

## Effect of Environmental Hydrogen Pressure on the Hydrogen Yield from X-Irradiated Polyethylenes\*

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### Synopsis

An experimental assembly incorporating a capacitance-type, differential pressure transducer, which provides resolutions of  $3 \times 10^{-4}$  torr at pressures extending to 30 torr, has been employed to monitor the effect of hydrogen environmental pressure on the hydrogen yield from x-irradiated polyethylenes. Contrary to the observations of previous investigators, the hydrogen yield is found to be independent of hydrogen environmental pressures extending over the critical range up to at least 30 torr. It is demonstrated that neglecting the temperature and density gradients inherent in closed-volume irradiation assemblies employing cryogenic traps to separate liberated gases into condensable and noncondensable fractions may lead to erroneous conclusions with respect to gas yields arising from the irradiation of materials. A homogeneous, variable-plate separation ion chamber consisting of a polyethylene body and utilizing flowing ethylene as the cavity gas was employed to obtain total volatile  $G$  values of  $3.6 \pm 0.4$ ,  $3.8 \pm 0.4$ , and  $4.0 \pm 0.4$  molecules/100 e.v., for Marlex 6002, Dow Ziegler (Q 917.5), and DuPont A-1410 polyethylenes, respectively. A hydrogen contribution of approximately 98 mole-% was obtained with this experimental method.

### INTRODUCTION

When polymeric systems are subjected to ionizing radiation, one common result is the liberation of various gases whose composition depends upon that of the parent material. If these gases are retained in the presence of the parent material during subsequent irradiation, the question arises as to whether or not they might initiate a new series of reactions which are not characteristic of the material during irradiation *in vacuo*. A secondary question is concerned with their ability to influence the relative rate at which particular reactions may progress.

In the case of the radiation chemistry of polyethylene, Dole et al.<sup>1</sup> have presented data from which they have deduced that the radiation-induced rate of hydrogen production is dependent upon the hydrogen pressure above the sample. They employed an initially evacuated, closed-volume irradiation assembly which incorporated a cryogenic cold trap to

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separate the liberated gases into condensable and noncondensable fractions with respect to liquid nitrogen. The pressure-time history of the build-up of the noncondensable fraction (presumed to be hydrogen) was monitored at constant radiation dose rate from a  $^{60}\text{Co}$  source, and the slope of the pressure-time curve was employed to deduce the time rate of hydrogen production as a function of environmental hydrogen pressure. The  $G$  value (molecules/100 e.v.) for hydrogen production was observed to fall very rapidly from 3.8 under limiting vacuum conditions (presumed  $<10^{-2}$  torr) to 3.2 at approximately 30 torr and to approach 2.7 asymptotically at 760 torr hydrogen pressure. The statistical spread in the  $G$  values as a function of pressure did not appear to satisfy the unambiguous assignment of the functional curve placed through the data for the purpose of justifying the reaction scheme proposed to explain their observation. The purpose of our study was to develop an experimental assembly with sufficient resolution to unequivocally establish or reject these earlier conclusions. This primary observation on the pressure dependence of the hydrogen yield was reiterated more recently by Cracco et al.<sup>2</sup>

In another experiment, Williams and Dole<sup>3</sup> used a  $^{60}\text{Co}$  source to irradiate thin Marlex 50 polyethylene films pressed between two aluminum plates. After post-irradiation melting of the sample to remove the dissolved gases, the hydrogen yield was measured with a Toepler pump, after freezing out any condensables at  $-196^\circ\text{C}$ . The integral of  $G(\text{H}_2)$  was reported to fall to 1.6 from the 3.8 value obtained for experiments in which the liberated hydrogen could more readily diffuse out of the film. No attempt was made to analyze the hydrogen concentration within the film pressed between the plates and only qualitative features of the data were explored. Our present study is concerned with minimizing the concentration gradients existing in a sample system in order that a measurement of the environmental hydrogen pressure will more readily correlate with the concentration of volatile hydrogen within the material.

A detailed analysis of the possible effect of environmental hydrogen on the hydrogen yield appears to be in order, since in addition to its interest from the standpoint of reaction mechanisms, it could also represent a biasing event which is responsible for the wide range of radiation-induced hydrogen yields from polyethylenes which are presently available in the literature.<sup>4-6</sup> The recorded gas yields would be sensitive to the pressure range over which the integral of the gas evolution rate was evaluated.

## EXPERIMENTAL

### Sample Materials

Three types of polyethylenes were employed in these studies. In the order of decreasing density and increasing branching, they were Marlex 6002, Dow Ziegler (Q 917.5), and DuPont A-1410 polyethylene. The Dow resin was fabricated into films by the Olin Matheson Corp. Sample masses ranged from 0.186 to 0.191 g.

### Gas Evolution Measurements

The problem of monitoring the rate of hydrogen liberation from x-irradiated polyethylenes in the presence of a variable-pressure hydrogen environment was resolved by irradiating samples in a sealed volume containing a cold trap section for separating the gases liberated during irradiation into condensable and noncondensable fractions with respect to liquid nitrogen temperature. The time rate of pressure rise together with absolute pressure was monitored, and the general gas law was applied to deduce the time rate of production of the average number of moles of condensable and noncondensable gas fractions. Post-irradiation, mass spectral analysis was employed to define the terminal composition of the gases in the sample irradiation volume.

The experimental assembly used in these studies is shown schematically in Figure 1. Weighed polyethylene samples consisting of layers of nominal 0.001-in. thick disks, 0.690 in. in diameter, were placed upon the 0.030-in. thick beryllium window in the sample-mounting section of the assembly. Sample to x-ray target geometry was maintained at 2.06 in. by an alignment jig consisting of a thin-walled stainless steel tube. The temperatures of the sample chamber walls were monitored and maintained at  $76 \pm 5^\circ\text{F}$ . by streaming laboratory air from a 35 cfm blower over the chamber during the calibration and irradiation experiments. The radiation source was a Machlett AEG-50T x-ray tube driven by full-wave rectified output of a G.E. XRD-5 transformer section. A 50-k.v.p. potential was employed with tube currents extending to the 50-ma. limit of the tungsten target.

The gases liberated by the sample under irradiation were distributed throughout a closed volume including a copper cold trap and one side of a capacitance type differential pressure sensor. That portion of the volume

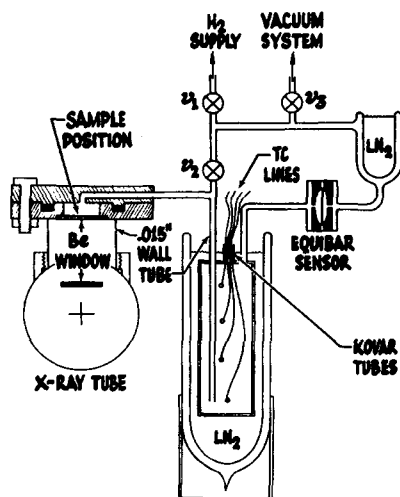


Fig. 1. Experimental irradiation and pressure monitoring assembly.

which may be submerged in a cryogenic fluid ( $\text{LN}_2$ ) to separate the gases into condensable and noncondensable fractions is approximately  $106 \text{ cm.}^3$  as determined from calculations based upon measured dimensions. The overall closed system volume is approximately  $147 \pm 2 \text{ cm.}^3$  as determined by gas-expansion techniques.

The differential pressure sensor consisted of a modified Trans-Sonics, Inc. Type 120 Equibar pressure meter which operates over eight full-scale pressure ranges from 0.01 to 30 torr and is independent of gas composition. The pressure sensor, called an Equibar, is a differential capacitance device consisting of a tightly stretched diaphragm which is clamped between two glass disks and forms two arms of an a.c. bridge circuit. The absolute pressure signal generated by the unbalance of the bridge due to diaphragm deflection may be suppressed electrically by means of a pressure-calibrated, zero-offset dial to allow the use of the lower ranges for accurate measurement of small pressure fluctuations about base pressures extending to 30 torr. In these studies, time rate of pressure changes were recorded by using the 0.01-torr scale (resolution 0.0003 torr) and electrical suppression of the base pressure up to absolute values of 30 torr. At pressures above approximately 0.5 torr, higher differential pressure scales and longer averaging were required due to temperature fluctuations of the gas within the closed volume. The output of the Equibar sensor was continuously monitored with a Brown Electronic strip-chart recorder from which the slopes of the pressure-time curves were deduced.

Although pressure may be considered uniform throughout the sealed volume for the modest rates of change employed in these studies, the same is not true of the temperature (and hence, the density distribution of the gas throughout the system) when the cryogenic ( $\text{LN}_2$ ) trap is employed. When  $\text{LN}_2$  is used to trap condensables, the rate of production of noncondensables is given by a modification of the general gas law

$$dn_1/dt = (1/R) (dP/dt) \sum V_i/T_i \quad (1)$$

where  $n_1$  is the number of moles of noncondensables,  $R$  is the universal gas constant,  $P$  is the chamber pressure in dynes per square centimeter,  $V_i$  is the  $i$ th volume (in cubic centimeters) into which the sealed volume may be arbitrarily subdivided to accommodate an analytical representation of the density gradient in the system, and  $T_i$  is the average absolute temperature of the gas in the  $i$ th volume element. In these studies the pressure range of interest extends from a fraction of a millitorr to tens of torr, corresponding to conditions in which the mean free path of the gas molecules range from an order of magnitude larger to a negligibly small fraction of a typical dimension of the irradiation assembly. For pressures at which the mean free path of the gas molecule is small compared to the volume dimensions, one may deduce the rate of production of noncondensables with eq. (1) when the cold trap volume is a principal fraction of the total volume, and the ratio of the trap volume to trap temperature is the principal term in the summation. An alternate and equally useful an-

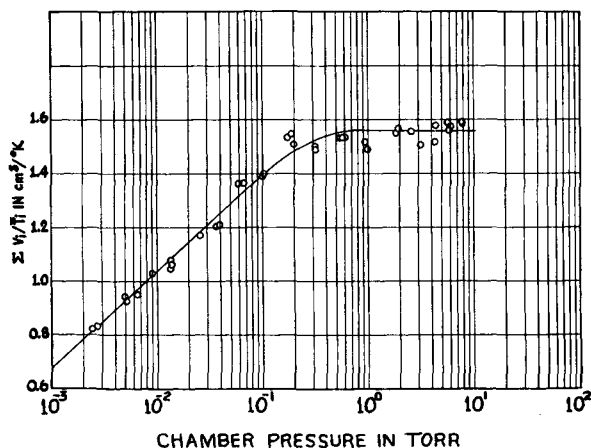


Fig. 2. Calibration of  $\sum V_i/T_i$  as a function of experimental chamber pressure.

alytical technique would be to make the trapped volume and associated gas fraction a small fraction of the total volume so that the density perturbation with respect to the room temperature volume is small. The former method was chosen in these studies because it provided for a maximum conductance element between the irradiation cell and the pressure sensor and maximized the response time of the experimental assembly. A typical response time of the pressure sensor and electronic circuitry itself is approximately 10 msec. to achieve 63% of a step pressure change at atmospheric pressure.

Four helically wound, 3-mil diameter, iron-constantan thermocouples were initially employed to obtain gas temperature measurements within the cold trap section of the assembly to evaluate the summation term in eq. (1). However, this did not prove dependable at pressures below 1 torr, where the couples were sensibly dependent upon the LN<sub>2</sub> level and heat conduction along the leads. Their use was subsequently restricted to measurements of gas temperature at higher pressures (>1 torr) during volume calibrations and pressure ratio analysis of the effective temperature of the volume during cryogenic trapping.

Evaluation of the summation term in eq. (1) was obtained by the method of pressure ratios. The experimental volume extending from valve V<sub>2</sub>, which included the irradiation cell, cold trap volume, and Equibar sensor, was filled with hydrogen gas at room temperature ( $T_0 \approx 297^\circ\text{K}$ .); valve V<sub>2</sub> was sealed and the pressure  $P_0$  in the assembly was recorded after achieving thermal equilibrium. The liquid nitrogen-containing Dewar was then raised to a fixed, constant level around the cold trap section and a final equilibrium pressure ( $P_f$ ) recorded for the system. From the experimentally determined relationship of the pressure ratio  $P_0/P_f$  to  $P_f$ , it was possible to obtain a calibration of  $\sum V_i/T_i$  as a function of  $P_f$  from the statement

$$nR = P_0 V_T/T_0 = P_f \sum V_i/T_i \quad (2)$$

where  $V_T$  is the total volume in the sealed experimental assembly and  $n$  is the number of moles of hydrogen filling the system. In filling the experimental assembly, the hydrogen gas was allowed to stabilize in the volume containing the  $\text{LN}_2$  auxiliary trap for several minutes in order to minimize condensable contaminants presented to the sealable volume. The calibration curve for eq. (2) is shown in Figure 2.

### Dosimetry

Dosimetry measurements were provided by an approximately homogeneous, variable-plate-separation ion chamber consisting of a polyethylene body and employing flowing ethylene as the cavity gas. The geometry of the ion chamber was such that dose rate profiles over the sample face could be obtained in addition to the depth-dose data required to specify the energy deposited in the material. The variable plate separation feature allowed one to specify the energy deposited exclusively in the ethylene cavity gas, from which the energy deposition in the polyethylenes could be deduced directly. Details of the ion chamber have been discussed,<sup>7</sup> and a publication is in preparation.

A  $w$  value for ethylene of 28.2 e.v. per ion pair, which is based upon the data of Jesse and Sadauskis<sup>8</sup> and Bortner and Hurst,<sup>9</sup> was employed in these studies. Whyte<sup>10</sup> has renormalized the earlier data on the basis of more dependable values which have been developed for air and suggests a  $w$  for ethylene of  $26.3 \pm 0.3$  e.v. per ion pair. If one accepts the latter value, then our quoted yields for hydrogen would be increased by approximately 7%. However, since the present paper is not dedicated to precision gaseous yield data, the choice is somewhat academic. Our average absorbed dose rates were approximately  $6.4 \times 10^{16}$  e.v./g.-sec.

### RESULTS

A composite display of some of the typical experimental data obtained with these techniques is presented in Figure 3. These data are normalized for the individual sample masses and dose rates. Reproducibility of the data with and without the cryogenic trap is approximately  $\pm 2\%$  of the particular average values. Intermittent temperature excursions attributed to mixing are responsible for the data variations at pressures extending above approximately 0.50 torr.

A qualitative comparison of the time rate of pressure increase for  $\text{LN}_2$ -trapped Marlex 6002 shown in Figure 3 with the evaluation of the summation term as a function of pressure presented in Figure 2 shows that the product of these two quantities, which is proportional to the time rate of production of moles of noncondensables, is approximately constant and independent of pressure. The failure of this product to exhibit a more precisely constant value is associated with the difficulties of assigning slopes to the pressure histories below  $10^{-2}$  torr and the inability to establish thermal equilibrium throughout the gas phase at these rates of pressure in-

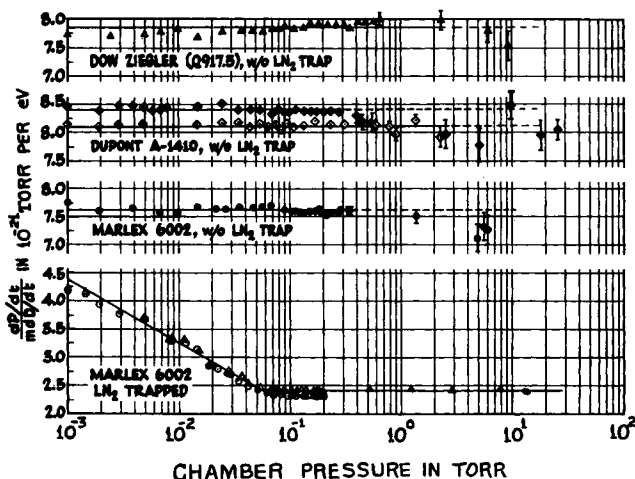


Fig. 3. Mass normalized ratio of pressure of volatiles per unit absorbed 50 k.v.p. x-radiation dose as a function of chamber pressure. Partial pressure of hydrogen  $\approx 98\%$  of chamber pressure.

crease. Rates of pressure rise of 1.4–3.2 mtorr/min. are typical of these data, while the summation calibration data in Figure 2 were allowed several minutes to achieve equilibrium. The data obtained with the entire irradiation assembly at room temperature, which are exempt from a pressure dependent correction, are quite satisfactory for demonstrating the independence of the rate of hydrogen production on the hydrogen environmental pressure of the polyethylene samples.

For pressures extending to approximately 0.50 torr, the gases liberated by the sample were employed to furnish the required changes in environmental pressure in order to maximize the probability of satisfying equilibrium conditions in the gaseous concentration gradients existing throughout the sample. Data at higher pressures were obtained by adding hydrogen to the system from an auxiliary reservoir and subsequently monitoring the rate of pressure increase until equilibrium was obtained. The additional hydrogen introduction was dictated by the observation that the rate of gas liberation began to fall a few per cent at absorbed doses above  $10^{21}$  e.v./g. As will be observed subsequently, the partial pressure of hydrogen in the volatiles is approximately 98% of the total gaseous yield in this experimental method.

Post-irradiation mass spectral analysis of the gases liberated during the room temperature runs (in the absence of the  $\text{LN}_2$  trap) are presented in Table I. Saturates and unsaturates are grouped together, and no absolute significance should be attached to the yields other than hydrogen. Cracking fraction data from the American Petroleum Institute Tables were used in the analysis.

Total and noncondensable gas yields are presented in Table II. The ratio of noncondensable to total gas liberation was checked with an inde-

TABLE I  
Mass Spectral Analysis of Gases Liberated from  
X-Irradiated Polyethylenes at 300°K.

Polyethylene type	Constituent, %				
	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub>	C <sub>3</sub>	>C <sub>4</sub>
Marlex 6002	98.3	0.9	0.4	0.2	0.2
Dow Ziegler (Q917.5)	96.7	0.9	1.6	0.5	0.3
DuPont A-1410	98.1	0.5	0.7	0.3	0.4

pendent series of experiments in which the time rate of pressure rise in the system without the LN<sub>2</sub> trap was compared to the rate obtained when the trap was added in the absolute pressure range above 0.50 torr. These values confirmed the mass spectral data to within  $\pm 1\%$ . Based upon the reproducibility of the data, the relative yields in Table II exhibit an uncertainty of  $\pm 2\%$  of the average values. Absolute yields, which include the uncertainties associated with the dosimetry and the specification of volume and pressure data are estimated to possess a maximum error of  $\pm 10\%$ .

TABLE II  
Total and Noncondensable (w.r.t. LN<sub>2</sub>) Gas Yields  
from X-Irradiated Polyethylenes at 300°K.

Polyethylene type	G, molecules/100 e.v.	
	Noncondensables	Total
Marlex 6002	3.5	3.6
Dow Ziegler (Q917.5)	3.7	3.8
DuPont A-1410	3.9	4.0

## DISCUSSION

It appears from the data developed in the present paper that the hydrogen yield from x-irradiated polyethylenes is independent of the environmental hydrogen pressure over the range extending up to at least 30 torr. The earlier reported observations by Dole and associates<sup>1,2</sup> can be explained by consideration of Figures 2 and 3, which demonstrate that although the monitored rate of pressure change with absolute pressure is real, the actual rate of production of hydrogen is constant when the appropriate correction for the density variation associated with the temperature distribution inherent in the cryogenically trapped system is applied.

The absolute values for the pressure dependence of  $\Sigma V_i/\bar{T}$ , presented in Figure 2 depend, of course, upon the geometries of the particular experimental assemblies employed, but the nature of the correction is well established. Even at higher pressures, where the summation approaches a constant value, it is necessary to correct for the gas density distribution in order to obtain absolute values for the number of moles of gas liberated.



The magnitude of the correction depends sensitively upon the partial volume of the cryogenic trap. The general literature available on gas liberation by irradiation materials is notably lacking in discussions of the details of the methods employed to evaluate the yields quoted on this topic.

The variations in the literature describing absolute hydrogen yields may also be biased by the type of pressure sensor employed in studies of this type. The operational characteristics of typical electronic gages, such as the Pirani, thermocouple, Alphanon, and other similar types, depend sensitively upon the composition of the gas being monitored (as well as its temperature in the first two cases). We observe that while the absence of statements regarding the calibration method employed in such cases does not necessarily imply a lack of attention to this detail, it does make subsequent attempts at data comparison difficult, if not impossible.

As previously mentioned, Dole et al.<sup>1</sup> quote a decrease in  $G(\text{H}_2)$  from 3.8 to 2.7 molecules/100 e.v. in irradiated Marlex-50 over the pressure range from vacuum (assumed  $<10^{-2}$  torr) to atmospheric hydrogen pressure. In consideration of the results of our present study, it is suggested that the lower  $G$  values associated with higher environmental pressures are those less susceptible to error providing that adequate calibration of the pressure sensor and density distribution has been supplied. The  $\Sigma V_i/T_i$  term approaches a constant value at the higher pressures, although the resolution of small pressure differences in the presence of large absolute pressures, which serve to establish the gaseous yields, may suffer from inherent temperature fluctuations in his range.

Williams and Dole's<sup>3</sup> value for  $G(\text{H}_2)$  of 1.6 for the polyethylene film irradiated while pressed between the two aluminum plates may be associated with a hydrogen pressure effect on the hydrogen yield. However, the dosimetry for this experimental configuration is extremely complex and this sensitively influences the quoted yield. Furthermore, in the absence of information on the volatile hydrogen contained within the sample, it is not possible to draw meaningful, quantitative conclusions concerning its influence. Our experimental study is restricted to an explanation of the results of their other experimental method.<sup>1</sup>

Lawton et al.<sup>11</sup> incorporated a cold-trap section in a closed volume of 140 cc. during irradiation of "commercial" polyethylene with 800 k.e.v. electrons and monitored the chamber pressure with and without the employment of the cryogenic fluid for separating the liberated gases into condensable and noncondensable fractions. Pressures of 1660 and 360  $\mu$  monitored with a thermistor type gage were reported for the contributions of the noncondensable and condensable (with respect to  $\text{LN}_2$ ) fractions, respectively, after a radiation dose of  $16 \times 10^6$  roentgen. A  $G$  value of 5.7 molecules/100 e.v. was offered,<sup>12</sup> subsequently, for the noncondensable fraction, which was attributed to hydrogen. Assuming the 1660  $\mu$  referred to the pressure of the noncondensable normalized to room temperature ( $\sim 300^\circ\text{K}$ .), we compute a  $G = 4.5$  molecules/100 e.v. for this fraction. If one assumes that the difference between the  $G$  values of 4.5 and 5.7 is

due to a correction of the density distribution in the cold-trapped system and, therefore, that the pressure of 1660  $\mu$  is measured under cold-trapped conditions, then we compute that for their irradiation assembly the ratio of  $\Sigma V_i/T_i$  to  $V_T/T_0$  is 5.7/4.5 or 1.27. Upon subsequent warming of the cold trap to room temperature, the pressure in the closed volume would rise under these conditions to approximately 2100 microns, which is slightly larger than the sum of the two reported pressure contributions (1660 + 360  $\mu$ ) and suggests the possibility of negligible condensable fractions. Furthermore, applying A.P.I. mass spectral sensitivities to their reported relative peak heights associated with the various hydrocarbon products, we deduce a hydrogen yield of approximately 94 mole-%, compared to the quoted 85%, which is based, presumably, on the ratios of the reported pressures attributed to the condensable and noncondensable fractions. The last observation is more reasonable in view of the later results<sup>13</sup> from the same laboratory, which reported hydrogen yields of approximately 98% in Marlex 50 polyethylene utilizing similar techniques.

There is insufficient information available in the other referenced literature<sup>4</sup> to allow a detailed comparison with the results of the present paper.

A fundamental question, which is inherently involved in the experimental technique common to the investigations under discussion, concerns the secondary effect of the radiation on the liberated gases which remain in the field. The association of the terminal products, which have been subjected potentially to such bias, with the primary reactions occurring in a sample system may also lead to erroneous conclusions. One of us<sup>14</sup> has employed a flow-calibrated mass spectrometer to monitor dynamically the rate of gas liberation by x-irradiated polyethylenes *in vacuo* ( $<10^{-5}$  torr), and we observe that a larger fraction of higher molecular weight products are obtained than is characteristic of studies employing the present technique. It requires  $1\frac{1}{2}$ -3 hr. to obtain an equilibrium mass spectrum for samples consisting of layers of nominal 0.001-in. thick polyethylene irradiated at a dose rate of approximately  $1.5 \times 10^{16}$  e.v./g.-sec. at room temperature. The relatively rapid buildup of hydrogen pressure in the closed volume irradiation assemblies and the subsequent short period of the exhaust into an analytical mass spectrometer may be expected to prevent the removal of other higher molecular weight generated gases from the sample in these cases.

We shall intentionally refrain from discussing the subject of dosimetry, which greatly influences the absolute  $G$  values reported in the literature. Comparative dosimetry techniques are particularly subject to criticism with respect to satisfying conditions of "electronic equilibrium" in sample systems. This is particularly true in the customary cases of high-energy sources and thin sample specimens, since massless radiation sources and sample containers are difficult to approximate.

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### Résumé

Un appareillage expérimental comprenant un dispositif de transmission de la pression différentielle du type capacitif, fournissant des résolutions de  $3 \cdot 10^{-4}$  torr à des pressions s'étendant jusque 30 torr a été utilisé pour enregistrer l'effet de la pression environnante d'hydrogène sur le rendement d'hydrogène au départ de polyéthylène irradié aux rayons-x. Contrairement aux observations de chercheurs précédents, le rendement d'hydrogène est trouvé indépendant des pressions environnantes d'hydrogène et ceci au delà du domaine critique jusque au moins 30 mm de mercure. Il est démontré que en négligeant les gradients de température et de densité inhérents dans les assemblages à volume clos soumis à irradiation en employant des trappes cryogéniques pour séparés les gaz libérés en fractions condensables et non-condensables cela peut amener à des conclusions erronées par rapport au rendement en gaz résultant de l'irradiation des matériaux. Une chambre homogène de séparation à plateau variable consistant en un corps en polyéthylène et utilisant l'éthylène comme gaz de cavité a été utilisée pour obtenir des valeurs  $G$  totales volatiles de  $3.6 + 0.4$ ,  $3.8 + 0.4$  et  $4.0 + 0.4$  molécules par 100 eV pour le Marlex 6002, Dow Ziegler (Q 917,5) et DuPont A-1410 respectivement. Une contribution d'hydrogène d'environ 98 mole % a été obtenue avec cette méthode expérimentale.

### Zusammenfassung

Eine Versuchsanordnung mit einem Kapazitäts-Differentialdrucktransducer der eine Auflösung von  $3 \times 10^{-4}$  Torr bei Drucken bis zu 30 Torr liefert, wurde zur Aufzeichnung des Einflusses des Wasserstoffdrucks auf die Wasserstoffentwicklung aus röntgenbestrahlten Polyäthylenproben verwendet. Im Gegensatz zu den Befunden früherer Autoren erweist sich die Wasserstoffentwicklung als unabhängig vom Wasserstoffdruck im kritischen Bereich bis zu mindestens 30 Torr. Es wird gezeigt, dass die Vernachlässigung der bei Anordnungen zur Bestrahlung in geschlossenem Volumen unvermeidbaren Temperatur- und Dichtegradienten bei Verwendung von Tieftemperatur-

fallen zur Trennung der in Freiheit gesetzten Gase in kondensierbare und nicht-kondensierbare Fraktionen zu irrtümlichen Schlüssen bezüglich aus der Bestrahlung von Stoffen stammenden Gasmengen führen kann. Mit einer homogenen Ionisationskammer mit variablen Plattenabstand aus Polyäthylen mit strömendem äthylen als Cavitygas wurden  $G$ -Werte für die Gesamtmengen an Flüchtigem zu  $3,6 \pm 0,4$  Moleküle pro 100 eV für Marlex 6002-, zu  $3,8 \pm 0,4$  für Dow-Ziegler (Q 917,5)- und zu  $4,0 \pm 0,4$  für Du Pont A-1410-Polyäthylen bestimmt. Mit der angegebenen Methode wurde ein Wasserstoffbeitrag von angenähert 98 Molprozent erhalten.

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