The Solubility of Small Permanent Gases in Polyethylene as Related to Its Morphological Structure

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ABSTRACT: The solubilities of hydrogen and helium in samples of bulk, extended-chain, and single crystal samples of polyethylene have been studied. Extraordinarily large amounts of hydrogen and helium when calculated on the basis of the amorphous content can be dissolved in the highly crystalline extended-chain and single crystal samples with the greatest amount in the single crystal samples. A greater anomaly for helium than for hydrogen suggests that the smaller the gas molecule the more marked is the phenomenon of enhanced solubility. A theoretical extrapolation of the solubility data in *n*-paraffin liquids to infinite molecular weight gives values close to the experimental solubilities in ordinary bulk samples and does not account for the observed anomaly of the highly crystalline samples. A thermodynamic calculation of the data indicates that the lower heat of solution is a major factor for the enhanced dissolution. These data are explained by the more open structure in the disordered regions of the highly crystalline samples. The effect of irradiation of the polyethylene on gas solubility has been studied and was found relatively small. Gas solubility in a perfect *n*-$C_{20}H_{44}$ crystal is effectively zero.

The sorption of gases can be used as a tool to investigate the structure of disordered regions in polymeric materials. In this paper data are given which demonstrate that per unit of amorphous content an extraordinarily large amount of small permanent gases such as helium and hydrogen can dissolve in highly crystalline pressure-crystallized polyethylene and solution-grown single crystalline polyethylene and the implication of these findings as especially related to the microstructure of the disordered zones is discussed.

It has been well established in the past[1-5] that in ordinary bulk polyethylene (PE) at constant gas pressure and temperature the solubility of a gas σ in terms of the two-phase model is proportional to the amorphous weight fraction of the PE as calculated from density measurements, that is

$$\sigma = \alpha_w \sigma_a \tag{1}$$

where σ is the gas solubility, here defined as g of gas/100 g of PE, α_w is the amorphous weight fraction, and σ_a is the solubility of the gas in the completely amorphous polymer. Equation 1 has been used, in fact, to evaluate the crystallinity of single crystal samples of PE using cyclopropane as the dissolving gas.[4]

Recently Toi, Kaminaga, and Tokuda[6] presented data which indicated that eq 1 is not universally applicable to all PE samples. They studied not only the rate of uptake of various gases, N_2, O_2, Ar, and CO_2, but also the final equilibrium solubility values in thin films of low- and high-density PE and found a marked difference in the rate of gas uptake between the two types of PE and in the final equilibrium values. For example, σ_a at 30° was 0.104 cm^3(STP)/cm^3 atm, for nitrogen in the case of a Ziegler-type PE of α_w equal to 0.30, but only 0.069 cm^3(STP)/cm^3 atm for a low-density PE film of α_w equal to 0.49. A more marked fact than the difference between the two samples is that the value of σ_a for the high-density PE sample was significantly higher than those previously reported, about 3-fold greater in an extreme case. In the case of the high-density PE film value quoted above, Toi *et al.*[6] corrected their final equilibrium solubility value for the amount of gas apparently adsorbed onto the surface. However, it should be noted that Deas *et al.*[5] using bulk PE samples found no significant variation in σ_a over a range of α_w values from 0.16 to 0.41 in their measurements of the solubility of hydrogen in PE.

Michaels *et al.*,[7] Vieth and Sladek,[8] and Vieth *et al.*[9] in their studies of the solubility of gases in glassy, semicrystalline, or rubbery samples of polyethylene terephthalate or polystyrene have proposed a "dual-Mode" of sorption, the regular type of dissolution in "compact amorphous" regions and a "hole-filling" type of sorption in microvoids. The hole-filling sorption was described in terms of a Langmuir adsorption isotherm and the regular type in terms of Henry's law. The linear constants of the Langmuir and Henry law equations were separately determined from data obtained from solubility measurements made over a range of pressures from low to high values. In the work of the present paper a linear sorption isotherm was obeyed at all pressures up to 1 atm; measurements were not made at high enough pressures to detect a Langmuir-type sorption. Michaels *et al.*[7] observed that the sorption of helium was of the same type, that is ordinary dissolution, whether in semicrystalline or rubbery polyethylene terephthalate.

Most recently Kubo and Dole[10] found a greatly enhanced solubility of hydrogen in single crystalline PE as calculated on the basis of eq 1. This observation has been further strengthened by measurements[11] of the catalytic effect of hydrogen on the alkyl radical decay in mats of PE single crystals where it was observed that the catalytic effect was about 10-fold greater than in ordinary bulk PE. Deas *et al.*[5] showed on one sample of extended-chain PE that the hydrogen solubility, σ_a, was also about 5-fold greater than that of ordinary bulk PE.

These findings suggested that the sorption of gases in PE is more complicated than originally thought and that a study of the solubility of hydrogen in PE samples of different morphologies would be of considerable interest. Because our original semimicro method[5] was not applicable to single crystals a new technique[10] was developed which enabled the solubility of hydrogen to be measured in single crystalline PE for the first time. In the present paper we have extended this work, we have made a theoretical estimate of the solubility in a hypothetical 100% amorphous PE from solubility data in *n*-paraffin liquids, and we have also studied the solubility in irradiated PE and some *n*-paraffin crystalline solids.

Although the study of hydrogen solubility was the major objective of this work as explained above, the study was extended to helium solubility for representative samples of different morphologies in the hope of clarifying the nature of gas sorption in PE. At the same time it was also of considerable interest to test the applicability of our new solubility method[10] to light gases other than hydrogen.

Experimental Section

Materials. Properties of the various PE samples used in this work are given in Table I. Sample F is as-received Marlex-6002

Table I
Properties of Polyethylene Samples Studied

Sample	Description of Sample	Density (g/cm³) at 25°	α_w	Wt (g)	Thickness (l), cm
		Bulk Polyethylene Samples			
K-1	Crystallized from the melt under atmospheric pressure	0.962	0.229	0.347	0.120
K-1-1	K-1 irradiated to 14 Mrads			0.208	0.142
F	Film as received	0.960	0.242	0.148	0.025
F-1	F irradiated to 7 Mrads			0.159	0.025
F-2	F irradiated to 13 Mrads			0.151	0.025
F-3	F irradiated to 22.8 Mrads			0.147	0.025
F-4	F irradiated to 30 Mrads			0.146	0.025
		Extended Chain Samples			
P-H[a]	Crystallized from the melt at 223° under a pressure of 4.8 kbars	0.977	0.136	0.263	0.099
P-M[b]	Crystallized from the melt at 216° under a pressure of 4.9 kbars	0.993	0.035	0.249	0.112
P-L[c]	Crystallized from the melt at 221° under a pressure of 4.8 kbars	0.989	0.059	0.312	0.115
P-69[d]	Crystallized from the melt under an elevated pressure and subsequently annealed at 230° under a pressure of 5.1 kbars	0.985	0.083	0.379	0.131
P-70[e]	Crystallized from the melt under an elevated pressure and subsequently annealed at 249° under a pressure of 5.1 kbars	0.986	0.078	0.435	0.172
		Single Crystal Samples			
S-1	Single crystals sample grown from p-xylene solution at 90°. A dried mat was cut into pieces with diameters less than 0.11 cm	0.978	0.124	0.172	
S-1-0	S-1 compressed into a cylinder with a diameter of 0.26 cm	0.978	0.124	0.0414	
S-1-1	S-1-0 irradiated to 16.8 Mrads			0.0325	

[a] Sample P-H described by R. B. Prime, Ph.D. Thesis, p 86, Rensselaer Polytechnic Institute, Troy (1968), as his sample 101. [b] Described in the above reference as sample 89. [c] Described in the above reference as sample 93. [d] Sample P-69 described in C. L. Gruner, B. Wunderlich, R. Bopp [*J. Polym. Sci., Part A-2*, **7**, 2099 (1966)] as their sample 69. [e] Described in the preceding reference as sample 70.

film, weight- and number-average mol wt 230,000 and 20,000, respectively, and was the starting material of the K- and S-series samples. Sample K-1 was recrystallized from the melt by cooling in air under vacuum in an 8-mm Pyrex tube. Sample S-1 was recrystallized from a 0.2 wt % solution of PE in p-xylene at 90°. The P-series samples are the extended-chain crystal samples supplied by Professor B. Wunderlich.

All irradiated samples were γ irradiated at 77°K and then stored at room temperature *in vacuo* for several months before making the solubility measurements. To prevent oxidation of the few remaining allyl radicals present in the PE the samples were transferred from the irradiation cell to the solubility cell in an atmosphere of nitrogen. The density data of Table I were determined at 25° in a toluene–monochlorobenzene density gradient column. The amorphous weight fraction of the samples, α_w, in terms of the two-phase model was calculated from the eq 2, where

$$\alpha_w = 5.882v - 5.888 \text{ at } 25° \qquad (2)$$

v is the specific volume of the sample. The numerical factors were calculated taking the specific volumes of the 100% crystalline and amorphous fractions equal to 1.001 and 1.171 cm³ per g, respectively.

In order to determine whether or not any hydrogen solubility could be detected in a perfect n-hydrocarbon crystal, it was decided to make, if possible, single crystals of eicosane (Matheson, Coleman and Bell, mp 35–36.5°) and of octacosane (Eastman, mp 59–61°). This was attempted by slowly drawing a crystal out of the molten bath of the material at a rate of 1 mm hr^{-1}. In the case of the n-C_{20} hydrocarbon a long narrow perfectly transparent prismatic crystal resulted, approximately 3 cm long and 0.2 cm thick. On being quenched to 77°K in the solubility cell this crystal (which had been cut to a shorter length to fit into the cell) shattered into several slivers less than 1 mm in thickness. In the case of the n-C_{28} hydrocarbon a polycrystalline opaque rod was obtained from pulling a seeded metal rod from the melt. An X-ray study showed that the long axis of the molecular chains was preferentially oriented in the longitudinal (pulling) direction. An isotropic polycrystalline sheet, 0.2 cm in thickness, was also made from n-octacosane by cooling a melted portion of it in air. Neither of the n-C_{28} samples shattered on cooling to 77°K. A condensed description of these n-paraffin samples is given in Table II.

The gases were Linde hydrogen and helium listed at 99.5 and 99.995% purity, respectively.

Apparatus and Technique. Two methods of solubility measurements have been utilized for this work. Both are of the static type and are based on a technique established previously in this laboratory which utilizes a gas chromatograph for the evaluation of the small quantity of the dissolved gas in semimicro size sam-

Table II
***n*-Paraffin Samples Studied**

	Sample			
Code	Material	Description	Wt (g)	Form
C-20	Eicosane ($C_{20}H_{42}$)	See text Single crystal	0.160	See text
C-28-3	Octacosane ($C_{28}H_{58}$)	See text Plane sheet	0.302	See text
C-28-6	Octacosane ($C_{28}H_{58}$)	See text Opaque rod	0.220	See text

ples.[5] The two differ in the method of eliminating the ambient hydrogen from the solubility cell with the polymer sample containing the equilibrium amount of the dissolved gas. In the first method which is hereafter called the flushing method, ambient hydrogen is swept out of the sample loop in a short period (3 sec) by a blast of nitrogen. This method is the same as the technique described by Deas *et al.*[5] except that the glass sample loop was changed into a loop of all-metal construction. The most important improvements due to this change were that the correction terms for residual gas decreased to an almost negligible amount and that the second injection could be eliminated by the appropriate choice of sorption and desorption conditions (see below). Although the amount involved was found to be almost negligible (a maximum of 1%), corrections for ambient gas remaining after flushing and any gas sorbed in the empty copper tube system as experimentally determined in blank tests were subtracted from the total gas measured in the gas chromatograph (gc).

In the second method which is hereafter called the liquid nitrogen quenching method, ambient gas is removed by pumping out at leisure after freezing the equilibrium mixture of gas and polymer at liquid nitrogen temperature. The dissolved gas is frozen in the polymer at this temperature and cannot be pumped out by evacuation.[10] To eliminate a possible contribution of gas sorbed by the solubility loop, blank tests of the empty copper tube system were carried out. In the case of hydrogen a small amount (1% maximum) was found and a correction was subtracted from the corresponding measurements. In the case of helium no sorption by the empty copper tube system was found and hence no correction was necessary.

The liquid nitrogen quenching method was primarily developed as a technique for measuring gas solubility in single crystal samples for which no previous technique appeared to be applicable. The other hope we had on developing this technique was that it would serve as a convenient way of separating the trapped or surface adsorbed gas, if any, from the dissolved gas. From this point of view the liquid nitrogen quenching method was applied also to samples other than the single crystalline samples. In the study of helium solubility the liquid nitrogen quenching method played a major role in the experiments.

The sorption and desorption conditions which are common for both methods at a given temperature were determined in the way described below.

The F-, K-, and P-series samples which were sheets with thicknesses shown in Table I with the dimensions in the other directions large as compared to the former can be roughly approximated as infinite sheets. In this case with the fact that sorption and desorption occurred at practically constant pressure, the equations for sorption and desorption are identical in form and are given by[12]

$$1 - \frac{Q_t}{Q_\infty} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\left\{\frac{(2n+1)\pi}{l}\right\}^2 Dt\right] \quad (3)$$

where Q_t is the amount sorbed or desorbed at time t, Q_∞ is that at infinite time, and l is the thickness of the sample. For t large, the series converges so rapidly that only the first term need be considered. In our experiments t was calculated for 99.9% approach to equilibrium using values of D estimated from those for branched PE with 0.56 volume fraction of amorphous content by Ash *et al.*,[13] by multiplying the latter values at each selected temperature by the ratio $\alpha_v/0.56$. The longest time required was 29 hr for the experiment with sample P-M at 0°. In practice at least 50% extra time was allowed for both sorption and desorption. The completeness of sorption and desorption in the period thus determined was checked and assured for each condition by means of a second injection into the gc after allowing the gas to diffuse out for an additional period.

Table III
Hydrogen Solubility in Bulk Samples

		Solubility at 1 atm (10^{-4} g of H_2/100 g of PE)			
		Flushing Method		Quenching Method	
Sample	Temp (°C)	σ	σ_a[a]	σ	σ_a[a]
F ($\alpha_w = 0.242$)	25	0.783^5	3.20^5	0.854	3.53
K-1 ($\alpha_w = 0.229$)	0	0.702	3.07		
	25	0.807	3.52	0.876	3.82
	35	0.811	3.55		
	45	0.846	3.69		

[a] σ_a values are σ/α_w, or the solubility of a gas in grams calculated for 100 g of 100% amorphous polymer.

For the S-series samples for which the apparent shape does not serve as a meaningful parameter, the determination of sorption and desorption times was empirical; a certain time was chosen based on the gross dimensions of the sample and the completeness of sorption and desorption in this period was tested by the method described above. Whenever the process was found incomplete, longer times, in which sorption and desorption were practically complete, were adopted. The sorption and desorption times thus determined for the S-series samples varied from 1 hr for S-1 at 45° to 6 hr for S-1-0 at 25°.

The gas chromatograph apparatus and the sampling system were the same as previously described.[5] The same gc column and measurement conditions were used for both hydrogen and helium.

Data and Discussion

Hydrogen Solubility. Ordinary Bulk Samples. Data for the solubility of hydrogen in the bulk film and in a melt-recrystallized sample as measured by both the flushing and the quenching method are given in Table III. The quenching method tends to yield somewhat higher values than the flushing method for these ordinary bulk PE samples. Since the flushing method involves an uncertain extrapolation to zero flushing time, we believe that the values from the quenching method give generally more reliable results. Nevertheless the values by the flushing method are useful for comparing our results in the present work with data in the literature obtained by similar techniques. The values of σ_a obtained previously[5] at 25° for eight different bulk samples of high-density PE, whose α_w varied from 0.157 to 0.297, were in the range from 3.20 × 10^{-4} to 3.56 × 10^{-4} g of H_2/100 g of amorphous PE. Solubility of hydrogen (σ_a) in a bulk sample of low-density PE at 25° measured by Ash *et al.*[13] was 3.58 × 10^{-4} g of H_2/100 g of amorphous PE which is nearly the same as our value for sample K-1 by the flushing method. Thus it appears that equation 1 is valid for the solubility of H_2 in ordinary melt-recrystallized bulk samples of PE with α_w more than 0.15. In the temperature range studied, the solubility increased with increasing temperature which was in accord with our previous result[5] for high-density bulk PE and the result by Ash *et al.*[13] for low-density bulk PE. Quantitative discussions of temperature dependence will be found in the next section.

Pressure-Crystallized Samples. Provisional data for the solubility of H_2 in an extended-chain crystal sample have been given in the previous publication.[5] The rather surprising fact that the solubility value for that sample was unusually high compared to the ordinary bulk samples when reduced to 100% amorphous content required further confirmation. Fortunately, several more samples whose α_w varied from 0.035 to 0.136 were kindly supplied by Professor B. Wunderlich of Rensselaer Polytechnic Institute and they enabled us to study in detail the solubili-

Table IV
Hydrogen Solubility in Extended-Chain Sample as Measured by the Flushing Method

Sample	Temp (°C)	Solubility at 1 atm (10^{-4} g of H_2/100 g of PE)	
		σ	σ_a
P-H	0	0.491	3.61
(α_w = 0.136)	25	0.547	4.03
	35	0.548	4.05
	45	0.568	4.17
P-69	0	0.783	9.43
(α_w = 0.083)	25	0.746	8.99
	35	0.768	9.25
	45	0.740	8.92
P-70	0	0.445	5.70
(α_w = 0.078)	25	0.467	5.99
	35	0.461	5.91
	45	0.474	6.08
P-L	0	0.719	12.19
(α_w = 0.059)	25	0.696	11.80
	35	0.664	11.29
	45	0.678	11.48
P-M	0	0.962	26.49
(α_w = 0.035)	25	0.934	26.68
	35	0.955	27.30
	45	0.924	26.40
Extended-chain crystals in ref 5 (α_w = 0.031)	25	0.559[5]	18.3[5]

ty of H_2 in highly crystalline (extended chain) samples of PE with α_w less than 0.15. Table IV lists the results as measured by the flushing method. The provisional data described above are also included in the table. It is evident that the original high value of 18.3×10^{-4} g of H_2/100 g of PE was by no means an experimental artifact because some of the new data are even higher. However, there is a possibility that the cause of these high values might be due to hydrogen molecules which were not really dissolved, but instead trapped in macrovoids. Thus, if the highly crystalline samples contained some macrovoids, removal of hydrogen by the flushing process might not have been complete in a few seconds and consequently hydrogen molecules which failed to diffuse out of the macrovoids during flushing would have been counted as dissolved gas. It is obvious, however, that there will be no such complication in the quenching method in which such molecules would have been easily removed by the lengthy evacuation process which characterizes this method. Sample P-M which is the most crystalline sample used in this work and whose solubility (σ_a) was the highest was subjected to this test. A mean value of 0.858×10^{-4} g of H_2/100 g of PE at 25° was obtained for this sample by the quenching method and σ_a was calculated to be 24.52×10^{-4} g of H_2/100 g of amorphous PE. These data are about 10% less than the corresponding values of Table IV as measured by the flushing method. This difference of 10% is small compared to the 8-fold greater value of σ_a as compared to σ_a for ordinary bulk PE. No dependence of evacuation time at 77°K on the result indicated that the value of σ obtained represents the true solubility. Additional support for this view came from a study of solubility as a function of hydrogen pressure. Figure 1 shows the value of σ as a function of H_2 pressure as measured for sample P-L by the flushing method. A linear sorption law which is usually obeyed by gases dissolved in a liquid is valid in the range of pressure studied.

Figure 2 illustrates values of σ_a at 25° as a function of α_w. Instead of σ_a remaining constant as α_w changes as required by eq 1, there is a marked trend of σ_a increasing as α_w decreases. Evidently, the character of dissolution of H_2 changes gradually, but drastically as the crystallinity of the sample exceeds 85%. If the data for samples P-69 and P-70 are compared, it can be seen that the σ and σ_a values for sample P-70 are considerably less than those for sample P-69 despite the fact that the measured densities and amorphous weight fractions (as calculated from the densities), Table I, are almost identical. Possibly the different annealing temperatures of these two samples caused the structure of the small, and therefore probably highly constrained, amorphous zones to be different enough to affect significantly the hydrogen solubility. If this is true, then the hydrogen solubility is a more sensitive indicator of the

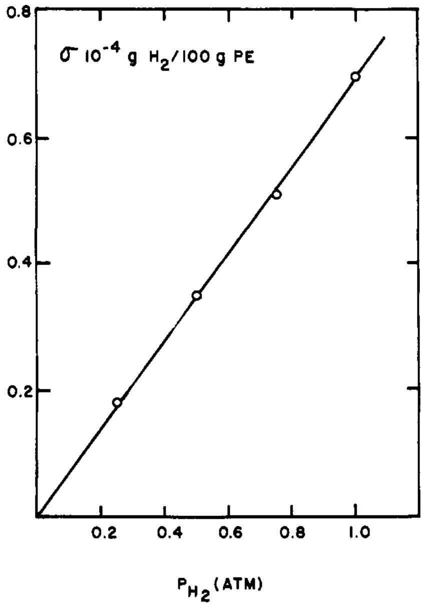

Figure 1. Solubility of hydrogen at 25° in sample P-L at different equilibrium pressures of hydrogen gas; flushing method.

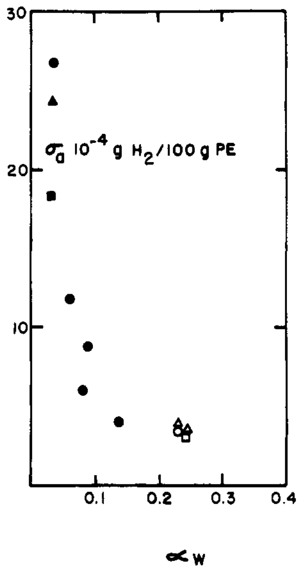

Figure 2. Plot of σ_a at 25° against α_w. Filled circle and filled triangle, data for pressure-crystallized samples by the flushing method and the quenching method, respectively. Filled square, data for pressure-crystallized sample reported in ref 5. Open circle and open triangle, data for ordinary bulk sample by the flushing method and the quenching method, respectively. Open square, data for ordinary bulk sample reported in ref 5.

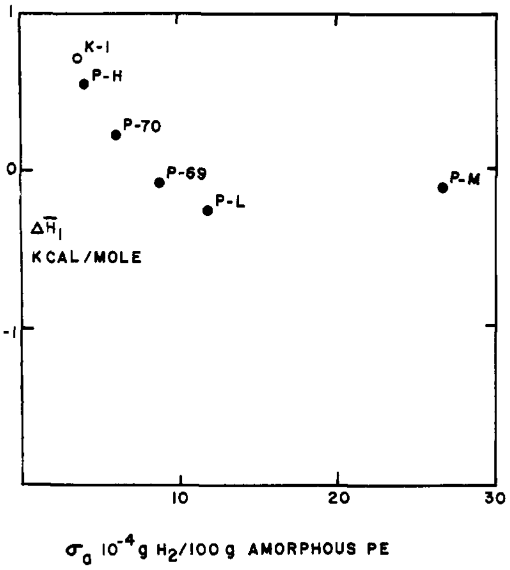

Figure 3. Plot of $\Delta\bar{H}_1$ against σ_a as measured by the flushing method at 25°.

amorphous structure and volume than are the density values.

A marked difference in the behavior of the dissolved hydrogen molecules is also found in the temperature dependence of solubility. In Figure 3 the heat of solution $\Delta\bar{H}_1$, calculated from the slope of the lines of the ln σ *vs.* $1/T$ plot, is shown as a function of σ_a at 25°. The endothermic heat observed for ordinary bulk PE decreases gradually as σ_a increases. For highly crystalline samples $\Delta\bar{H}_1$ is a small negative value very close to zero. This fact is further evidence that the character of the dissolution of the gas changes as the PE samples become highly crystalline. Further discussion concerning this problem will be made in a later section.

Solution-Grown Crystals. From the foregoing experiments it is now apparent that the solubility of H_2 in PE in the highly crystalline range is a morphology-sensitive property. From this point of view it is of considerable interest to study the solubility of H_2 in solution-grown single crystalline samples which are usually more crystalline than ordinary melt-recrystallized bulk samples and, more importantly, whose morphological details are known to be quite different in character.

Table V shows the data. We had previously shown[10] that a linear sorption isotherm holds in the range of equilibrium pressures of hydrogen of 1 atm or less. A remarkable fact is that the solubility of H_2 in these samples reduced to 100% amorphous content is higher by an order of magnitude than that in ordinary bulk PE. Furthermore the σ_a values are even higher than the largest observed for the pressure-crystallized samples. The values of σ_a depend, of course, on the estimate of α_w. Our density value for the single crystal mat, 0.978 g cm^{-3} at 25°, is close to that given by Namada *et al.*[14] for an unfractionated Marlex-50 sample of viscosity-average molecular weight equal to 60,000. However, the solubility values, σ, for the single crystals are so high compared to ordinary bulk PE *that there are no values* of α_w *which when introduced into eq 1 would give a value of* σ_a *for the single crystals even remotely close to* σ_a *for the bulk PE.*

Table V
Hydrogen Solubility in Single Crystals of Polyethylene (Quenching Method)

Sample	Temp (°C)	Solubility at 1 atm (10^{-4} g of H_2/100 g of PE)	
		σ	σ_a
S-1	0	4.86	39.2
(α_w = 0.124)	25	4.90	39.5
	35	4.75	38.3
	45	4.91	39.6
S-1-0	25	4.96	40.0

When we consider the relatively high value of σ_a compared with the pressure-crystallized samples we are forced to recognize that the high capability of single crystals to dissolve H_2 is by no means an extension of the type described in the preceding section. Yet the data indicate that such an unusually high solubility is a real solubility as based on the validity of a linear sorption isotherm. The possibility of the occlusion of hydrogen gas in the interlamellar space which might have given rise to the apparent high value of σ is discarded by the fact that the compression of the sample has not at all changed the value of σ (compare the results of S-1 and S-1-0) and by the fact that prolonged evacuation at 77°K did not reduce σ. Also the fact that the alkyl radical decay in single crystalline PE as compared to ordinary bulk polyethylene is enhanced at equal hydrogen pressures[11] is a further demonstration of the enhanced hydrogen solubility.

From the slope (by the least-squares method) of the ln σ *vs.* $1/T$ plot, the heat of solution for the single crystal sample is calculated to be -0.01 kcal/mol. This small negative value is closer to the values for the highly crystalline pressure-crystallized samples than to the larger positive value for ordinary bulk polyethylene. This suggests that the enhanced dissolution of hydrogen gas in the single crystalline PE involves a significant change in the character of the dissolution similar to the case of highly crystalline pressure-crystallized samples. Considerable differences in the character of the disordered regions, however, seem to exist between melt-grown and solution-grown samples so that a significant difference in their capability to dissolve hydrogen results.

In a study of the sorption of N_2, O_2, and Ar in high-density inflation films of PE Toi *et al.*[6] obtained sorption curves showing some instantaneous sorption of gases at the start of the sorption process. Their curves were explained by two concurrent mechanisms, ordinary dissolution and Langmuir monolayer type of sorption originally proposed by Michaels *et al.*[7] for sorption of gases in polyethylene terephthalate. A maximum of 30% of the total take-up was attributed to the contribution by the latter.

A linear sorption curve at low pressures does not necessarily mean that a Langmuir-type adsorption or that other types of sorption would not prevail at higher pressures. Some years ago Dole[15] derived a general adsorption equation on the basis of statistical thermodynamic reasoning as follows

$$n/n_s = x\phi'/\phi \qquad (4)$$

where n is the number of molecules sorbed/g of sample, n_s is the number of sorption sites/g, x is the activity of the vapor, or P/P_0. ϕ' is the first derivative of ϕ with respect to x and ϕ is given by the series

$$\phi = 1 + xc_1 + x^2c_1c_2 + \ldots \qquad (5)$$

in which c_1 *is the ratio of the partition function of the sorbed molecule in the first layer to that in its pure liquid phase,* c_2 is a similar ratio for the sorbed molecule in the second sorption layer, etc. In the present situation where we are dealing with gases and not vapors, x is set proportional to the pressure and the various partition function ratios proportional to the partition function of the sorbed

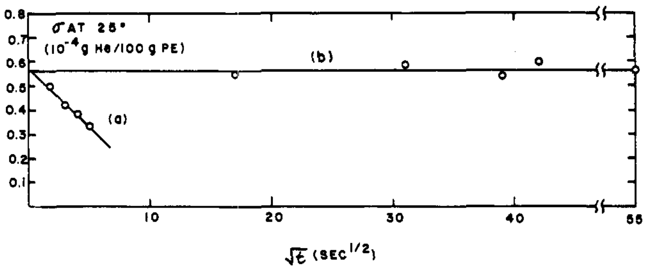

Figure 4. Grams of helium gas per 100 g of polyethylene × 10^4 as a function of the square root of the time of (a) flushing nitrogen gas through the solubility cell (b) evacuation at −196° after quenching in liquid nitrogen.

molecule. If the partition functions, c, of the sorbed molecules are equal in all layers, eq 4 becomes

$$n/n_s = Pkc/(1 - Pkc) \qquad (6)$$

which at low pressures is a linear sorption isotherm. In eq 6 k is a constant at constant temperature. If the partition functions are zero in all layers above the first, Langmuir-type adsorption, eq 4 becomes

$$n/n_s = Pkc_1/(1 + Pkc_1) \qquad (7)$$

which again is a linear isotherm at low pressures. If the partition functions, c, are all equal beyond the first layer, we obtain an expression similar to the BET adsorption equation[16]

$$n/n_s = Pkc_1/[(1 - Pkc)(1 - Pkc + Pkc_1)] \qquad (8)$$

This sorption equation also becomes a linear sorption isotherm at low pressures. Finally, if the partition functions decrease harmonically with each layer, that is if

$$c_2 = \tfrac{1}{2}c_1$$
$$c_3 = \tfrac{1}{3}c_1, \text{ etc.}$$

then a strictly linear adsorption isotherm results

$$n/n_s = Pkc_1 \qquad (9)$$

valid at all pressures. This analysis shows that at low pressures it is impossible to distinguish between the four types of sorption equations given above. However, Michaels *et al.*[7] observed deviations from linearity in the sorption of CO_2 by polyethylene at 25° at pressures below 200 Torr, hence if a Langmuir- of BET-type sorption prevailed in our work there is a possibility that some evidence of it could have been detected although this question cannot be answered definitively without sorption measurements at much higher pressures.

Helium Solubility. It is known that the Langmuir type of sorption becomes less important as the molecular size of the gas decreases.[7] Hence we decided to study the solubility of helium in the representative samples examined in the previous section. To begin with, we compared the flushing and quenching methods using sample K-1. Results are shown in Figure 4. This was a first test of the quenching method for a gas other than hydrogen and it turned out to be quite successful. It is seen that σ is independent of the evacuation time at −196°. Extrapolation to zero time of the flushing method data yielded a value for the helium solubility in good agreement with that of the quenching method. From the slope of the flushing method line the diffusion coefficient of helium was calculated to be 15.1 × 10^{-6} cm^2/sec as compared to the diffusion coefficient of hydrogen equal to 4.5 × 10^{-6} cm^2/sec which was also determined for the sample by the same flushing method. Thus helium diffuses about 3.3 times more rapidly than hydrogen out of this ordinary bulk sample. Ash *et al.*[13] found the ratio to be 2.1 in a low-density bulk PE at 20°.

Table VI
Solubility of Helium in Polyethylene at 25°

Sample	Solubility at 1 atm (10^{-4} g of He/100 g of PE) Flushing Method σ		Quenching Method σ	
	σ	σ_a	σ	σ_a
	Bulk Polyethylene Samples			
K-1	0.575	2.51	0.564	2.46
Ref 2		2.51[a]		
Ref 13		1.84[b]		
	Extended Chain Sample			
P-M			1.45	41.4
	Single Crystal Sample			
S-1-0			8.29	66.9

[a] Average value from both the static method and the time lag method. [b] Time lag method.

Table VI contains helium solubility data for samples of different morphologies along with helium solubility data reported in the literature. While our result for K-1 is in reasonable agreement with those reported previously (note all are ordinary bulk PE), there exist surprisingly high differences between the solubilities for samples with different morphologies. It is to be noticed that the selection of helium as a sorption gas has not reduced, but rather increased the differences in solubility between the samples with different morphologies. We also tested the validity of a linear sorption isotherm, and found it was valid over the range of helium pressures used, 1 atm or less. Thus the results do not favor the possibility that the sorption involved is of a Langmuir or BET type, at least in this range of pressures. Note that the solubility per mole rather than per gram indicates that helium is slightly less soluble than hydrogen at equal temperature and pressure.

If a larger gas is used, the differences in solubility between samples of different morphology are likely to decrease and will perhaps disappear eventually at a certain molecular size. In fact this view is supported by the experimental results reported by Toi *et al.*, namely that the differences decrease with the size of the sorption gas molecule.[6] Further, the previous assumption of Lowell and McCrum[4] that eq 1 is valid for the solubility of cyclopropane in single crystal mats is consistent with this view. Thus an important result has emerged from the study of helium solubility: small gases are much more affected by the detailed morphological differences between samples than big molecules. This suggests an association of the phenomena with the sizes of open spaces in the disordered regions.

Sorption of Gases in n-Paraffin Solids. In connection with the solubility of gases in highly crystalline PE, it is interesting to study the sorption of gases in n-paraffin crystalline solids. First of all we wanted to check if any large single crystals of n-paraffins can absorb any significant quantity of hydrogen or helium. This would be a test of the *a priori* assumption that ideal crystals of PE cannot absorb hydrogen or helium. A study with the large prismatic crystals of n-eicosane indicated that no hydrogen or helium is sorbed by these crystals. Thus the assumption of no sorption in perfect crystals of PE seems to be valid. The next experiment was concerned with the sorption of hydrogen and helium in a polycrystalline bulk solid of a n-paraffin, the counterpart of our bulk sample of PE. We studied sorption of gases in two different samples of n-oc-

Table VII
Solubility of Gases in *n*-Paraffin Solids at 25° as Compared with the Data for Polyethylene

Sample	H_2 Solubility at 1 atm σ in 10^{-4} g of H_2/100 g of Sample Flushing Method	 Quenching Method	He Solubility at 1 atm σ in 10^{-4} g of He/100 g of Sample Quenching Method	He/H_2 Ratio
C-20	0	0	0	
C-28-3	0.808			
C-28-6	0.403	0.389	0.364	0.94
K-1	0.807	0.874	0.546	0.64
P-M	0.934	0.858	1.45	1.69
S-1-0		4.96	8.29	1.67

Table VIII
Solubility of Hydrogen in γ-Irradiated[a] Samples as Compared with the Data for Original Samples

Sample	σ at 25°, 1 atm[b] (10^{-4} g of H_2/100 g of PE) 0°	 25°	 35°	 45°
K-1 (original sample)	0.702	0.807	0.811	0.846
K-1-1	0.696	0.758	0.778	0.828
S-1-0 (original sample)		4.96		
S-1-1		5.25		

[a] Irradiation data in Table I. [b] K series by the flushing method, S series by the quenching method.

tacosane. One was an opaque rod, sample C-28-6, which was carefully crystallized from the melt by the crystal-pulling method and the other was a sheet, sample C-28-3, which was quickly crystallized by cooling the melt in air. The results of measurements of hydrogen and helium solubility are listed in Table VII in comparison with some data for PE. We found that prolonged periods of evacuation at −196° had no effect on σ in the quenching experiment for sample C-20-3. Hence there is no evidence that the sorbed gases have the characteristics of adsorption. From Table VII, it is seen that a significant amount of gas is sorbed even by the carefully crystallized bulk sample, C-28-6. The difference between the two samples of C-28 indicates the existence of more imperfections in the sample, C-28-3, prepared by fast crystallization. The relative magnitude of solubility per unit weight of the whole sample compared with the bulk PE sample is considerably larger than we expected, but a comparison of the He/H_2 solubility ratios in the various samples indicates that the octacosane is intermediate in behavior between the bulk PE and the extended-chain and single crystalline PE. The almost equal He/H_2 ratios for samples P-M and S-1-0 are interesting. In other words, the increase in the number of sorption sites in going from bulk PE to the extended chain and single crystalline PE is practically identical for both hydrogen and helium (quenching method data).

Irradiated Samples. Sample F-0, an orignal bulk polyethylene film, was subjected to γ irradiation at 77°K for doses of 7, 13, 22.8, and 30 Mrads and then allowed to stand *in vacuo* at room temperature to produce samples F-1, F-2, F-3, and F-4, respectively. We measured the hydrogen solubility in these samples all by the same quenching technique. Figure 5 shows the hydrogen solubility in these samples as a function of the dosage of γ irradiation. The slope of the line calculated by the linear least-squares method is slightly negative which indicates a decrease of solubility with increasing dosage. However, the difference is so small that it is probably better to say that there is no significant effect of γ irradiation in this sample in the range of dosage studied. Results of a further study with two other selected samples are shown in Table VIII. The slightly decreased solubilities observed for sample K-1-1 are consistent with the above data for a similar bulk sample. From the slope of the line of the ln σ *vs.* $1/T$ plot, the heat of solution of hydrogen in sample K-1-1 is calculated to be about 0.6 kcal/mol which is to be compared with 0.7 kcal/mol for sample K-1. In contrast, the solubility in S-1-1 is slightly higher than that for S-1-0, the original sample. If these results are correct the irradiation effect appears to be opposite for the solution-grown single crystalline sample, but the differences are so small that any attempt to explain them at this time would be rather meaningless.

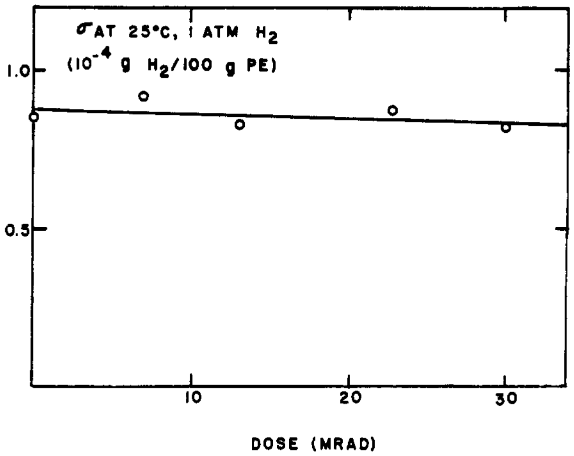

Figure 5. Grams of hydrogen in 100 g of polyethylene × 10^4 as a function of the dosage of γ irradiation. Original sample F-1.

Thermodynamics of the Sorption of Hydrogen by Polyethylene. Free Energy of the Sorption Process. Dole and McLaren[17] have given equations for the free energy, heat, and entropy of the sorption of water vapor by proteins and high polymers for the cases of linear, Langmuir, and BET sorption. Because the change in free energy per mole, ΔG, for sorption at equilibrium is zero, the free energy can be computed by integrating the following equation

$$\Delta G = \int V\mathrm{d}P = \int nRT(\mathrm{d}P/P) \tag{10}$$

or since by Henry's law n, the number of moles of hydrogen sorbed per 100 g of PE, is proportional to P, eq 10 (which assumes the validity of the perfect gas law for hydrogen) becomes

$$\Delta G = RT\int_n^0 (nRTk_{\mathrm{H}}\mathrm{d}n/k_{\mathrm{H}}n) = RT\int \mathrm{d}n$$

or

$$\Delta G = -nRT \tag{11}$$

where in eq 11 k_{H}, the Henry's law constant should be expressed in units of mol atm^{-1} if P is in atmospheres. The limits of integration are from n to zero as these limits represent the moles of gas taken from the gas phase.

Enthalpy of the Sorption Process. The so-called isosteric heat of sorption, q, can be calculated from the equation

$$-q = \Delta\overline{H}_1 = (\partial\Delta H/\partial n) = r\ln(P_1/P_2) \tag{12}$$

where P_2 is the pressure at the higher temperature T_2 which produces the same moles of sorption as at the lower temperature T_1, and $r = RT_1T_2/(T_2 - T_1)$. If Henry's

Table IX
Molar Volumes of *n*-Paraffin Liquids and Solubility Data at 25°

n-Paraffin				
Name	Formula	Molar Vol, V_2 (ml)	H_2 Solubility Mole Fraction $x_1 \times 10^4$	He Solubility Mole Fraction[g] $x_1 \times 10^4$
n-Hexane	C_6H_{14}	131.6[a]	6.18[d]	2.57
n-Heptane	C_7H_{16}	147.5[a]	6.88[e]	2.49
n-Octane	C_8H_{18}	163.5[a]	6.83[e]	2.42
n-Nonane	C_9H_{20}	179.7[a]		2.41
n-Decane	$C_{10}H_{22}$	195.6[b]		2.39
n-Dodecane	$C_{12}H_{26}$	227.8[c]		2.24
n-Tetradecane	$C_{14}H_{30}$	260.6[b]		2.26
n-Hexadecane	$C_{16}H_{34}$	293.8[b]	8.78[f]	

[a] "Selected Values of Properties of Hydrocarbons," National Bureau of Standard Circular C461 (1947). [b] "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1928. [c] Estimated by interpolation using other values listed. [d] Estimated by extrapolation from the data at lower temperatures in J. A. Waters, G. A. Mortimer, and H. E. Clements, *J. Chem. Eng. Data*, **15,** 174 (1970). [e] M. W. Cook, D. N. Hanson, and B. J. Alder, *J. Chem. Phys.*, **26,** 748 (1957). [f] P. M. Cukor and J. M. Prausnitz, *J. Phys. Chem.*, **76,** 598 (1972). [g] H. L. Clever, *J. Phys. Chem.*, **61,** 1078 (1957).

Table X
Comparison of the Experimental Solubility Data with the Values Obtained by Extrapolation of the Solubility Data of Gases in *n*-Paraffin Liquids at 25°

Gas	Sample	Solubility at 1 atm[a]
H_2	Theoretical estimation	4.3
	K-1	3.82
	P-M	24.5
	S-1-0	40.0
He	Theoretical estimation	1.9
	K-1	2.46
	P-M	41.4
	S-1-0	66.9

[a] Solubilities as measured by the quenching method; in 10^{-4} g of gas/100 g of amorphous PE.

law is obeyed, the ratio P_1/P_2 can be replaced by k_H''/k_H', the inverse ratio of the Henry's law constants at the two temperatures, or if the pressure is kept at 1 atm at the two temperatures, the ratio k_H''/k_H' can be replaced by σ_2/σ_1, the solubilities at 1 atm pressure at the two temperatures.

In the case of the sorption of polar molecules such as water on polar substrates such as proteins, the heat of sorption drops rapidly with the extent of sorption sites covered by the water molecules, but in our case, the ratio σ_2/σ_1 is independent of the extent of sorption so that the partial molal heat of sorption $\Delta\bar{H}_1$ is independent of n and is readily determined in the usual way from the slope of a ln σ *vs.* reciprocal temperature plot.

Entropy of the Sorption Process. From the usual thermodynamic expression for an isothermal process, $\Delta G = \Delta H - T\Delta S$, the integral entropy of sorption of n mol of gas/100 g of PE can be expressed by the equation

$$\Delta S = nR + n\Delta\bar{H}_1/T \qquad (13)$$

so that ΔS can be obtained by simple adding nR to $n\Delta H/T$. For the sorption of an infinitesimal amount of gas at equilibrium, ΔG is equal to zero and the partial molal entropy of sorption at equilibrium, $\Delta\bar{S}$ is equal to $\Delta\bar{H}/T$. From Figure 3 it is seen that in the case of the high-pressure-crystallized samples the $\Delta\bar{H}$ values are fairly close to zero. Setting $\Delta\bar{H}$ equal to zero in eq 13, the integral entropy of sorption per mole then becomes equal to R. However, no special significance is attached to this result.

Theoretical Estimate of the Solubility of Hydrogen and Helium in Polyethylene. According to the Flory-Huggins theory of polymer solutions,[18] the partial molal free energy of a solute liquid denoted by the subscript 1 in the amorphous region of a polymer denoted by the subscript 2 as compared to its free energy in its pure state is expressed by

$$\Delta\bar{G}_1/RT = \ln \phi_1 + \phi_2(1 - V_1/V_2) + \chi_1\phi_2^2 \qquad (14)$$

where the ϕ's represent volume fractions, V_1 and V_2 molar volumes and χ_1 is an interaction parameter. As the volume fraction of the solute in our system is negligible with respect to unity, eq 14 can be simplified to

$$\Delta\bar{G}_1/RT = \ln \phi_1 + 1 + \chi_1 - V_1/V_2 \qquad (15)$$

At equilibrium the chemical potential of the solute molecule in the gas and polymer phases must be equal, so that if we compare the solubility of hydrogen or helium in a number of different solvents all at 1 atm of gas pressure, $\Delta\bar{G}_1$ will be a constant and if χ_1, the interaction parameter is nearly the same for the different mixtures, then ln ϕ_1 should be linear function of $1/V_2$ for either hydrogen or helium as the solute, and we can write eq 15 in the form

$$\ln \phi_1 = A + B/V_2 \qquad (16)$$

However, we do not know the actual volume of the gas as sorbed in the liquid or polymer phase. In terms of our measured quantity, g of hydrogen or helium sorbed per 100 g of polymer, eq 16 can be rewritten in the form

$$\begin{aligned}\ln\,[\text{g(gas)/100 g of solvent}] &+ \\ \ln \rho_{\text{solvent}} &= \ln \phi_1 + \ln \rho_{\text{solute}} \\ &= A' + B/V_2 \qquad (17)\end{aligned}$$

Hence by plotting the left-hand side of eq 17 as a function of $1/V_2$ and by extrapolating to infinite V_2, we can obtain an estimate of the solubility of hydrogen or helium in PE based on their solubilities in low molecular weight *n*-paraffin liquids.[19]

Table IX lists the data for the solubility of hydrogen and helium liquids at 25° as collected from the literature while in Table X it is interesting to note that the solubility values obtained by the extrapolation to infinite molar volume in Figure 6 agree within 10% in the case of hydrogen and within about 20% in the case of helium with the measured values calculated for the amorphous regions of bulk polyethylene, but differ by an order of magnitude from similar values calculated for the amorphous zones of single and extended-chain crystals. We conclude from these considerations that the structure of the amorphous regions in ordinary bulk PE is similar to that in *n*-paraffinic liquids.

Partial Molal Entropies of Mixing and Conclusions. The molal entropy of mixing of the Flory-Huggins theory to the first approximation can be expressed by the equation[20]

$$S_1 - S_1^\circ = -R \ln \phi_1 - R\phi_2[1 - (V_1/V_2)] \qquad (18)$$

Imagine the hydrogen or helium gas to condense to a liquid with the loss of entropy $-\Delta S_c$. Adding this term to eq 14, setting the ratio V_1/V_2 equal to zero and ϕ_2 equal to

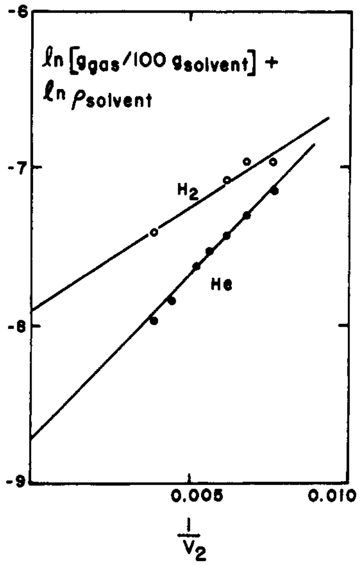

Figure 6. Logarithm of gas solubility plus logarithm of the density of the solvent in *n*-paraffin liquids as a function of the reciprocal molar volume of the *n*-paraffin liquids.

unity, eq 18, becomes

$$\Delta\bar{S}_1 = S_1 - S_1^\circ = -R \ln \phi_1 - R - \Delta S_c \quad (19)$$

Thus $\Delta\bar{S}_1$, which in the entropy of mixing at equilibrium or the partial molal entropy, should be proportional to ln ϕ_1, or inasmuch as we do not know the volume of the dissolved gas, ln ϕ_1 can be replaced by ln $[g_{\text{gas}}/100g_{\text{solvent}}]$ + ln ρ_{solvent} − ln ρ_{solute} and $\Delta\bar{S}_1$ plotted as a function of ln $[g_{\text{gas}}/100g_{\text{solvent}}]$ + ln ρ_{PE} or ln σ_a + ln ρ_{PE} similarly to the plot of Figure 6. From eq 19 the slope of the line should be equal to $-R$. Figure 7 illustrates such a plot where the solid line has been drawn with a slope of $-R$ and the symbols on the points designate the type of polyethylene to which we refer. With the exception of the result for the single crystal sample the relative entropies of mixing the gas with the amorphous zone of the PE agree fairly well with those calculated from the measured solubilities.

The decrease in the entropy of solution of the gas molecules in the amorphous zones of the polyethylene can be seen to be related to the increase in the local concentration of the dissolved gas molecules. The enhanced solubility of hydrogen in the pressure-crystallized samples must be the result, therefore, not of an increased entropy of mixing, but of a decrease in the partial molal heat of solution, ΔH_1, as illustrated also in Figure 3. We picture the disordered regions in the pressure-crystallized samples as having a more open structure than in the ordinary bulk PE so that on dissolution of the gas in the solid there is less of the endothermic effect of the gas molecules forcing the polymer chains apart in order to be accommodated into the amorphous structure. The exothermic van der Waals forces of attraction thus have a relatively greater effect on the heat of solution in the extended-chain crystal samples. In addition, one can imagine that the number of "holes" that can accommodate such small molecules as hydrogen and helium per cm³ of the disordered regions is greater in the extended chain and single crystal samples than in bulk PE. Defining the free volume per gram as the difference between the actual volume per gram and the volume of a gram of a perfect PE crystal, one can calculate that at an amorphous weight fraction of 0.242 (bulk PE) there is a free volume of 0.041 cm³ per gram. The density[21] of solid hydrogen (at 4.2°K) is 0.09 g cm^{-3}. The volume of the hydrogen dissolved at 1-atm pressure in 1 g of amorphous bulk PE, if it had a density equal to that of the solid, in PE of α_w = 0.242 is 3.5 × 10^{-6}/0.09 or 3.9 × 10^{-5} cm³ g^{-1}. This is smaller by about a factor of 1000 than the free volume as calculated above. On the other hand if we calculate the volume that 3.5 × 10^{-6} g of H_2/g of PE would have from the perfect gas law at 1-atm pressure and 298°K, the answer is 3.5 × 10^{-3} cm³, still smaller than the free volume by an order of magnitude. In the single crystals of α_w equal to 0.124 and free volume estimated to be 0.021 cm²/g^{-1}, σ_a is 10-fold greater and the volume of the dissolved hydrogen assumed to be a solid would be still two orders of magnitude less than the free volume; but the volume calculated on the basis of the perfect gas law would be about 50% greater than the free volume. These calculations are not meant to prove that the dissolved hydrogen is to be conceived either as a solid or a perfect gas, but merely to show that in the single crystals, at least, the volume of the dissolved hydrogen is intermediate between what it would have as a solid or a perfect gas.

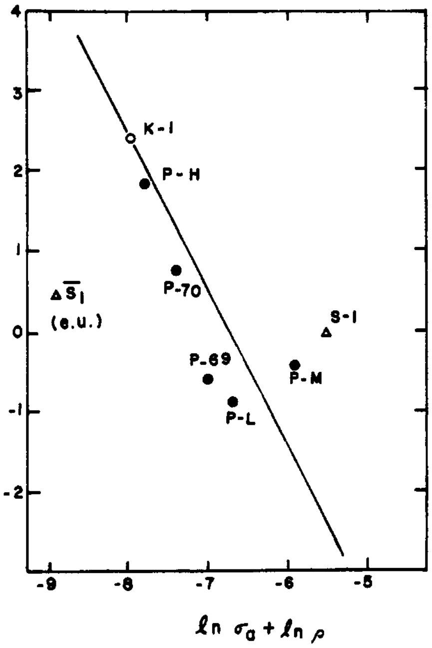

Figure 7. $\Delta\bar{S}_1$ as a function of the logarithm of the solubility at 25° of hydrogen in amorphous polyethylene plus the logarithm of the amorphous PE density.

Turning now to the single crystal sample of PE we see that the net entropy of dissolution is practically zero. We also have to consider the extraordinarily rapid diffusion of the hydrogen or helium into and out of the single crystal mats. This suggests to us that the gas molecules can penetrate rapidly into the amorphous zones between the single crystal lamellae. Such penetration could cause a forcing apart of the lamellae with a smaller endothermic heat effect than in the case of the bulk PE, and there would be no crystalline zones or barriers between the lamellae to impede the diffusion of the gas molecules into or out of the single crystal mats. In this connection Udagawa and Keller[22] have recently studied the swelling of single crystals of PE when wetted with a drop of solvent, such as xylene. They observed that the crystal mat almost instantaneously became transparent which is another indication of the rapidity with which other molecules can penetrate into the single crystal mats. They conclude that "the material responsible for the swelling is a variable component of surface looseness overlying the rest of the fold surface which contains other, possibly more intrinsic sources of crystallinity deficiency."

Because of the large specific surface area of single crystals,[23] $\sim 10^6$ cm^2 g^{-1} one might imagine that the hydrogen solubility in the single crystals could be accounted for by assuming complete surface coverage to the depth of one layer. However, taking the molecular diameter of the hydrogen molecule[24] as 2.19 A° it is easy to calculate that a surface of 10^6 cm^2 g^{-1}, would accommodate 9×10^{-1} g of H_2/100 g of the single crystals. This is almost three orders of magnitude larger than the actually observed solubility (Table V) and demonstrates that the interlamellae surfaces are certainly sufficiently great enough in area to sorb the dissolved hydrogen. Of course, there is nothing approaching a surface coverage at 1-atm pressure otherwise a Langmuir sorption isotherm would be deduced from the data. Furthermore, one would hardly expect the simple Flory-Huggins mixing theory to be applicable to the mixing of hydrogen or helium molecules with the interlamellae folded-chain structure of the polyethylene. The entropy of mixing from Figure 7 is surprisingly high for the single crystal sample, and if this result is correct, it would indicate that more configurations are available to the system of gas molecules and polyethylene segments than in the case of the other PE samples; in other words per gram of amorphous polymer there are more sorption sites for the hydrogen and helium molecules in the case of the single crystals.

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References and Notes

(1) A. S. Michaels and R. B. Parker, Jr., *J. Phys. Chem.*, **62**, 1604 (1958).
(2) A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 393 (1961).
(3) N. G. McCrum, *Polymer*, **5**, 319 (1964).
(4) P. N. Lowell and N. G. McCrum, *Polym. Lett.*, **5**, 1145 (1967).
(5) T. M. Deas, Jr., H. H. Hofer, and M. Dole, *Macromolecules*, **5**, 223 (1972).
(6) K. Toi, T. Kaminaga, and T. Tokuda, *Kogyo Kagaku Zasshi*, **73**, 1467 (1970).
(7) A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1 (1963).
(8) W. R. Vieth and K. J. Sladek, *J. Colloid Sci.*, **20**, 1014 (1965).
(9) W. R. Vieth, C. S. Frangoulis, and J. A. Rionda, Jr., *J. Colloid Interface Sci.*, **22**, 454 (1966).
(10) S. Kubo and M. Dole, *Macromolecules*, **6**, 774 (1973).
(11) W. Y. Wen, D. R. Johnson, and M. Dole, to appear in *Macromolecules*.
(12) P. Meares, "Polymers: Structure and Bulk Properties," D. Van Nostrand, London, 1965, p 320.
(13) R. Ash, P. M. Barrer, and D. G. Palmer, *Polymer*, **11**, 421 (1970).
(14) F. Namada, B. Wunderlich, T. Sumida, S. Hayashi, and A. Nakajima, *J. Phys. Chem.*, **72**, 178 (1968).
(15) M. Dole, *J. Chem. Phys.*, **16**, 25 (1948).
(16) S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, **69**, 651 (1947).
(17) M. Dole and A. D. McLaren, *J. Amer. Chem. Soc.*, **69**, 651 (1947).
(18) See, for example, E. A. Guggenheim, "Mixtures," Oxford Univ. Press, Oxford, 1952, p 252.
(19) This treatment is similar in some respect to that of R. J. Roe, H. E. Bair, and C. Gieniewski, to be published. See also *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **14**, 530 (1973).
(20) See ref 18, p 253.
(21) V. S. Kogan, B. G. Lazarev, and R. F. Bulatova, *Zh. Eksp. Teor. Fiz.*, **37**, 678 (1959).
(22) Y. Udagawa and A. Keller, *J. Polym. Sci., Part A-2*, **9**, 437 (1971).
(23) B. Wunderlich, "Macromolecular Physics," Academic Press, New York, N. Y., 1973, Vol. 1, p 387.
(24) W. J. Moore, "Physical Chemistry," Prentice Hall, Inc., Englewood Cliffs, N. J., 1962, 3rd ed, p 229.

Radiation Chemistry of Polyethylene. XIII.[1] Alkyl Radical Decay Kinetics in Single Crystalline and Extended-Chain Samples of Linear Polyethylene

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ABSTRACT: In this paper the previous kinetic study of alkyl free-radical decay in bulk polyethylene (PE) has been broadened to include a study of single crystalline and extended-chain samples of PE. At room temperature and above the decay kinetics can be quantitatively expressed in terms of two simultaneous first-order decay reactions. The catalytic effect of hydrogen gas on the radical decay rate is very much greater in single crystalline PE than in bulk, but the enhanced catalytic activity is in line with the approximately 10-fold greater solubility (per unit of amorphous content) of hydrogen in the single crystal samples. In the extended-chain samples the hydrogen catalytic effect was less than expected. Activation energies decrease with increasing crystallinity of the samples and the activation energies of the fast decay approach those of the slow decay with decreasing crystallinity.

Using samples of bulk polyethylene (PE) of different amorphous volume fractions, α_v, Johnson, Wen, and Dole[1] showed that the decay of alkyl radicals at room and higher temperatures could be expressed in terms of two first-order decay reactions with constants k_f for the fast decay and k_s for the slow decay. Both of these constants increased as α_v increased. Furthermore, molecular hydrogen had a pronounced catalytic effect on both the slow and fast decays. Inasmuch as hydrogen is soluble only in the amorphous regions of the PE[2,3] it appears that most, if not all, of the alkyl decay at room or higher temperatures must occur in the amorphous regions. This last statement is also supported by the fact that allyl radicals produced at room temperature by the reaction of a free-radical center and a double bond are mostly (70% or higher) of the chain end type when the decay is studied after γ-ray doses of 27 Mrads or less where the vinyl groups still have a significant concentration.[4] It is known that 90% of the vinyl end groups are located in the amorphous zones, at least in single crystalline (SC) PE.[5]

With respect to other papers dealing with the decay kinetics of alkyl radicals in PE, several reviews[6-8] have been published so that older work will not be referred to here unless pertinent.