated DE-2450-I).

9. Inversion Temperatures Involving Irradiated Polyethylene.

If, as has been suggested, E_p's (and $\log P_o$'s) for a given penetrant in different polyethylenes increase in the order

$$\text{DE-2450-I} < \text{DE-2400} < \text{DE-2450} < \text{Alathon 10,}$$

then at low temperatures ($e^{-E_p/RT}$ the dominant term), P-Factors should be least for Alathon 10 and greatest for DE-2450-I, but just the reverse of this at very high temperatures (where P_o is the dominant term). There are indications that something like this is actually what one observes in practice.

Referring back to section 4, one sees that the observed P-Factors fall precisely in the low temperature order suggested above, with the exception that DE-2400 and DE-2450 have already generally swapped places at 70^oF, and for non-polar penetrants with fairly large P-Factors, DE-2450-I and DE-2450, which are nearest neighbors at 70^oF, start to switch positions around 100^oF.

Low inversion temperatures such as these are not entirely unexpected; there should be inversions, as will be argued later, at temperatures below the final melting point of the partially crystalline polymer, particularly in the case of the more soluble penetrants like the hydrocarbons xylene, benzene, and heptane, the two acetates, and dibutyl ether.

Thus, continuing observations begun in section 4, hydrocarbon P-Factors for DE-2450-I are greater, at 70^oF, than those for DE-2450, but less for the irradiated polymer at 130° and 165^oF, with inversion temperatures for the three hydrocarbons investigated (xylene, benzene, and heptane) falling, for all three, almost exactly at 100^oF. For slightly less soluble dibutyl ether, there appears to be an inversion for the DE-2450-I - DE-2450 pair at about 130^oF, and at about 165^oF for the still less soluble acetates (amyl and ethyl).

Table III illustrates these inversions in even larger measure. Column three labelled P_2 lists extrapolated P-Factors for $1000/T = 2.80$, which

corresponds to a temperature of about 183°F. At this temperature irradiation has decreased the P-Factors for the aromatic hydrocarbons about 35%. Note also that this temperature is clearly above the acetate - DE-2450-I - DE-2450 inversion temperature and near that for aniline and benzaldehyde. In fact, with the exception of methyl ethyl ketone, whose P-Factors did not plot smoothly on the master logP vs. 1/T plot, only for methyl alcohol is the P-Factor for the unirradiated polymer DE-2450 still appreciably less than that for DE-2450-I. It is apparent, too, that in several cases one is approaching an inversion temperature for the DE-2450-I - DE-2400 pair and, indeed, even the DE-2450-I - Alathon 10 pair, whose P-Factors, as a rule, are most widely separated at room temperature. The pronounced effect of a difference of about only 2 kcal/mole in E_p, such as exists for hydrocarbon penetrants in the DE-2450-I - Alathon 10 pair, on relative P-Factors over a protracted temperature interval is shown below in Table IV.

TABLE IV

P-FACTORS FOR THREE HYDROCARBONS IN DE-2450-I AND ALATHON 10 AT 9° AND 183°F

Penetrant and Polyethylene	P(183°F)	P(9°F) *	E_p	$\log P_o$
n-Heptane				
DE-2450-I	15,700	16.4	13.00	12.15
Alathon 10	14,100	5.4	14.88	13.25
Benzene				
DE-2450-I	35,500	34.7	13.18	12.63
Alathon 10	28,000	8.0	15.45	13.90
o-Xylene				
DE-2450-I	25,300	12.5	14.42	13.23
Alathon 10	23,600	4.1	16.40	14.41

* 9°F corresponds to the low temperature intercept in Method I (Table III).

Notice that irradiated DE-2450 is slightly over three times as permeable as Alathon 10 to these hydrocarbon penetrants at 9°F, but only about 10% more permeable at 183°F.

10. Summary of Inversion Temperatures.

Figure 1 below summarizes schematically the existing information on inversion temperatures for hydrocarbon-polyethylene (1) - hydrocarbon-polyethylene (2) pairs. The figure is based largely on data for 6,7, and 8 carbon hydrocarbons (benzene, n-heptane, and o-xylene), and drawn with slopes increasing in the order: DE-2450-I, DE-2400, DE-2450, and Alathon 10 (the greatest).

FIGURE 1

LOG P-FACTOR-TEMPERATURE PLOT TO INDICATE INVERSION

Temp:	Low	Room	165°F	Very High
Order of P-Factors	1. 2450-I	1. 2450-I	1. 2450	1. Alathon
	2. 2400	2. 2450	2. 2450-I	2. 2450
	3. 2450	3. 2400	3. 2400	3. 2400
	4. Alathon	4. Alathon	4. Alathon	4. 2450-I
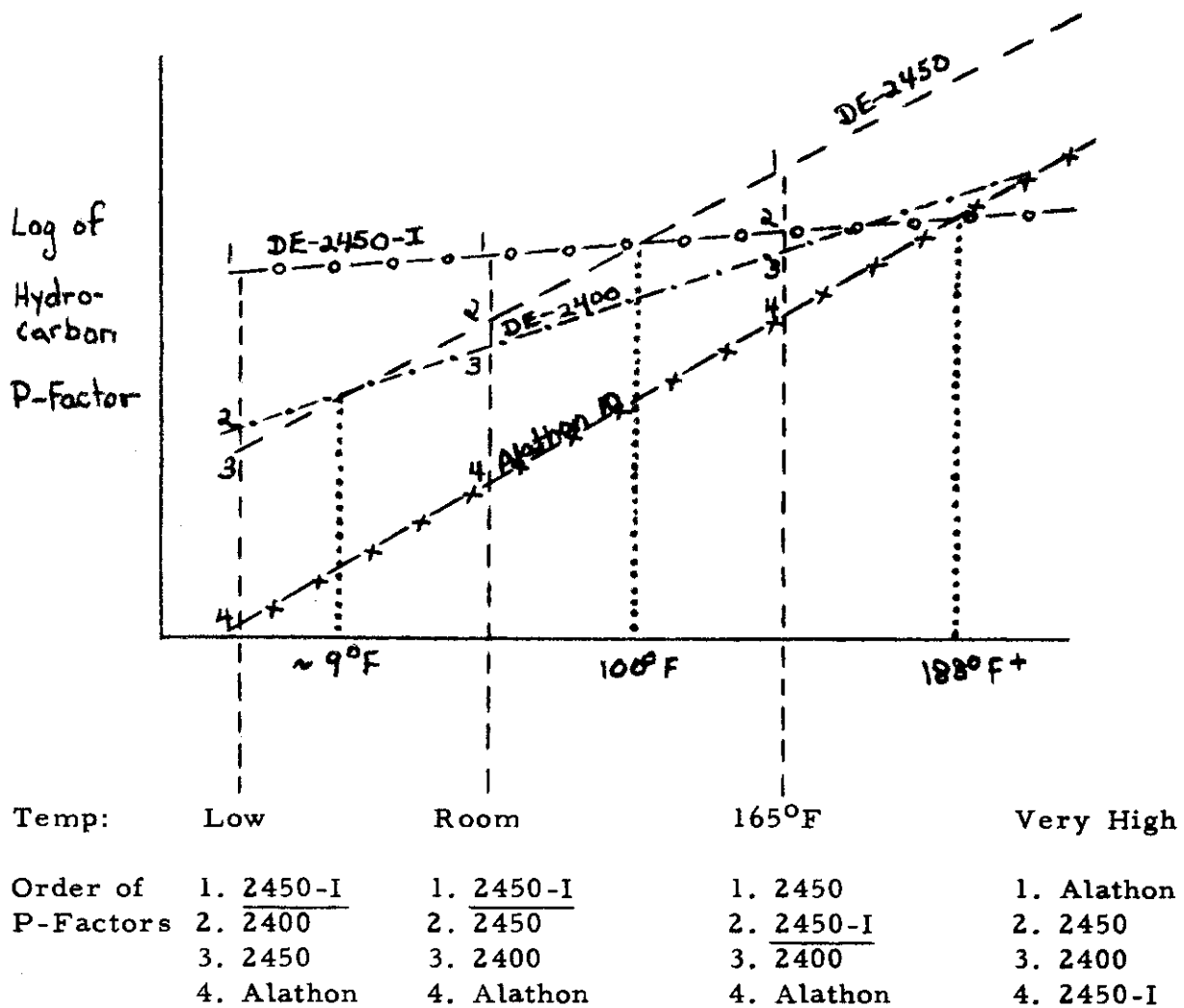
Remarks on Figure 1.

Low Temp. Sequence: The order observed at 9°F (extrapolated).
                       See P_1 column of Table III.

Rm. Temp. Sequence: See section 4. DE-2400 and DE-2450 have
                       switched positions.

165°F   Sequence: See remarks concerning hydrocarbons in
                       section 4.

High Temp. Sequence: A complete inversion of the low temp. sequence.

As the temperature is raised, all P-Factors increase, but the slow ones faster than the fast ones, until eventually the slowest becomes the fastest, and the fastest the slowest. At low temperatures, the order of the P-Factors is precisely the opposite of the E_p's, whereas at high temperatures the two sequences are identical.

Figure 1 shows, incidentally, why the hydrocarbon inversion temperature for the pair DE-2450-I - DE-2400 is greater than the inversion temperature for the pair DE-2450-I - DE-2450, even though at 9°F the hydrocarbon P-Factors for the former pair are closer together than the latter.

To see this analytically, one might note that a total of six independent parameters is required to characterize three straight lines, say their slopes and two of the intersections (this gives at least one point for each of the curves); the third intersection is then determined.

Presentation of the Solubility Data

11. The Solubility Data

Table V lists data and calculations on the solubilities of four penetrants (methyl alcohol, ethyl acetate, n-heptane, and benzene) in four different polyethylenes (DE-2400, DE-2450, DE-2450-I, and Alathon 10) at two different temperatures (70° and 130°F). The notation follows the earlier report (Part 2).

Q = grams of penetrant absorbed per gram of polyethylene;

ϕ_2 = the volume fraction of the penetrant in the swollen polymer at equilibrium; and

χ = the Flory-Huggins polymer interaction parameter.

Values for methyl alcohol are included, although its solubility is small and near the limit of experimental error.

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TABLE V

SOLUBILITIES OF METHYL ALCOHOL, ETHYL ACETATE, n-HEPTANE, AND BENZENE IN DE-2400, DE-2450, DE-2450-I, AND ALATHON 10 AT 70°F AND 130°F.

Penetrant and Polyethylene	70°F			130°F		
	Ω	Φ_2	χ	Ω	Φ_2	χ
Methyl Alcohol						
DE-2400*	0.001	0.001	5.80	0.001_2	-----	----
DE-2450	0.001_1	0.001_2	5.70	0.012_5	0.014	3.37
DE-2450-I	0.001_6	0.001_8	5.33	0.019_4	0.022	2.93
Alathon 10	0.001_2	0.001_4	5.61	0.0027	0.003	4.82
Ethyl Acetate						
DE-2400	0.027	0.027	2.77	0.042	0.046	2.33
DE-2450	0.029_5	0.030	2.70	0.046_5	0.048_5	2.29
DE-2450-I	0.033	0.034	2.60	0.051	0.053	2.22
Alathon 10	0.026_0	0.026_7	2.80	0.044_5	0.046_9	2.33
n-Heptane						
DE-2400	0.113	0.134	1.52	0.220	0.236	1.17
DE-2450	0.106	0.125	1.57	0.194	0.210	1.20
DE-2450-I	0.113_5	0.132	1.53	0.190	0.208	1.21
Alathon 10	0.091	0.111	1.65	0.163	0.181	1.33
Benzene						
DE-2400	0.150	0.138	1.50	0.290	0.237	1.17
DE-2450	0.137	0.125	1.57	0.376	0.288	0.92
DE-2450-I	0.147	0.135	1.52	0.252	0.213	1.18
Alathon 10	0.119	0.112	1.64	0.241	0.205	1.25

* The data on DE-2400 are taken from Parts 1 and 2.

Interaction parameters not corrected for polymer crystallinity and cross-linking.

12. Observations on the Solubility Data.

These data are difficult to assess. Owing to the nature of the measurements, precise reproducibility is difficult and not to be expected; which

leaves one wondering, however, with only four compounds to consider, whether small differences from polymer to polymer are real or illusory. Bearing this in mind, we venture the following generalizations.

> In every case irradiation increases the solubility, except for heptane and benzene at 130°F.

> In five cases out of six among the non-alcoholic compounds, the solubility is smallest in Alathon 10.

These generalizations cover DE-2450 and DE-2450-I and Alathon 10 against the others, but overlook any comparison between DE-2450 and DE-2400. As they stand, the six comparisons between DE-2450 and DE-2400 among ethyl acetate, heptane, and benzene are evenly divided. At both temperatures ethyl acetate is more soluble in DE-2450, but for the hydro-carbons, with the exception of the benzene value in DE-2450 at 130°F (which looks a bit out of line), the solubility is greatest in DE-2400. Perhaps the polarity of the acetate is a factor here, but lacking further information, we conclude, rather tentatively, that

> For the hydrocarbons the solubility is greater in DE-2400 than in DE-2450.

Summarizing then, the order of solubility, at least so far as the hydro-carbons are concerned, seems to be

> DE-2450-I > DE-2400 > DE-2450 > Alathon 10

with two qualifications: i)   DE-2400 should perhaps be left out of the list; and

ii)   DE-2450-I and DE-2450 switch positions at 130°F.

Further Development on the Theory of Mass Transfer Through Polyethylene

13. Factors to Consider Regarding Irradiated Polyethylene.

Prior investigations of irradiated polyethylene, primarily published reports by Charlesby in England and Dole in this country (see bibliography), suggest that one should consider the following factors when polyethylene is irradiated while exposed to the air.

1. Decrease in crystallinity. (Eventually the polycrystalline opaque polymer becomes transparent.)

2. Cross-linking. (Sharp rise in melting point.)

3. Change in molecular weight. (From studies on H_2 evolution.)

4. Increase in unsaturation. (From studies on Br_2 absorption.)

5. Surface oxidation. (Material more ink-receptive, as are polymers treated with acid dichromate.)

6. Bulk oxidation.

Such changes as occur in molecular weight are probably not important. Three Du Pont polyethylenes of varying melt indices were investigated in Part III, with similar results all along the line.

If unsaturation was caused, as in fact seems likely, we have not been able to definitely attribute any appreciable change in either diffusion or solubility to it.

Past Plax studies have indicated that surface oxidation by acid di-chromate appears to increase slightly the permeability to polar substances, presumably due to enhanced solubility in the oxidized surface, but that the effect is not large. We assume, likewise, that radiation-induced oxidation in the interior is probably not an important factor in this problem.

The irradiation effects left to consider are 1: decrease in crystallinity and 2: increase in cross-linking. We believe that both effects are important.

14. Discussion of Solubility Data and Correlation With Activation Energies.

If we assume, as in Part 3 (section 22), that penetrants are insoluble in the crystalline regions of partially crystalline polyethylene, then solubility coefficients should increase as crystallinity decreases, other things remaining the same. From the information in Table I and the notion that irradiation destroys crystallinity, one predicts solubility coefficients running in the order

$$DE-2450-I > DE-2400 > Alathon \; 10,$$

as observed in section 12.

The inversion of DE-2450-I with DE-2450 for heptane and benzene at $130°F$ arises in part from the "anti-freeze" effect, which diminishes crystal-linity, probably by the greatest amount for the relatively highly crystalline unirradiated DE-2450, thereby tending to equalize amorphous contents, and hence, also, solubility coefficients. The actual inversion is undoubtably caused by the irradiation induced chemical cross-links, which inhibit the swelling of the irradiated polymer (Part 3, section 22, part d). Thus, the two effects together, the decrease in crystallinity and the increase in cross-linking, seem to account for the solubility data.

It will be noted, however, that whereas the reported crystallinities in Table I differ by less than 4%, some of the solubilities in Table V differ by more than 4%. The explanation is perhaps as follows. Crystallinity depends on the side-chain branching ratio; the less the side-chain branching, the

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greater the crystallinity (Table I). Thus, although on crystallization side-chain molecules are probably preferentially concentrated in amorphous regions, it seems reasonable to suppose, without detailed inquiry, that a decrease in overall side-chain branching decreases the concentration of the side-chain molecules in the amorphous polymer. In fact, to take a particularly simple case, suppose that all of the side chains are concentrated in amorphous polymer during crystallization. If the figures in Table I are correct, the concentration of side-chains in amorphous DE-2450 would be 2.2/(100-58) = 0.0525, but only 1.6/(100-60) = 0.040 in Alathon 10, which could easily account for the difference in swelling (the greater the side-chain branching in amorphous polymer, the greater the solubility of penetrants in that polymer).

Finally, it is to be noted that the order of the solubility coefficients is precisely the order of the activation energies, in this sense: large solubilities go with small activation energies; thus penetrants are most soluble in DE-2450-I and least soluble in Alathon 10, but their activation energies are least in the former and greatest in the latter. Trends such as this were observed in Part 2, but there it was the penetrant that was changing, and here it is the polymer. We are led to inquire into this matter further.

15. Mechanism of Mass Transfer in Polyethylene. I. Diffusion-Induced Melting.

One obvious explanation for the correlation between low solubilities and high activation energies is this: The greater polymer crystallinity, the less the solubility of penetrants, but the greater the contribution the heat of fusion makes to E_p as the polymer gradually melts with rising temperature.

We digress slightly at this point to observe that decreasing polymer crystallinity not only operates in the direction of the E_p - Q correlation, but also explains, in part, the surprisingly large values of penetrant permeability activation energies in polyethylene, compared to anticipated diffusion activation energies. The explanation is that E_p is equal to E_d plus contributions from polymer crystallinity (and also the heat of solution of the penetrant).

But again we come back to the fact that the crystallinity of DE-2450 and Alathon 10 may differ by less than 4%, and the activation energies sometimes differ by more than that. Apparently here too one must look to the amorphous regions for an explanation.

A clue is given when one examines rather expanded plots of the E_p and $logP_o$ values listed in Table III. For a given penetrant, the points frequently fall nicely on a straight line, much as happened in Figure 10, Part 2. Moreover, the slopes of these lines are remarkably constant from one penetrant to the next, suggesting that a change in crystallinity (i.e., side-chain branching ratio) affects one penetrant very much like the next, at least

insofar as E_p and P_o are concerned.

The constancy of $dE_p/d(\log P_o)$ probably arises from the fact that as side-chain branching decreases and the amorphous regions collapse, activated diffusion requires increasingly great reorganization of the now more nearly crystalline amorphous polymer matrix. This is presumably true for all penetrants; hence the constancy of $dE_p/d(\log P_o)$. Moreover, as side-chain branching decreases, ΔH^* for the diffusion process (essentially E_p) -- and with it, as usual, ΔS^* (essentially $R\log P_o$) -- should increase; hence the increase in E_p with decreasing solubility -- and also the increase in $\log P_o$ with E_p.

On slight extension, these statements concerning the mechanism of diffusion in polyethylene can be checked semi-quantatively. We have assumed that the increase in ΔH^* and ΔS^*, say from DE-2450 to Alathon 10, reflects the greater need, as chain branching decreases, for re-organization in that part of the polymer associated with activated complexes, much of which may normally be on the verge of crystallizing. That is to say, we are suggesting that, at least in so far as the polymer is concerned, changes that occur in ΔH^* and ΔS^* are similar to those changes that normally occur on melting ΔH_{fusion} and ΔS_{fusion}). Now if the only change is the polymer (penetrant constant), then, although certainly ΔH^* and ΔS^* are not equal to the polymer fusion values ΔH_f and ΔS_f, at least we suspect that changes in ΔH^* are proportional to ΔH_f as changes in ΔS^* are proportional to ΔS_f (under the conditions specified above: different polyethylenes, but same penetrant). That is, we suspect that perhaps (penetrant constant) $d(\Delta H^*)/d(\Delta S^*) = \Delta H_f/\Delta S_f$, or, what is probably nearly the same, that

$$\left[\partial(E_p)/\partial(R\log P_o)\right]_{\substack{\text{penetrant} \\ \text{constant}}} = \Delta H_f/\Delta S_f.$$

The fusion values (subscript f) refer to the polymer. The heat of fusion, ΔH_f, probably changes little with temperature, but the entropy of fusion of the polymer, ΔS_f, increases as the percentage crystallinity increases (melting releases more and more configurational "strain" in amorphous regions). That is to say, the ratio $\Delta H_f/\Delta S_f$, which is just the melting temperature (in degrees Kelvin) of the region under consideration, has a spectrum of values, for polyethylene, about 60 - 114°C. Thus it is not entirely certain exactly what to expect from the left-hand side of the equation above; presumably something in the range 60 - 114°C. And this is found to be the case. The common slope to the E_p vs. $\log P_o$ curves referred to earlier in this section is 1700. Dividing by 4.6 (= 2.3R), one finds 370°K = 97°C, which is reasonably good semi-quantitative agreement between theory and experiment.

We might summarize by saying that activated diffusion through polyethylene seems to induce structural changes in the polymer not unlike local melting.

16. Condensation of Information Obtained From P-Factors and Swelling Measurements.

We pause at this point to collect in one place the principal conclusions presented in previous sections of this report.

The following properties increase in the order indicated.

Swelling by Organic Solvents

at low temperatures . . . . DE-2450-I $>$ DE-2450 $>$ Alathon 10

at high temperatures . . . . DE-2450-I $<$ DE-2450

Crystallinity . . . . DE-2450-I $<$ DE-2450 $<$ Alathon 10

Side-Chain Branching. . . . .   DE-2450 $>$ Alathon 10

Activation Energy, E_p . . . . DE-2450-I $<$ DE-2450 $<$ Alathon 10

Frequency Factor, $\log P_o$ . . . . . . DE-2450-I $<$ DE-2450 $<$ Alathon 10

P-Factor at low temperatures . . . . DE-2450-I $>$ DE-2450 $>$ Alathon 10

          at high temperatures . . . . DE-2450-I $<$ DE-2450 $<$ Alathon 10

DE-2400 could probably in most cases be inserted between DE-2450-I and DE-2450.

17. Mechanism of Mass Transfer in Polyethylene. II. A Kinetic Model: Chain Branching, Porosity, and Diffusion.

Certain features of the diffusional process in polyethylene are most easily expressed in kinetic language. Up to this point we have described mass transfer through polyethylene in rather different, thermodynamical terms, drawing particularly on the terminology of the activated complex or transition state theory, since that language was peculiarly well adapted to the problem of giving expression and perspective to the temperature dependence of P - Factors -- activation energies and frequency factors, particularly the correlation between their increments and the melting point spectrum of polyethylene. The following kinetic description is in part equivalent to, but perhaps in larger measure complementary to the thermodynamic description. It is presented for the easy and natural way it treats the importance, at different temperatures, of side-chain branching.

First, diffusion through DE-2450 is compared with that through less branched, more highly crystalline Alathon 10. The comparison is quite simple. At low temperatures and high crystallinities, the greater porosity of more highly branched DE-2450 is the dominant diffusional feature of the two polyethylenes; at low temperatures DE-2450 has the larger P-Factor.

But at high temperatures, where both polymers have loosened up and crystallinities are low, chain-branching, which before made for comparatively rapid diffusion, now becomes a hindrance; i.e., at high temperatures DE-2450 has the smaller P-Factor.

The obstacle-course effect of side-chain branching is perhaps most easily seen in terms of the random walk model of activated diffusion.   In this model, the diffusion coefficient of the penetrant is given by the expression

$$D \;=\; v\lambda\Delta^2,$$

where v = the number of jumps a penetrant molecule makes per second when there are no others around to clog up naturally occurring defects in the polymer structure, λ = essentially the reciprocal of the coordination number of the polymer structure, and Δ = the elementary jump distance.

Now, to simplify the picture somewhat, imagine a particle freely vibrating back and forth with a frequency v in a box of length Δ.   Without changing the velocity of the particle (temperature constant), we halve the length of the box (double the number of side-chain branches). The frequency of vibration doubles, but Δ^2 is only one-fourth as great, and D drops by a factor of two.   That is to say, an increase in the side-chain branching ratio should tend to decrease P-Factors, all other things the same (such as polymer crystallinity and over-all density). This is not the case at low temperatures, but things tend toward that with rising temperature.

The comparison between DE-2450-I and DE-2450 is similar in a way to that between the latter and Alathon 10.   At low temperatures the greater porosity of the less highly crystalline DE-2450-I causes it to have the larger P-Factor.   But at high temperatures, where both polymers have loosened up and crystallinities are in any case low, irradiation induced cross-links, which before were associated with reduced crystallinity and hence comparatively rapid diffusion, now limit swelling and interfere with diffusion; i.e., at high temperatures DE-2450-I has a smaller P-Factor than the unirradiated material.

18.   Mechanism of Mass Transfer in Polyethylene.   III.   Factors Influencing the Frequency Factor.

This section is a sequel to section 25 of Part 2, "An Empirical Treatment of the P_o Data".   The problem of concern is the explanation for the useful empirical observations given in section 25, Part 2.   No new data are considered here, although the way is prepared for a comparison between theory and recent experiments on carbon tetrachloride (section 20). We begin by comparing frequency factors and permeabilities of two penetrants, decane and o-xylene, which have nearly identical activation energies (Table VI).

TABLE VI

DATA ON DECANE AND O-XYLENE

Substance	E_p	$\log P_o$	P(32°F)	P(70°F)	P(100°F)	P(130°F)	P(165°F)
Decane	15.56	13.41	9.49	71.2	297.	1220.	4120.
o-Xylene	15.60	14.03	36.1	284.0	1167.	4270.	16600.

Although these two hydrocarbons have nearly identical activation energies, $\log P_o$ is 0.42 units larger for o-xylene, making its P-Factor almost exactly four times greater than that of decane (at all temperatures!). We are led to inquire: "What is there about xylene that makes its frequency factor four times larger than that of decane?"

Recalling that $\log P_o$ is essentially equivalent to ΔS^* for diffusion, the question is one of explaining why the entropy of activation is greater for xylene than decane. The answer becomes apparent when one considers the structures of the two molecules: xylene is rigid and inflexible, decane just the opposite. Thus decane stands to lose more entropy in going to the activated state -- or perhaps it is a case of xylene gaining more entropy during activation. In any event, the more rigid a molecule, the greater its frequency factor (and P-Factor) compared to flexible molecules of similar polarity and over-all activation energy.

This rigidity effect explains why simple derivatives of benzene are fast permeators. Cyclohexane and carbon tetrachloride are bad for the same reason. Note also that pentene-2 diffuses more rapidly than normal pentane. In all cases it is relatively easy to get all atoms in the molecule going in the same direction at the same time when they are rigidly bound one to another. Such is not the case, however, with a flexible molecule like decane, and diffusion is less rapid. The effect is one of entropy, and shows up in the frequency factor, as seen in Table VI.

Thus it is not at all surprising that rigid aromatic hydrocarbons fall above the flexible aliphatic hydrocarbons on a $\log P_o$ vs. E_p plot (larger $\log P_o$ for given E_p; See Figure 10, Part 2), with the cyclic aliphatic hydrocarbon cyclo-hexane actually belonging with the aromatic family, and the essentially straight chain, flexible, and not too polar ethers, esters, ketones and aldehydes with their aliphatic analogues.

On the other hand, the aliphatic alcohols form a distinct family of their own. For given $\log P_o$ (indicating size of hole required, rigidity, and probably

other miscellaneous effects), polarity augments E_p, boosting it above the "normal" hydrocarbon value, thereby displacing the family $\log P_o$ vs. E_p curve off to the right (see again figure 10, Part II). Polarity also pulls (or pushes) phenol off to the right, landing it nearly on the curve for the alcoholic aliphatic family; aniline too is displaced far to the right of the aromatic family.

To summarize, we recast slightly the concluding remarks to section 25 of Part 2 as follows:

Generic relationships on a $\log P_o$ vs. E_p plot are to some extent determined by molecular rigidity and, perhaps to a larger extent, by polarity. Thus non-polar but rigid cyclohexane falls in with the also non-polar rigid aromatic ring compounds; and the flexible straight chain ethers, esters, ketones, and aldehydes are grouped somewhat with the straight chain hydrocarbons of comparable flexibility. But highly polar phenol clearly belongs with the polar aliphatic alcohols off to the right, and the strongly hydrogen-bonded aliphatic acids fall in a class by themselves, rather than with the paraffins.

To conclude this section, we consider briefly the heavy atom effect, a factor that influences frequency factors and calculated P-Factors.

Imagine two molecules, essentially the same size, shape, polarity, and rigidity, but composed of atoms with nuclei of different mass numbers; that is, two molecules, essentially identical with regard to solubility and diffusion in polyethylene, but of different molecular weight. Clearly by our methods we would calculate identical P-Factors (in _grams_ per unit), but probably measure different weight losses experimentally (assuming that _molecule for molecule_ the two substances permeate with essentially identical _rates_). To allow for this effect, P-Factors should be expressed in number units (moles) rather than weight units (grams).

The correction from grams to moles is not a significant one in so far as Part 2 of this study is concerned; for there, within any one $\log P_o$ vs E_p family, molecular masses increased more or less linearly with size (and E_p). The correction would merely decrease the slopes of the curves in Figure 10, without changing their essential linearity. But there may be cases where atoms other than mainly carbon and hydrogen, with an occasional oxygen, nitrogen, or halogen atom mixed in, are involved, making it necessary to allow for the heavy atom effect when calculating weight P-Factors. (Carbon tetrachloride is such a case.)

19. Permeability of Polyethylene to Some Aqueous Solutions.

In this section we take a look at some data, not previously considered, on aqueous solutions of sulfuric acid, sodium hydroxide, nitric acid, hydro-

chloric acid, and ammonia. The hypothesis to be checked is this: That, at least in so far as the water is concerned, there should be weight losses (or gains) recorded whenever the vapor pressure of the water over the solution is greater (or less) than the partial pressure of the water vapor outside.

The data on weight losses are taken from Part 1 of this study, those on vapor pressures largely from the International Critical Tables (Volume III).

Part A. Weight Loss Data.

The data under consideration are listed in Table VII, where it is indicated whether the bottles gained or lost weight.

TABLE VII

MASTER DATA ON AQUEOUS SOLUTIONS OF H_2SO_4, NaOH, HNO_3, HCl, AND NH_3. WEIGHT LOSSES AND GAINS

Substance	32°F	70°F	100°F	130°F	165°F
Water	Erratic	Loss	Loss	Loss	Loss
Sulfuric Acid					
36% (By Weight)	Gain	Loss	Loss	Loss	Loss
50%	Gain	Erratic	Loss	Loss	Loss
68%	Gain	Gain	Erratic	----	Loss
93%	Gain	Gain	Gain	Erratic	Loss
Sodium Hydroxide					
10%	Erratic	Loss	Loss	Loss	Loss
40%	Gain	Erratic	Loss	Loss	Loss
Solid	Gain	Gain	Gain	Gain	Gain
Nitric Acid					
20%	Erratic	Loss	Loss	Loss	Loss
67%	Gain	Loss	Loss	Loss	----
Hydrochloric Acid					
20%	Gain	Loss	Loss	Loss	Loss
36%	Gain	Loss	Loss	Loss	----
Ammonia					
10%	Loss	Loss	Loss	----	----
28%	Loss	Loss	Loss	----	----

We notice that in every case low temperature gains, or erratic behavior, tend to be followed at higher temperatures by systematic weight losses.

Part B.   Theory.

P-Factors at 70°F were determined from bottles standing in a room thermostated at 70°F, relative humidity constant at 50%; those at higher temperatures in ovens through which air from the room was circulated.

At 70°F the vapor pressure of water is 18.7 mm of Hg. Thus the partial pressure of the water vapor in the room air conditioned as mentioned above (R.H. = 50% at 70°F), was one-half this, or approximately 9.3 mm of Hg. Assuming that there was no water added to or removed from the air as it entered and circulated through the ovens, this is also the partial pressure of the water vapor outside those bottles whose P-Factors were determined at 100°, 130°, and 165°F.

Therefore, when the aqueous tension inside a bottle was greater than 9.3 mm, water should have permeated outwards, and vice-versa. When water was the only penetrant, this means weight losses whenever the aqueous tension was greater than 9.3 mm, and weight gains whenever the aqueous tension was less than 9.3 mm. Actually, owing to small variations in temperature -- which have rather pronounced effect on aqueous tensions, and fluctuations in relative humidity, erratic behavior is perhaps to be expected (alternating small gains and losses), for bottles containing solutions whose aqueous tensions are close to 9.3 mm.

(The argument above is essentially based on the fact that diffusion must vanish with the gradient of the chemical potential, for which we may use the vapor pressure as a measure.)

In the following sections C through G we consider the facts individually for aqueous solutions of H_2SO_4, NaOH, HNO_3, HCl, and NH_3.

TABLE VIII

AQUEOUS TENSIONS OVER SULFURIC ACID SOLUTIONS
(ICT, III, p303)

t°C \ Wt.%	95	90	70	65	50	40	35	30
0 (32°F)	-----	-----	0.15	0.38	1.55	2.55	3.06	3.43
15								
20 (68°F)	-----	0.005	0.72	1.61	6.20	9.95	11.8	13.2
25								
35								
40 (104°F)	0.002	0.026	2.75	5.66	20.3	31.8	37.3	41.7
50								
55 (131°F)	0.009	0.08	6.89	13.4	45.5	69.0	80.2	91.0
60								
70								
75 (167°F)	0.042	0.327	20.3	37.0	115.	171.	198.	222.
80								

PREDICTIONS (Based on loss of water)

36%   Gain at 32°F. Loss at 70°F and above. (O.K. See
                                               Table VII)

50%   Gain at 32°F and 70°F. Loss at 100°F and above. (O.K.)

68%   Gain at 32° and 70°F. Probably erratic at 100°F.
       Loss at 130°F and above. (O.K.)

93%   Gain at all temperatures. (165°F value anomalous)

DISCUSSION

Water loss predictions in good agreement with experiment, except for concentrated acid at highest temperature, which might be diffusion of SO_3, although its tension is small (ICT, vol. III, page 304).

CONCLUSIONS

Diffusion of H_2SO_4 (or SO_3) negligible over the temperature and concentration range studied.

TABLE IX

AQUEOUS TENSIONS OVER SODIUM HYDROXIDE SOLUTIONS
(ICT, III, p370)

C \ $t^{o}C$	20 (68°F)	40 (104°F)	60 (140°F)	80 (176°F)
0	17.5	55.3	149.5	355.5
5	16.9	53.2	143.5	341.5
10	16.0	50.6	137.	325.
20	13.9	44.2	120.5	288.5
50	6.3	20.7	62.5	160.5
60	4.4	15.5	47.	124.
70	3.0	10.9	34.5	94.

C = grams of NaOH per 100 grams of H_2O (ICT, III, p351)

= approximately 11.1 for 10% NaOH, and

= approximately 66.6 for 40% NaOH.

PREDICTIONS (Based on water loss)

10%	Loss at 70°F and above. (O.K.)

40%   Gain at 70°F. Probably erratic at 100°F. Loss at 130°F and above. (Essentially O.K.)

Solid   Gain at all temperatures (O.K.)

DISCUSSION

Water loss predictions in good agreement with experiment.

CONCLUSIONS

Diffusion of NaOH (or hydrated Na^+ and OH^-) negligible over the temperature and concentration range studied, in agreement with expectation, since the tension of NaOH is negligible.

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Part E. Nitric Acid.

TABLE X

H$_2$O AND HNO$_3$ TENSIONS OVER NITRIC ACID SOLUTIONS
(ICT, III, p304-5)

t$^{\circ}$C	Wt. %	20	25	65	70
0 (32°F)		4.1	3.8	1.3 (0.41)	1.1 (0.79)
20 (68°F)		15.2	14.2	4.9 (1.68)	4.1 (3.00)
40 (104°F)		47.5	44.	15.5 (5.7)	12.8 (9.68)
55 (131°F)		100.0 (0.09)	94. (0.18)	33.0 (12.8)	27.3 (21.0)
75 (167°F)		250.0 (0.38)	234. (0.77)	86. (35.)	70. (43.3)

HNO$_3$ tensions in parentheses.

PREDICTIONS (Based on water loss)

20%   Loss at 70°F and above. (O.K.)

67%   Gain at 70°F. Loss at 100°F and above. (Experimental bottle weights showed erratic behavior for first month at 70°F, followed by steady loss)

DISCUSSION

Prediction at 70°F for 67% solution perhaps in error.

CONCLUSIONS

Volatility of HNO$_3$ may be a factor for 67% solutions. As the tension of one component rises, the other drops. At 75°C (167°F), HNO$_3$ tension over 67% acid almost 100 times greater than that for 20% acid at same temperature.

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Part F.   Hydrochloric Acid.

TABLE XI

H_2O AND HCl TENSIONS OVER HYDROCHLORIC ACID SOLUTIONS
(ICT, III, p301)

Wt. %	t°C	20 (68°F)	40 (104°F)	50 (122°F)	60 (140°F)	70 (158°F)	80 (176°F)
20		10.3 (0.2)	33.3 (1.06)	57.0 (2.21)	93.5 (4.4)	150. (8.5)	230. (15.6)
36		3.1 (105.)	11.4 (322.)	20.4 (535.)	34.8	57.0	90.0

HCl tensions in parentheses.

PREDICTIONS (Based on water loss)

20%   Loss at 70°F and above.   (O.K.)

36%   Gain at 70°F.   Loss at 100°F and above.   (70° prediction incorrect).

DISCUSSION

20% solution falls in line, but water loss predicts gain at 70° for 36% acid, whereas in fact a substantial loss is observed.   In fact, the P-Factors for 36% HCl are greater than those for pure water.

CONCLUSIONS

The diffusion of hydrochloric acid is appreciable at 70°F and above for the more concentrated acid.

TABLE XII

NH₃ TENSIONS OVER AMMONIA SOLUTIONS
(ICT, III, p362)

t°C	Wt. %	5	10	15	20	25	30
0 (32°F)		14.6	28.8	49.6	81.8	127.5	195.8
20 (68°F)		51.8	87.8	142.9	224.7	335.5	494.5
40 (104°F)		131.8	227.5	353.5	543.0	766.9	1143.5
50 (122°F)		207.5	348.0	530.2	783.5	1109.	1554.5
60 (140°F)		314.5	517.2				
70 (158°F)			748.0				

DISCUSSION AND CONCLUSIONS

P-Factors for aqua ammonia, both 10 and 28%, greater than those for pure water. Weight losses in these cases obviously due primarily to NH_3.

Part H. P-Factors for Aqueous Solutions and Henry's Law.

If the solubility of water in polyethylene is proportional to its partial pressure (Henry's Law):

$$S = k(V.P.),$$

where k = Henry's Law Constant and V.P. is the vapor pressure or aqueous tension of the solution (which is the partial pressure of the water at saturation), then

$$P = S.D \qquad \text{(Part 2, Introduction)}$$

$$= k(V.P.)D;$$

that is to say, at a given temperature P-Factors for aqueous solutions should be proportional to their aqueous tensions if Henry's law is obeyed.

In Table XIII we have collected the data for pure water and those solutions examined in Parts C through G where it seems probable that water is the only component that penetrates the polyethylene to any appreciable extent.

TABLE XIII

P-FACTORS AND AQUEOUS TENSIONS

Solution and Property	70°F	100°F	130°F	165°F
Pure Water				
P-Factor x 100	27.9	83.5	394.	1840.
Tension	18.7	48.9	114.8	276.
Ratio*	1.5	1.7$_1$	3.4	6.7
20% Nitric Acid				
P-Factor x 100	16.1	64.8	374.	147$_5$.
Tension	15.2	44.5	100·	250·
Ratio	1.1	1.4	3.7	5.9
10% Sodium Hydroxide				
P-Factor x 100	19.6	72.3	364.	1508.
Tension	15.8	46.4	110.	243.
Ratio	1.2	1.4	3.6	6.2
40% Sodium Hydroxide				
P-Factor x 100	----	27.0	192.	642.
Tension	3.6	12.0	31.	84.
Ratio	----	2.2	6.3	7.6
36% Sulfuric Acid				
P-Factor x 100	----	57.	304.	----
Tension	11.	35.	79.	190.
Ratio	----	1.6	3.8	----
50% Sulfuric Acid				
P-Factor x 100	----	23.8	204.	603.
Tension	6.2	19.	45.	111.
Ratio	----	1.3	4.4	5.4
68% Sulfuric Acid				
P-Factor x 100				121.
Tension				26.
Ratio				4.6

Although no allowance has been made in Table XIII for the fact that diffusion of the water is against a back pressure of 9.3 mm of Hg, and although reliable P-Factors on even pure water itself are difficult to obtain, it seems likely that Henry's Law is obeyed over the temperature range covered by Table XIII. Note that the ratio of the P-Factor to the aqueous tension increases with rising temperature, in accordance with the following facts:

$$P = P_o e^{-E_p/RT}, \text{ and}$$

$$(V.P.) = (const)e^{-\Delta H_{vap}/RT}; \text{ therefore}$$

$$P/(V.P.) = (const)e^{-(E_p - \Delta H_{vap})/RT},$$

which increases with rising temperature since for water E_p (about 18 kcal/mole) is greater than ΔH_{vap} (about 10 kcal/mole).

20. **P-Factor Calculations for Carbon Tetrachloride and Comparison With Recent Experimental Data.**

The vital statistics for carbon tetrachloride are

Molecular Weight	153.8
Density (gms/cc)	1.595
Molar Volume (in cc)	96.45
Length of Fisher Model (in cm).	5.5
Shape Index (96.45/5.5)	17.5
Boiling Point (°C. For use with Dreisbach) .	76-7
Heat of Vaporization (Dreisbach, chart 13) .	7.9
$\Delta\Delta H$ (comparison with pentane)..	1.3

From these data, we calculate that for carbon tetrachloride (equation 14-1, Part II)

$$E_p = 0.0348(96.45) + 0.75(17.5) + 2.4(1.3)$$
$$= 3.36 + 13.12 + 3.12$$
$$= 19.60 \text{ kcal/mole.}$$

From the slope of a logP vs 1/T plot for CCl_4 in DE-2400 (data reported in Part 3), an experimental activation energy of 18.9 kcal/mole was found. The agreement is not bad considering the fact that the shape factor for carbon tetrachloride, 17.5, is considerably greater than that for any of the compounds

on which the original study (Part II) and equation 14-1 were based (most values ran between 9 and 12, with 15.6 for cyclohexane and 15.9, the previous high, for ter-butyl alcohol).

Next, following the discussion of section 18, we assume with some confidence that CCl_4 belongs with the aromatic $logP_o$ vs. E_p family and estimate for the frequency factor (Table 20, Part 2) that

$$logP_o = 0.661(19.60) + 3.74 = 16.69,$$

and hence that

$$logP(70°F) = -19,600/(4.6)(294.3) + 16.69$$

$$= -14.47 + 16.69 = 2.22, \text{ with}$$

$$P(70°F) = 166 \quad \text{Observed: } 500 \text{ gms per ... (using the initial slope of the wt. loss - time curve at } 70°F)$$

The calculated value is of the right order of magnitude, but not directly comparable to the observed value of 500. One or the other of the values should be corrected to allow for the fact that weight-loss-wise CCl_4 has a large P-Factor owing to the fact that four of its five atoms are chlorine atoms, which are more than twice as dense as methyl groups. Multiplying the 166 by the ratio of the molecular weight of carbon tetrachloride (154) to the molecular weight of carbon tetramethyl (72), we obtain 350, compared to 500.

Finally, were we to allow for the fact that once three of the four chlorine atoms in CCl_4 make it to an activated state the remaining one probably tags along with little trouble, and subtract 1 kcal from E_p (the para or torpedo effect; see section 12, Part 2), using therefore 18.6 and $0.661(19.6) + 3.74 = 16.03$ for $logP_o$, we should calculate for P at 70°F the value 200 times (as before) 154/72, or 420, which is within 16% of the observed value at this temperature.

A list of some recent articles concerned with irradiation and crystallinity of polyethylene.

Irradiation

1. "The Cross-linking and degradation of paraffin chains by high energy radiation."
   A. Charlesby, Proc. Roy. Soc. A 222, 60 (1954)

2. "The effect of cross-linking on the elastic modulus of polyethylene."
   A. Charlesby, Proc. Roy. Soc. A 218, 245 (1953)

3. "The effect of cross-linking on the Density and Melting of polythene."
   A. Charlesby and M. Ross, Proc. Roy. Soc. A 217, 122(1953)

4. "The Pile Irradiation of Polyethylene."
   M. Dole, C. D. Keeling, and D. G. Rose, J. Am. Chem. Soc. 76, 4304 (1954)

Crystallinity

1. Special High Polymer Issue, J. App. Phys., 25, 820-854 (1954)
   "Molecular Structure and the Crystallinity of Long-Chain Polymers" by C. W. Bunn.

   "Relationship of First- to Second-Order Transition Temperatures for Crystalline High Polymers" by R. F. Boyer.

   "Crystallization Kinetics in High Polymers. I. Bulk Polymers" by L. Mandelkern, F. A. Quinn, and P. J. Flory.

   "X-Ray and Infrared Studies on the Extent of Crystallization of Polymers" by J. B. Nichols.

   "An Infrared Study of the Crystallization of Polyethylene" by F. P. Reding and A. Brown.

   "Crystallization in Butadiene-Styrene Copolymers" by L. A. Wood.

2. "Thermodynamics of Crystallization of High Polymers: Natural Rubber."
   D. F. Roberts and L. Mandelkern, J. Am. Chem. Soc. 77, 781 (1955)