

MECHANISM OF THERMAL DEGRADATION OF POLYMERS

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I. INTRODUCTION

No mathematical analysis of the kinetics of the thermal degradation of polymers can be regarded as adequate until all of the contributing elementary rate processes have been considered in a model which predicts the measurable changes which occur during degradation. Therefore, research in this field falls into four general categories:

1. Identification of contributing rate processes,
2. Collection of data for describing these processes,
3. Synthesis of this data into a model which predicts the measurable changes, and
4. Measurement of these changes.

This report is broken down into three sections corresponding to the first two and last of these categories.

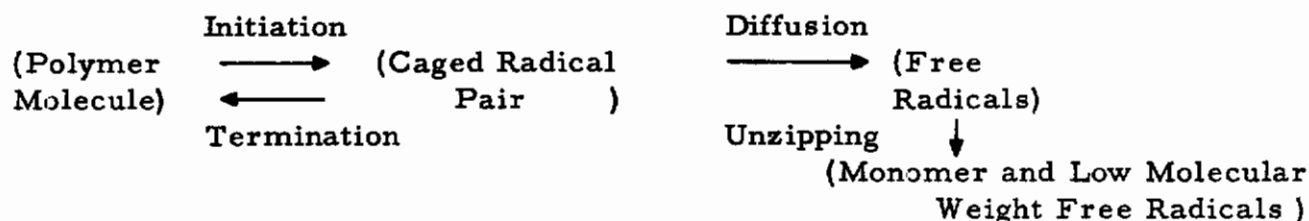
II. IDENTIFICATION OF CONTRIBUTING RATE FACTORS, THE "CAGE EFFECT"

In thermal degradation studies, the "cage effect" has been completely ignored. In order to demonstrate that this effect is a contributing rate factor, an extremely simple mathematical model including it is discussed below.

Assume that a polymer degrades by random chain scission followed by complete unzipping of both radicals to very low molecular weight radicals and monomer, which diffuse out of the sample before undergoing further reaction. Also, assume that the density of the polymer sample stays constant during degradation.

Contrails

Polymer radicals formed during initiation in an amorphous polymer sample should have a higher probability of immediate termination before unzipping than the similar initiation of linear molecules in the gas phase. Radical pairs which have just formed and have not separated to any extent will be called "caged radical pairs." Using this definition, the process of degradation may be represented in the following manner.



From this it follows that the rate of increase of concentration of "caged radical pairs" is

$$\frac{d[R_p]}{dt} = \alpha N K_i [P] - K_T [R_p] - K_D [R_p] \quad (1)$$

where $[R_p]$ is the concentration of "caged radical pairs," t is time, N is the number average degree of polymerization of polymer molecules, $[P]$ is polymer molar concentration and K_i , K_T , and K_D are rate constants for initiation, termination of "caged radical pairs" and separation of caged radical pairs. α is the number of carbon-carbon bonds contributed by each monomer unit. For vinyl polymers, the case considered here, α is equal to two.

The rate of formation of uncaged free radicals per unit volume is,

$$\frac{d[R]}{dt} = 2K_D [R_p] \quad (2)$$

Assuming the steady state for "caged radical pairs", $d[R_p]/dt=0$,

$$\frac{d[R]}{dt} = 2K_D \left(\frac{2NK_i [P]}{K_T + K_D} \right) = \left(\frac{K_D}{K_T + K_D} \right) \left(4NK_i [P] \right) \quad (3)$$

The rate of formation of monomer is

$$\frac{dM}{dt} = -\frac{1}{M} \frac{dw}{dt} = \frac{N}{2} \left(\frac{d[R]}{dt} \right) V \quad (4)$$

where V is the sample volume, m is the molecular weight of a monomer unit, and w is the weight of the sample. Substituting 3 into 4 and then substituting the rela-

$$\text{tion } [P] = \frac{w}{VmN}$$

$$\frac{dw}{dt} = -\left(\frac{K_D}{K_T + K_D}\right)(2NK_i)w \quad (5)$$

If K_D is much greater than K_T , $K_D/(K_T + K_D)$ will equal one and $dw/dt = -2NK_i W$, (6)

the rate equation for the case where the cage effect is negligible.¹

In order to find $K_D/(K_T + K_D)$ for the other case where K_D is not much greater than K_T , one utilizes the fact that the rate constants may be expressed in terms of an Arrhenius equation, that is

$$K_D = A_D e^{-E_D/RT}$$

$$K_T = A_T e^{-E_T/RT}$$

Also it is assumed that a liquid cell model holds where molecules may move only in six perpendicular directions and that once one of the free radicals in a "caged radical pair" makes a jump which does not lead to termination, the probability of termination of the radical pair is zero. Therefore, for this model $A_D = 5A_T$.

In order to put numbers into these expressions, polytetrafluoroethylene is taken as an example. E_T for radical recombination is generally quite small, and in this case due to the high degree of orientation given the free radical, it will be assumed that $E_T = 0$. From diffusion data in a following section of this paper E_D may be estimated to be 9 kcal for tetrafluoroethylene. Therefore,

$$K_D/(K_T + K_D) \approx 5e^{-9\text{kcal}/RT} = .015$$

at 500° C. It is to be expected that a chain end would have a much higher activation energy for diffusion due to the stiffness of a polytetrafluoroethylene chain. In any case, the cage effect appears to make a significant contribution to the overall rate even if one of the free radicals is as small as tetrafluoroethylene.

In order to give an example of the type of effect that the "cage effect" may have on a rate expression, the rate expression obtained from substituting values into equation 5 and 6 are compared. Comparison with the experimental rate expression is interesting also because the theoretical expression including the "cage effect" is in surprisingly good agreement with experiment.

The three expressions are:

1. Theoretical, neglecting the "cage effect"

$$\frac{dw}{dt} = \left[-2 \times 10^{18} e^{-74,000/RT} \right] W$$

2. Theoretical, including the "cage effect"

$$\frac{dw}{dt} = \left[-10^{19} e^{-83,000/RT} \right] W$$

3. Experimental²

$$\frac{dw}{dt} = - \left[9.4^{+7.4}_{-4.2} \times 10^{18} e^{-81,400/RT} \right] W$$

The first two expressions were obtained from substituting the values $N=10^4$ and $K_1 = 10^{14} e^{-74,000/RT}$ for gas phase reactions into equations 6 and 5 respectively. The experimental expression is the least square line of the Arrhenius plot of the data of Madorsky, and Siegle and Muus.

While this theoretical model is in good agreement with significant experimental results, it is open to question. Nevertheless it is felt that the cage effect itself cannot be ignored.

III. COLLECTION OF DATA FOR DESCRIBING DEGRADATION PROCESSES

A. Diffusion

The purpose of this part of the research program is to obtain diffusivity and solubility coefficients of the evolved products of degradation in parent polymer. At the present, the time-lag method³ is being used to study the flow of hexafluoropropene and tetrafluoroethylene in polytetrafluoroethylene. This type measurement is begun by evacuating a polymer sample from both sides. Then a vapor of a known pressure is introduced on one side and the increase in pressure of the other side is recorded against time.

At very high temperatures the time-lag is very short and difficult to measure, but permeabilities can be obtained. These permeabilities can be combined with independently determined solubility coefficients to yield diffusivity coefficients. Solubility coefficients can be determined by both theoretical and experimental techniques. A theoretical method is described later in this paper.

Theory

Published derivations of the equations used in this work are more complex than necessary because other authors have tried to maintain a high degree of generality.⁴ For this reason a comparatively simple derivation is presented.

The basic hypothesis of the mathematics of diffusion is Fick's First Law,

$$F = -D \frac{dC}{dx} \quad \text{where}$$

F is the rate of diffusion per unit area, C is the concentration of the diffusing gas, x is distance measured normal to the above area and parallel to the path of the diffusing vapor, and D is a constant called the diffusion coefficient and diffusivity. From this law, Fick's Second Law follows,

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad \text{where } t \text{ is time}$$

In this experiment both sides of the polymer film are evacuated for a long period before the gas is admitted to the chamber on one side of the film. Since diffusion is slow this vapor stays effectively at a constant pressure ϕ_0 . Therefore, its concentration C_0 , at the surface of the sample is assumed to be constant.

Since the pressure on the other side is always less than one thousandth of ϕ_0 , the concentration of gas at this surface of the polymer film can be assumed to be zero.

From this discussion we can write the boundary conditions.

1. At all time at $x = 0$, $C = 0$
at $x = l$, $C = C_0$ where l is film thickness.

Contrails

2. At $t = 0$ and at $0 \leq x \leq l$, $C = 0$

A solution of Fick's Second Law is

$$C = Ax + \sum_n (B_n \sin \lambda_n x) e^{-\lambda_n^2 Dt} \quad (7)$$

where A , B_n , and λ_n are to be determined.

Applying condition 1. starting with $t \rightarrow \infty$ equation (7) reduces to $C=0$ at $x = 0$ and to $C = C_0$ at $x = l$ if $C_0 = Al$. Therefore, $A = \frac{C_0}{l}$. At other values of t , $C = 0$ at $x = 0$ and $C = C_0$ at $x = l$ if $0 = \sum_{n=1}^{\infty} (B_n \sin \lambda_n x) e^{-\lambda_n^2 Dt}$ which is true if $\lambda_n = n \pi / l$.

Applying condition 2 where $0 \leq x \leq l$ at $t = 0$ and $C = 0$ we find $0 = \frac{C_0 x}{l} + \sum_{n=1}^{\infty} (B_n \sin \frac{n\pi x}{l})$. By multiplying this equation by $\sin p \frac{\pi x}{l}$

and integrating from $x = 0$ to $x = l$ we find that $B_n = \frac{2C_0(-1)^n}{n\pi}$.

On substituting these relations into equation (7) we find $C = \frac{C_0 x}{l} + \sum_{m=1}^{\infty} \frac{2C_0}{m\pi} (-1)^m (\sin \frac{m\pi x}{l}) e^{-\frac{(m\pi)^2}{l^2} Dt}$. From this relation the rate of flow at the surface $x = 0$ is found to be

$$D \left(\frac{dc}{dx} \right)_{x=0} = \frac{DC_0}{l} + \frac{2DC_0}{l} \sum_{m=1}^{\infty} (-1)^m e^{-\frac{(m\pi)^2}{l^2} Dt}$$

The overall quantity Q_t which has diffused out of side $x = 0$ at any time is

$$Q_t = \int_0^t D \left(\frac{dc}{dx} \right)_{x=0} dt = \frac{Dc_0 t}{l} - \frac{2C_0 l}{\pi^2} \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2} e^{-\frac{(m\pi)^2}{l^2} Dt} + \frac{2C_0 l}{\pi^2} \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2}$$

As $t \rightarrow \infty$ and equilibrium is reached Q_t becomes a linear function of time,

$$Q_t = \frac{DC_0 t}{l} + \frac{C_0 l}{6}$$

This line may be extrapolated back to Q_t equals 0 to give an intercept, L , on the time axis. Therefore, the diffusion coefficient may be obtained from this intercept and the thickness of the sample.

$$D = \frac{l^2}{6L}$$

At a given temperature the equilibrium concentration of dissolved vapor in a high polymer may be related to the pressure in the following manner,⁵ $C = (S_0 e^{QC}) \phi = S \phi$ where Q is a constant, S is the solubility coefficient and S_0 is the zero concentration solubility coefficient. For highly volatile vapors at low vapor activities e^{QC} approaches one and the ratio C/P is nearly equal to the constant S_0 . Even at fairly high concentrations $S/S_0 = 1$ due to the low magnitude of Q.

On substituting the relation $C = S \phi$ into Fick's First Law, $F = -SD \frac{d\phi}{dx}$. The product SD is defined as P, the permeability or $SD = P$.

It follows from Fick's Second Law that, at the steady state, concentration varies linearly, therefore, if $C = S \phi$ the following relation holds:

$$F = P(\phi_2 - \phi_1)/x \text{ where } \phi_1 \text{ and } \phi_2 \text{ are two pressures } x \text{ distance apart.}$$

With these assumptions, we can find P from the slope of the ϕ vs T plot at steady state and D from the intercept of the steady state line with the t axis. From these two values we can calculate S.

B. Diffusion Measurements

A schematic diagram of the vacuum apparatus used is shown in Figure I. Volume 1 is filled with the specimen gas and volumes 2 and 3 are evacuated overnight. Then stopcock D is closed and B is opened. The increase in pressure in volume 3 is then measured with a McLeod gauge. The "leak rate" is determined by measuring the increase in pressure in volume 3 before opening B to admit the specimen gas to volume 1.⁶

Figure II shows a typical plot of experimental data. The gas is admitted to volume 2 at the time indicated by the arrow. It is assumed that the established "leak rate" stays the same through the diffusion run so that subtraction from the observed pressure yields the pressure increase due to diffusion.

Two diffusion cells were used. The first was a very crude arrangement. The area was small, and stopcock grease was used to seal in the polymer film.

Contrails

The second diffusion cell is shown in Figures III and IV. This cell was constructed from stainless steel and put together with silver solder. The polymer film was put between the two halves of the cell and the two halves were bolted tightly together. The closed cell was put in a carefully machined copper block inside a specially built furnace.

The temperatures in the copper block, in the stainless steel cell and inside the cell where the high pressure vapor is stored were measured with thermocouples. The temperature differences and fluctuation were less than $\pm 1^{\circ}\text{C}$.

The measurements were made between 25 and 350°C . The latter being the highest temperature at which a polytetrafluoroethylene film can be maintained without its collapsing.

The tetrafluoroethylene was prepared by degrading polytetrafluoroethylene slowly and collecting the vapor. The vapors which could not be condensed with liquid nitrogen were pumped off and vapors which could be condensed with dry ice were removed from the tetrafluoroethylene. This procedure gives better than 96.7% pure tetrafluoroethylene.⁷ The pressure ϕ_0 was varied from 12 to .1 cm Hg.

The polytetrafluoroethylene films were provided by Dilectrix Corporation and designated as Type C Teflon Films. They varied from 1 to 5 mil in thickness.

It was found necessary to develop a reliable pressure measuring technique. The measurements were made with a carefully calibrated McLeod gauge. Five minutes were allowed for the mercury level in the gauge to settle down after it was brought up to a proper height. To save time no attempt was made to exactly zero the mercury in the standard column. As a result, it was necessary to measure the height of both columns with a cathetometer and calculate each pressure.

Table I and Figure V present the data collected to the present. Since both systems used with each of the two cells were completely different, the maximum absolute error should be indicated fairly well by differences in values of the room temperature permeabilities, $\pm .7 \times 10^{-9}$ (cc x mm)/(cmHg x cm² x sec)

C. Theoretical Determination of Zero Concentration Solubility Coefficients of the Low Molecular Weight Homologs of Vinyl Polymers in the Parent Polymer

In the following paragraphs, the zero concentration solubility coefficients of the low molecular weight homologs of vinyl polymers in the parent polymer are related to known properties of the vapor and polymer in order that the value of the solubility coefficients may be theoretically determined. This is necessary because at high temperatures solubility coefficients become very small and difficult to measure.

The following assumptions are made:

1. The enthalpy of solution of the condensed vapor with polymer at a given temperature is zero, i. e. $\Delta H = 0$
2. The ideal gas law is assumed for the gaseous state.
3. The total number of available sites for vapor molecules inside the polymer sample is equal to the difference in volume between the given polymer sample, and a hypothetical polymer sample of 100% crystallinity of the same mass, divided by the volume of a vapor molecule.
4. All of these sites are equivalent.

The difference in chemical potential of the vapor in equilibrium with the solution and the vapor in equilibrium with pure condensed vapor can be shown to be equal to

$$RT \ln \frac{P_i}{P_i^0} = \left[\frac{d(\Delta H - T \Delta S)}{dn_i} \right] \quad P, T, n_p$$

where P_i^0 is the equilibrium vapor pressure of pure vapor i , P_i is the vapor pressure of component i in equilibrium with the solution, n_i is the number of moles of vapor component i in the solution, n_p is the number of moles of polymer, and P , T , R , ΔH , and ΔS have their usual meaning.

Since $\Delta H = 0$

$$RT \ln \frac{P_i}{P_i^0} = - \left[\frac{d(T \Delta S)}{dn_i} \right] \quad P, T, n_p$$

Contrails

The difference in entropy between vapor in the solution and the pure condensed state equals

$$\Delta S = K \text{Ln} \Omega$$

where Ω is the number of distinguishable arrangements of vapor molecules in the polymer sample. The configurational entropy of the vapor in the pure condensed state at the same temperature is taken as zero.

If Z is the number of sites in the polymer sample and V is the number of dissolved vapor molecules, then

$$\Omega = \frac{Z!}{V! (Z-V)!}$$

Using Stirling's Formula, $\text{Ln} N! = N \text{Ln} N - N$

$$\begin{aligned} K \text{Ln} \Omega &= Z \text{Ln} Z - Z - V \text{Ln} V + V - (Z-V) \text{Ln} (Z-V) + (Z-V) \\ &= Z \text{Ln} Z - V \text{Ln} V - (Z-V) \text{Ln} (Z-V) \end{aligned}$$

The difference in chemical potential is

$$\begin{aligned} RT \text{Ln} \frac{P_i}{P_i^0} &= -N \left[\frac{d(T\Delta S)}{dV} \right]_{P, T, n_p} \\ &= -NKT \left[\frac{(\text{Ln} \Omega)}{dV} \right]_{P, T, n_p} \\ &= -RT \left[-\text{Ln} V - 1 + \text{Ln} (Z-V) + 1 \right] \\ &= RT \text{Ln} \left(\frac{V}{Z-V} \right) \end{aligned}$$

and $\frac{P_i}{P_i^0} = \frac{V}{Z-V}$

If $Z \gg V$, then

$$\frac{P_i}{P_i^0} = \frac{V}{Z}$$

The fraction of sites occupied is equal to

$$\frac{V}{Z} = \frac{P_i}{P_i^0} = \frac{C}{d_v \left(\frac{1}{d_p} - \frac{1}{d_c} \right)}$$

where C is the concentration of vapor (gm vapor/gm polymer), d_v is the density of the vapor, d_p is the density of the polymer after dissolving the vapor, and d_c is the density of the hypothetical 100% crystalline polymer.

The solubility coefficient at zero concentration is equal to

$$\begin{aligned} \text{Limit} \quad \frac{C}{P_i} &= S_0 \\ C \rightarrow 0 & \\ \text{or} \\ S_0 &= \frac{d_v}{P_i^0} \left(\frac{1}{d_p} - \frac{1}{d_c} \right) \end{aligned} \quad (8)$$

Equation 8 was used to calculate the theoretical solubility coefficients of low molecular weight homolog vapors of polyethylene in polyethylene as shown in table II.

The assumption was made that the degree of crystallinity does not change over the temperature range considered.⁸ The specific volume of the amorphous polyethylene was taken as $\bar{V} = 1.192 + 8.8 \times 10^{-4}T$ and the specific volume of crystalline linear polyethylene was taken as $\bar{V}_c = .993 + 3.0 \times 10^{-4}T$.⁸

From Table II it is apparent that all of the calculated values are in good agreement with experiment. The higher molecular weight vapors are in better agreement as would be expected from theory. While neither of the papers from which the experimental solubility coefficients were taken have a complete discussion of error, Brandt⁶ gives a 6% precision for his diffusion coefficients and states that solubility coefficients have a larger error than the corresponding diffusion coefficients.

While none of the vapors compared in Table II were above their critical temperatures it is possible to extrapolate equilibrium vapor pressures of pure vapors above their critical temperatures to obtain fair estimates of solubilities.⁹ Also the experimental data in Table II consists of measurements from both linear and branched polyethylenes. This theory seems to be adequately general to cover both cases. The greatest advantage of this theory is that it involves no parameters and the experimental data required for its application are, relatively speaking, readily available.

IV MEASUREMENT OF CHANGES WHICH OCCUR DURING DEGRADATION

A. Gradient Elution

Since it is necessary to obtain molecular weight distributions of the residue of the polymer after degradation, some work has been started to develop a gradient elution analysis apparatus. This apparatus is based on the principle that addition of solvent progressively dissolves fractions of precipitated polymer of increasing molecular weight. Superimposed upon this concentration gradient is a temperature gradient.

The apparatus which is being developed is shown in Figure VI. The design of this apparatus has some improvements over other apparatus used up to the present while still remaining as inexpensive as a gravity flow system. Since there will be no air space in the apparatus, there will be no need to adjust separate flow rates.

In a gravity feed system there is a rate controlling capillary at the bottom of the column which can become clogged with polymer and change the flow rate. In this apparatus, the rate controlling parts are the nitrogen pressure and the sinter filter. The pressure may be easily regulated and the sinter filter is not in danger of becoming clogged during the run since only pure solvent passes through it.

The major problem encountered has been to find suitable greases for joints and stopcocks.

B. High Vacuum Therman Balance

In order to measure weight changes of polymers undergoing thermal degradation as well as the temperature of the polymer, the apparatus shown in Figures VII and VIII was constructed. The polymer is suspended from an automatic recording balance by a fine thermocouple into a "Vycor" pyrolysis tube. The balance is mounted in a bell jar, has a 350 milligrams capacity and can measure weight changes over a range of 100 milligrams with .05% accuracy. The furnace is a cylindrical polished aluminum reflector with eight one kilowatt infrared heating lamps mounted inside. This method of heating raises the polymer to a constant degradation temperature before much reaction can occur at

intermediate temperatures.

Since it is quite unlikely that a polymer undergoing degradation is at the same temperature as its surroundings, it is desirable to measure the temperature of the polymer itself. Therefore, thermocouple wires are used to suspend the sample and contact is made intermittently by raising the level of the cups of mercury so as to make contact with the thermocouple wires.

With this apparatus it will be possible to measure the rate of weight loss and the volatile products formed during degradation of polymers at well defined temperatures.

TABLE I
DIFFUSION DATA FOR TETRAFLUOROETHYLENE
IN POLYTETRAFLUOROETHYLENE

Cell	Temperature	Permeability $\times 10^9$	Diffusivity $\times 10^9 \text{ cm}^2/\text{sec}$	Solubility Coefficient $\text{cc}/(\text{cc}\times\text{atm})$	Density of Polymer gm/cc
		$\frac{\text{cc} \times \text{mm}}{(\text{cm Hg}) \times \text{cm}^2 \times \text{sec}}$			
1	25.	2.7	7.2	2.2	2.18 \pm 01
	28.	2.2	7.9	2.1	"
	24.	2.5	6.7	2.9	"
	24.	2.5	7.2	2.7	"
2	25.	1.80	8.0	1.7	2.184 \pm .0006
	24.	1.85	8.5	1.65	"
	114.	14.4			"
	118.	21.8			2.161
	119.	23.6			"
	121.	16.5			2.184
	175.	63.9			2.161
	182.	73.1			"
	183.	79.0			"
	198.	87.0			"
	229.	164.0			2.161
	241.	167.0			2.184
	252.	171.0			"
	338.	1340.0			"
342.	1310.0			2.161	

TABLE II
COMPARISON OF THEORETICAL AND EXPERIMENTAL
SOLUBILITY COEFFICIENTS OF ALKANE VAPORS IN POLYETHYLENE

Vapor	Temperature °C	Density of Polyethylene	Solubility Coefficients x10 ⁴		Source of Experimental Data
			(gm vapor/(gm Polymer x cm Hg) Experimental	Theoretical	
Ethane	-5	.9511	.0483	.123	6
	0	.9505	.147	.110	6
	0	.9185	.173	.188	6
	0	.9103	.206	.209	6
	7	.9505	.106	.0945	6
	8	.9185	.138	.155	6
	25	.9505	.0743	.0549	6
	25	.9511	.0557	.0542	6
	25	.9508	.0538	.0546	6
	25	.9637	.0733	.0396	6
	25	.9182	.114	.0944	6
	25	.9639	.0787	.0394	6
	25	.9103	.112	.104	6
	25	.9206	.0997	.0913	6
	25	.9185	.127	.0940	6
Propane	25	.9511	.248	.339	6
Butane	25	.9511	.197*	1.53	6
Pentane	25	.9220	11.0	10.2	5
	25	.9505	6.24	6.25	6
	27	.9185	8.76	9.97	6
	50	.9185	4.61	4.77	6
	50	.9505	2.54	2.79	6
Hexane	0	.9540	67.0	65.3	5
	0	.9220	110.0	115.	5
	0	.9380	87.0	89.8	5
	25	.9220	39.0	36.4	5
	30	.9220	36.0	29.7	5
	30	.9540	20.0	16.9	5
	30	.9380	23.0	23.2	5
Heptane	25	.9220	140.0	125.0	5
Octane	25	.9220	460.0	420.	5

*Comparison of experimental data with itself indicates possible decimal error here.

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DIFFUSION APPARATUS

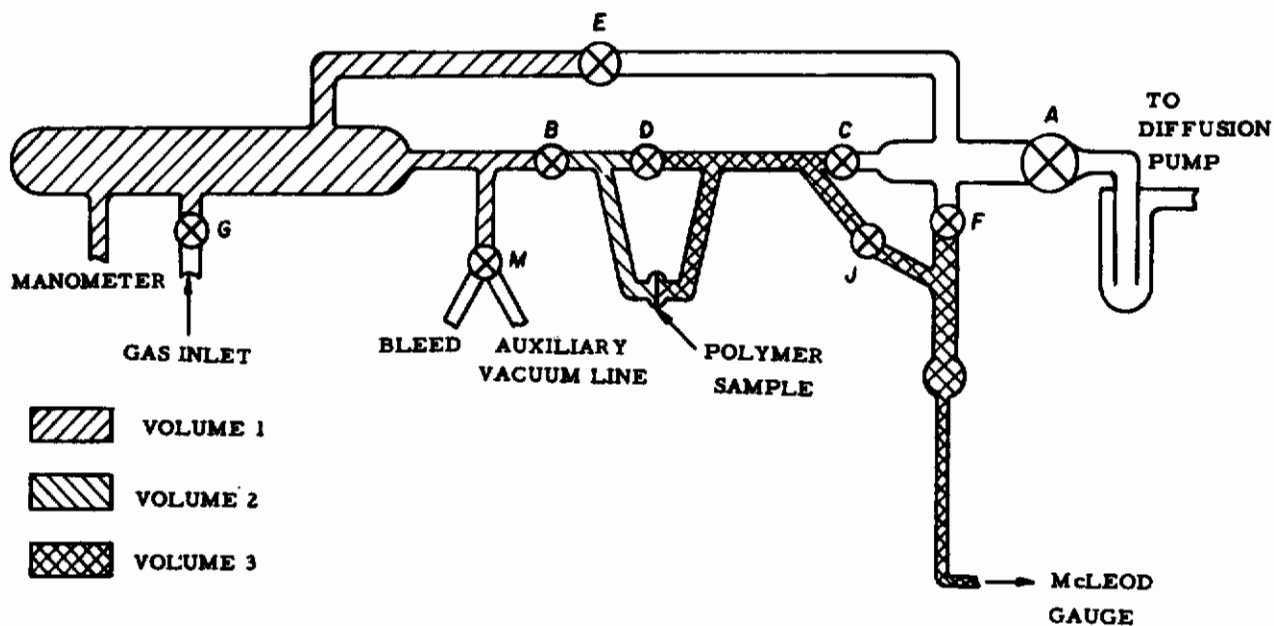


Figure I. Diffusion Apparatus

DIFFUSION OF C_2F_4 THROUGH TEFLON

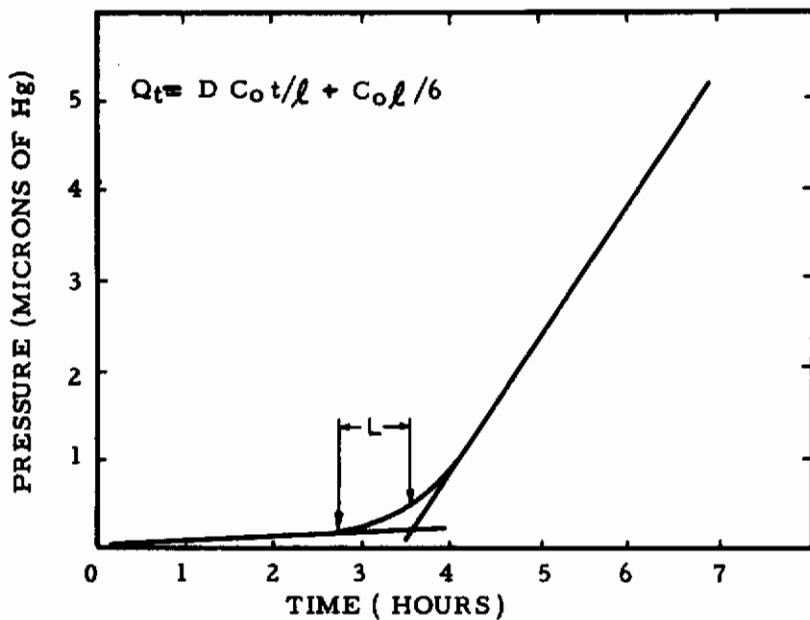


Figure II. Diffusion of C_2F_4 Through Teflon

HIGH TEMPERATURE DIFFUSION APPARATUS

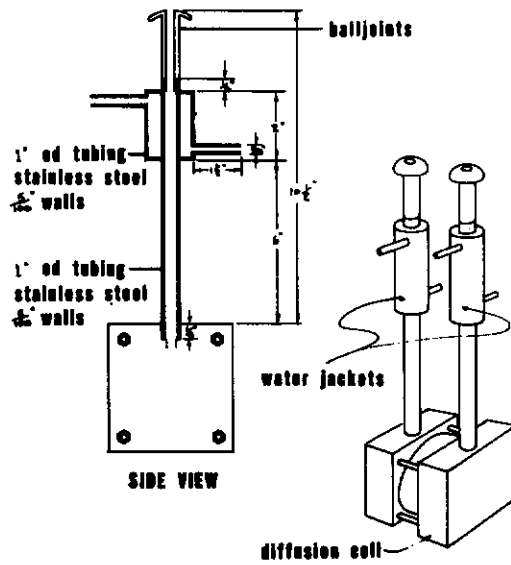
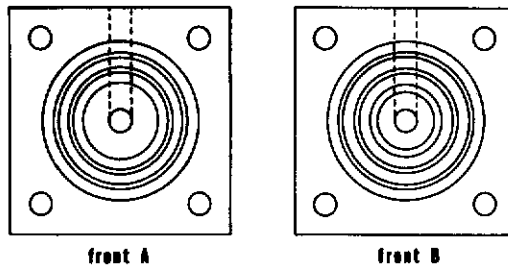


Figure III. High Temperature Diffusion Apparatus



HIGH TEMPERATURE DIFFUSION CELL

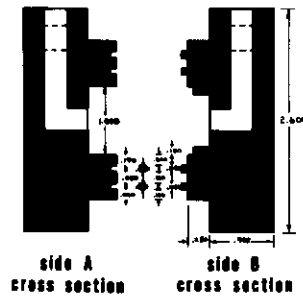


Figure IV. High Temperature Diffusion Cell

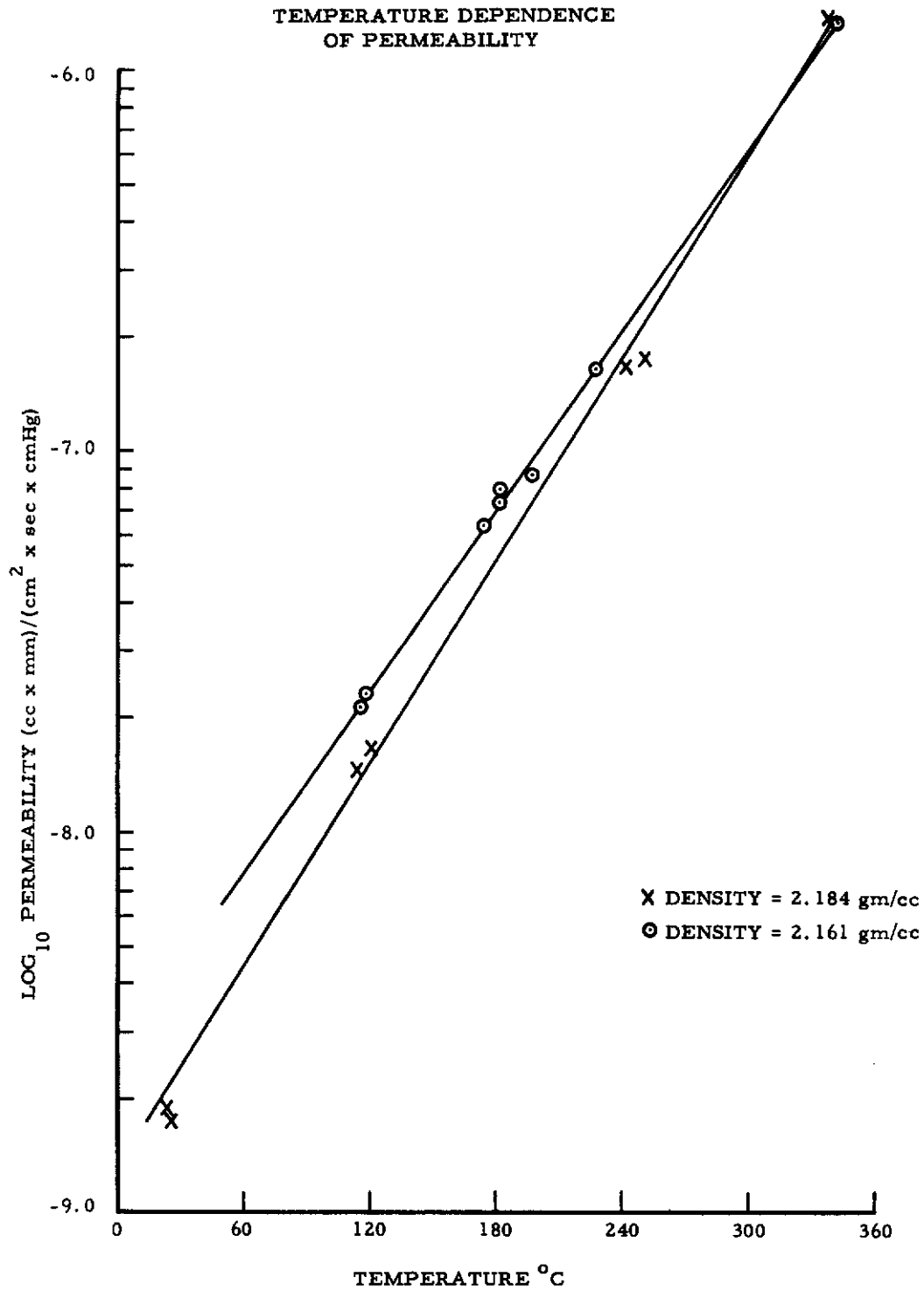


Figure V. Temperature Dependence of Permeability

APPARATUS FOR GRADIENT ELUTION

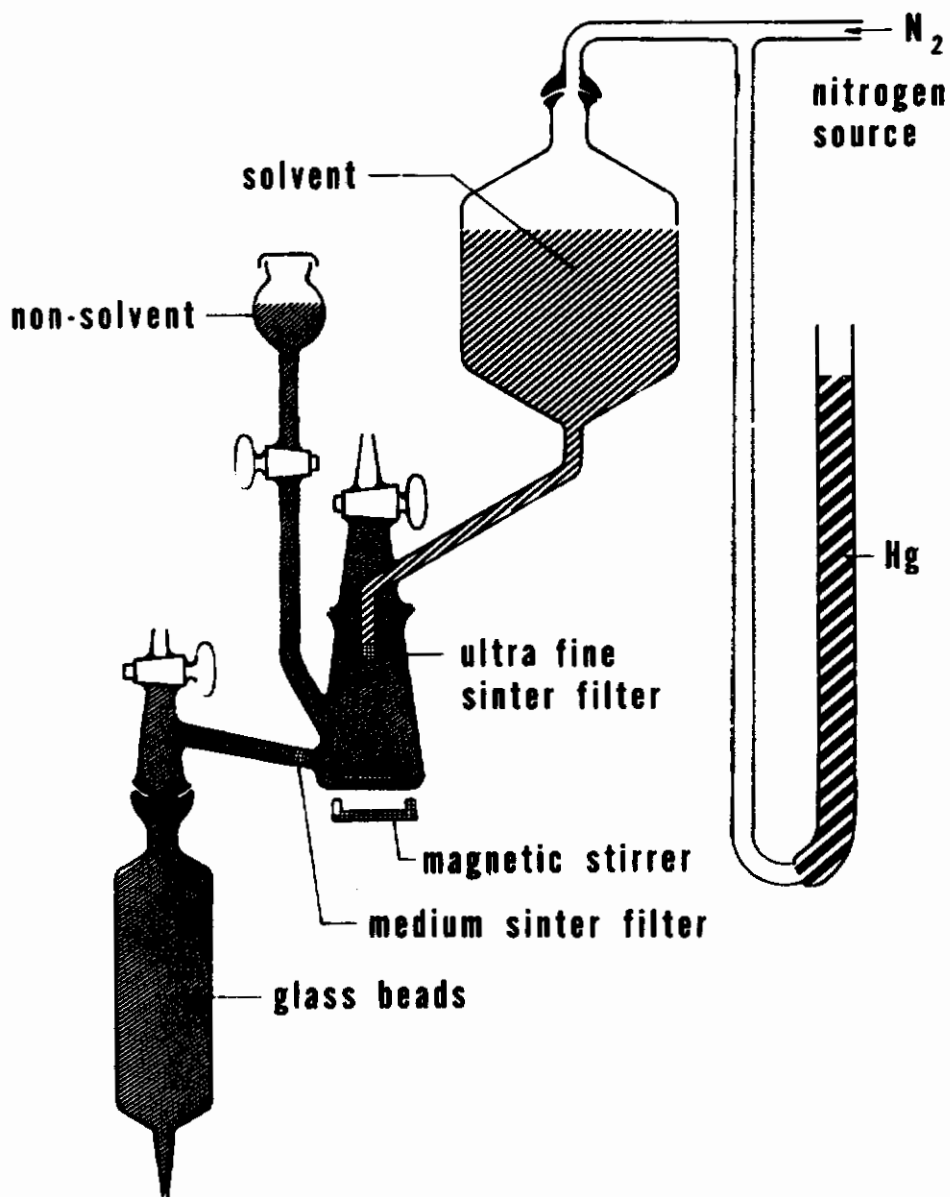


Figure VI. Apparatus for Gradient Elution

THERMAL BALANCE

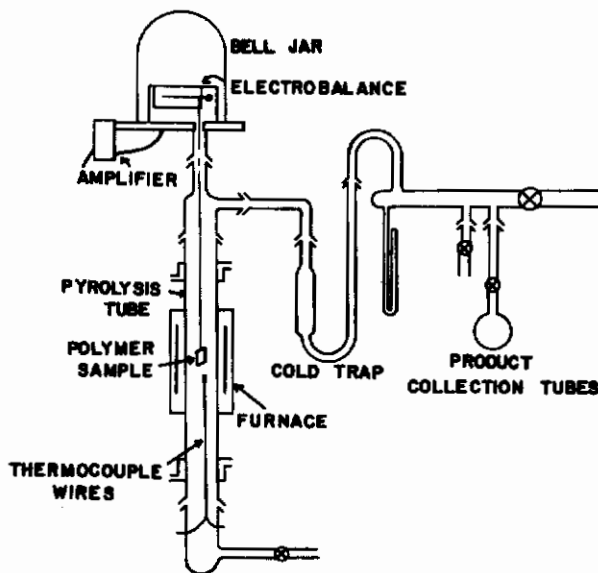


Figure VII. Thermal Balance

HIGH VACUUM THERMALBALANCE

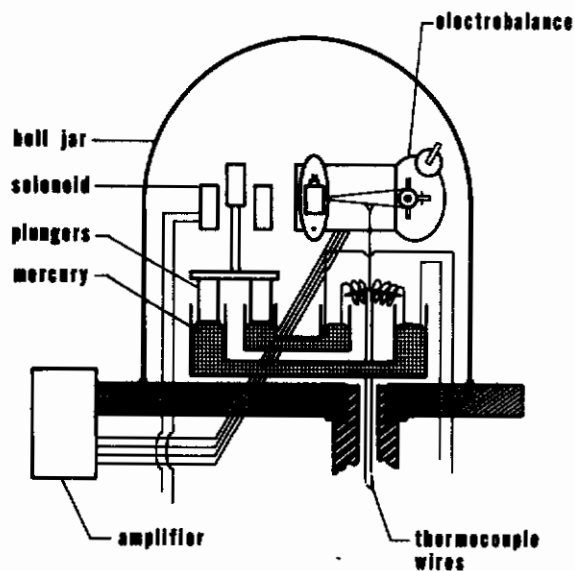


Figure VIII. High Vacuum Thermalbalance