

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

The Chemisorption of Ethylene on Nickel-Silica

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The sorption of ethylene on a nickel-silica catalyst was investigated over the temperature range 0 to 130°. The methods used were the change of magnetization in the nickel and analysis of the products of hydrogenation. There seems little doubt that at the lower temperature on this system the ethylene is adsorbed associatively. But as the temperature of adsorption is raised dissociation and rupture of the carbon-carbon bond became increasingly significant. Self-hydrogenation is negligible at the lower temperature but becomes important as the temperature is raised. It was confirmed that large additional volumes of ethylene may be taken up by the nickel if the ethane formed by self-hydrogenation is removed. In the neighborhood of 130° flowing ethylene quickly converts all the nickel to a non-magnetic carbide. Treatment of the carbide with hydrogen at 130° restores the magnetization with the liberation of virtually pure methane.

Introduction

In an earlier paper¹ it was shown on the basis of magnetic, and other data that the chemisorption of ethylene on reduced nickel-silica catalysts in the room temperature region proceeds primarily by two-site attachment involving, most probably, the Horiuti-Polanyi mechanism.² It was also pointed out that this conclusion was not in complete agreement with the infrared absorption spectra data given by Pliskin and Eischens³ and that the associative mechanism gives no explanation for the well known poisoning effect of ethylene on nickel for the hydrogen-deuterium exchange reaction⁴ and no confirmation for the view that hydrogen under these conditions cannot be chemisorbed as atoms.

Some evidence was, however, presented to show that at moderately elevated temperatures the adsorption of ethylene may proceed by quite a different mechanism and that this resolves some of the discrepancies mentioned above. This observation was also shown to be consistent with that of Schissler, *et al.*,⁵ who found that the poisoning effect of ethylene on the H-D exchange reaction is much less for ethylene adsorbed below room temperature than for ethylene adsorbed somewhat above room temperature.

The purpose of the work described in the present paper was to explain some of the remaining discrepancies and to study in rather more detail the change in adsorption mechanism which occurs for ethylene on nickel as the temperature of adsorption is raised.

Experimental

All experimental details were as previously described except that analyses were made on a Consolidated Electro-dynamics Corporation No. 21-611 mass spectrometer. The absorbent was Universal Oil Products Company nickel-kieselguhr hydrogenation catalyst reduced at 360° for 12 hr., evacuated to 10⁻⁶ mm. for 2 hr. at 360°, then cooled to temperature *in vacuo*. A description of this catalyst and a comparison of results obtainable with this and coprecipitated nickel-silicas has been given.¹ The magnetic measurements were made by the induction (low frequency AC permeameter) method.⁶

(1) P. W. Selwood, *J. Am. Chem. Soc.*, **79**, 3346 (1957).

(2) J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(3) W. A. Pliskin and R. P. Eischens, *J. Chem. Phys.*, **24**, 482 (1956).

(4) G. H. Twigg and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A171**, 55 (1939).

(5) D. O. Schissler, S. O. Thompson and J. Turkevich, "Advances in Catalysis," Vol. IX, edited by D. D. Eley, W. G. Frankenburg and V. I. Komarewsky, Academic Press, Inc., New York, N. Y., 1957, p. 6.

(6) P. W. Selwood, *J. Am. Chem. Soc.*, **78**, 3893 (1956).

Results

The work consisted of a long series of exploratory studies of which those yielding significant results are reported below.

(A) **H₂ Adsorption.**—The magnetization-volume isotherm of hydrogen on nickel-silica shows a slope which is somewhat dependent on the temperature of measurement. This is true even at temperatures well above those at which appreciable Van der Waals adsorption may take place. This is thought to be related to the distribution of particle sizes in any nickel-silica preparation. It was, however, thought prudent to investigate other possibilities before starting the ethylene adsorptions. One of these possibilities is that hydrogen may show a progressive change of bond type with time and that such a change would be reflected in a change of magnetization.

A catalyst sample weighing 5.86 g. and containing 3.09 g. of reduced nickel was treated with 29.5 cc. STP of hydrogen at 76°. The pressure over the sample remained less than 1 mm. After a brief thermal transient the magnetization reached a steady state at 88.8% of the initial magnetization. This remained constant within experimental error over a 2 hr. period.

(B) **C₂H₄ at 0°.**—A comparison was made of the change of magnetization produced by equal volumes of hydrogen and of ethylene adsorbed at 0°. The pressure was held below 1 mm. to lower the possibility of significant ethylene self-hydrogenation.

A catalyst sample weighing 7.06 g. was allowed to take up 30.6 cc. STP of hydrogen. This corresponded to 8.21 cc. STP per g. of nickel, and the magnetization fell to 88.8% of the original value. This is a change of 1.36% per cc. of hydrogen.

The same sample was re-evacuated at 360° and ethylene was then admitted at 0°. There is a fairly large Van der Waals adsorption under these conditions; it was, therefore, necessary to evacuate the sample as previously described to obtain the volume chemisorbed. The initial volume adsorbed was 9.7 cc. before correction. The volume desorbed and collected in a Toepler pump without change of magnetization was 2.8 cc. The desorbed gas was found to be almost pure ethylene. The residual chemisorbed ethylene on the catalyst was then 1.68 cc. STP per g. of nickel, and this caused the magnetization to fall to 97.7%. This is a change of 1.34% per cc. of ethylene.

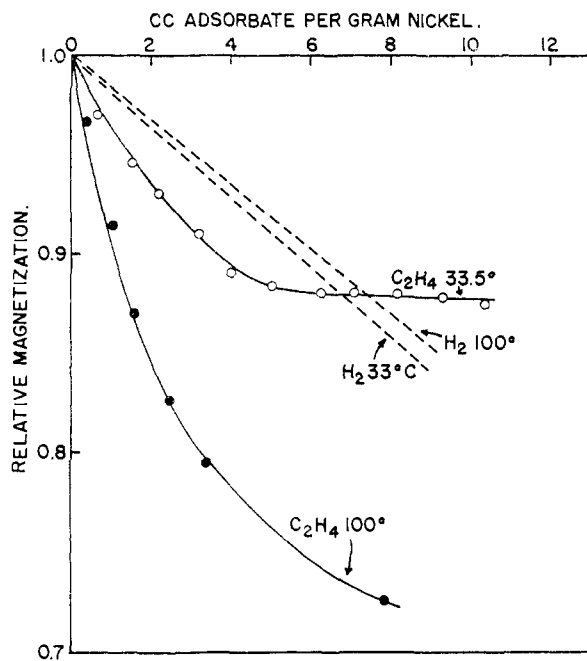


Fig. 1.—Magnetization-volume isotherms for the adsorption of hydrogen and of ethylene on nickel-silica at 33° and at 100°.

Hydrogen was now allowed to flow over the sample while the temperature was raised slowly to 100°. The effluent hydrogen was passed through a silica gel trap at -196° . The vapor so trapped contained ethane and, so far as could be determined, no methane or other hydrocarbon. The volume of hydrocarbon recovered was not measured but is given in connection with another run reported below.

(C) C_2H_4 at Room Temperature.—Although ethylene adsorbed in the room temperature region had been investigated previously, it was thought necessary to re-investigate the possibility of self-hydrogenation in this system and also to study further the products formed by hydrogenating pre-adsorbed ethylene.

A catalyst sample weighing 6.47 g. was treated with ethylene to a pressure of 300 mm. at 28° . The excess ethylene was evacuated and found to contain no appreciable fraction of ethane.

The residue of adsorbed ethylene amounting to 15.5 cc. STP was now treated with flowing hydrogen at a space velocity of about 0.1 per sec. for 2 hr. Toward the end of this period the temperature of the sample was raised to 100° . The effluent hydrogen was passed through a silica gel trap at -196° . The trap was evacuated briefly to remove most of the hydrogen and the trapped vapors were collected in a Toepler pump. The volume of vapor collected was 10.1 cc. STP and this proved to be about one-third methane and two-thirds ethane.

The above experiment now was repeated in slightly different form. Ethylene was allowed to flow over a fresh sample at 1 atm. and 27° until no further magnetization change could be observed. The sample was now evacuated and treated with flowing hydrogen as before. The effluent con-

tained, in addition to hydrogen, only ethane plus a little methane.

(D) Heating Pre-adsorbed C_2H_4 .—To see if heating pre-adsorbed ethylene had any irreversible effect on the magnetization of the nickel, the following experiment was performed.

About 6 cc. STP of ethylene was adsorbed on a 5.86 g. fresh catalyst sample to a pressure of 17 mm. at 26° . The magnetization fell to about 98%. The sample was now heated to 100° for 1.5 hr. and then cooled to 26° . The final magnetization was found to be 98%, as before.

This experiment was repeated, but this time the temperature was raised to 180° for 1 hr. before being returned to room temperature. Under these conditions the loss of magnetization was found to have increased by a factor of 2.6.

(E) C_2H_4 Isotherm at 33.5° .—An attempt was made to extend the previously determined ethylene magnetization-volume isotherm by evacuation after what seemed to be complete coverage had been reached, followed by re-admission of fresh ethylene. An isotherm was obtained in the usual manner at 33.5° . The results are shown in Fig. 1.

The point shown at 10.40 cc. STP C_2H_4 per g. Ni was reached at a pressure of 392 mm. It will be understood that part of this volume was physically adsorbed. The sample was now evacuated with no change of magnetization. The volume of ethylene desorbed after correction for the gas in the dead-space was found to be 3.1 cc. per g. Ni, which left 7.3 cc. per g. on the nickel. The gas so evacuated was found to be virtually pure ethylene.

Ethylene was now re-admitted to the sample to a pressure of 360 m. The quantity adsorbed by the catalyst was 5.7 cc. per g. Ni but this caused no change of magnetization.

The same sample now was evacuated once more to the same state of coverage, namely, 7.3 cc. C_2H_4 per g. Ni, and at this point the sample was heated to 100° . The pressure rose to 100 mm., the gas evolved was evacuated and fresh ethylene was admitted. This process resulted in a large additional sorption of ethylene and in a further drop of magnetization.

In view of the above result the process of evacuation and readmission of ethylene was repeated until no further sorption could be observed. At this point the total take-up of ethylene was well in excess of 20 cc. per g. Ni, and the magnetization had fallen to 70% of the initial value at the same temperature.

(F) C_2H_4 at 78° .—The simple experiment described was performed to determine whether ethylene adsorbed at 78° suffers any progressive change subsequent to the adsorption process. A fresh sample weighing 5.86 g. was treated with 6.0 cc. STP C_2H_4 at 78° . The pressure rose to 13 mm. and the magnetization fell to 85%. No further change occurred over 1.5 hr.

(G) C_2H_4 Isotherm at 100° .—A magnetization-volume isotherm for ethylene on nickel was obtained at 100° , and the effect of evacuation and re-admission of ethylene was determined as already described in part (E) for the isotherm at 33.5° . The results are shown in Fig. 1.

After the point shown at 7.9 cc. STP C_2H_4 per g. Ni had been obtained the sample was evacuated and then fresh ethylene was admitted. The cumulative total volume of ethylene sorbed after three such evacuations and re-admissions was 25.4 cc. STP per g. Ni, after correction for the evacuated gas. The magnetization fell to 54%.

(H) H_2 Isotherm at 100° .—The peculiar results reported above suggested that a hydrogen isotherm should be obtained on a fresh catalyst sample at 100° . The results of significance were that adsorption to a pressure of 746 mm. was 13.5 cc. per g. Ni and that the magnetization dropped to 81%.

(I) Flowing C_2H_4 at 87.6° .—Flowing ethylene has the effect of removing any volatile products such as those obtained through self-hydrogenation. An attempt was made to compare the flowing ethylene treatment at 87.6° with that already given in part C. The result was that the magnetization fairly rapidly fell to 58%. Evacuation had no further effect.

Hydrogen now was allowed to flow over the sample at 87.6° for 2.5 hr. The magnetization rose rapidly, then more slowly until it became almost constant at 73%. Evacuation raised it to 81%. The effluent hydrogen was passed through a silica gel trap at -196° and the hydrocarbons so obtained proved to be over half methane plus some ethane and a little higher hydrocarbon mixture.

(J) Flowing C_2H_4 at 126° .—The experiment with flowing ethylene was repeated on a fresh catalyst sample at 126° . The space velocity was about 1 per sec. In a 3 minute period the magnetization fell to 2%. This almost negligible value of the magnetization was not changed by evacuation.

Flowing hydrogen at 126° now caused a slow increase of magnetization. After 2.5 hr. this had reached 38% and was still rising slowly. Evacuation raised it to 45%. The vapors trapped out from the effluent hydrogen proved to be almost pure methane.

(K) Flowing C_2H_4 over Pre-adsorbed C_2H_4 .—The flowing ethylene experiment was repeated under somewhat different conditions. A fresh sample of catalyst weighing 6.25 g. was treated with 10 cc. STP of ethylene at 49° . The magnetization fell to 90% and remained constant over 2.5 hr. The sample was cooled to room temperature and then ethylene was allowed to flow over the sample while the temperature was raised to 170° . The magnetization as measured at room temperature fell to 4%.

(L) Flowing D_2 over Carbided Sample.—An attempt was made to determine whether the result with flowing ethylene at 126° was caused by complete nickel carbide formation, or rather by methide, methylene or methyl ions or groups.

A sample of catalyst was treated with flowing ethylene at 126° as above until the magnetization was almost zero. Deuterium was now allowed to flow over the sample at 135° for 3 hr. until the magnetization became nearly constant at 40%. The effluent deuterium was passed through a silica gel trap at -196° . The vapor so trapped con-

tained a very large fraction of CD_4 , with only a trace of higher hydrocarbon.

(M) Miscellaneous Results.—A sample carbided to completion as above was heated *in vacuo* at 135° for 1 hr. No change of magnetization occurred. But on being heated *in vacuo* to 355° for 2 hr. the sample regained 70% of its magnetization as measured at room temperature.

An attempt at comparing the catalytic activity of fresh *vs.* carbided samples for the H_2/D_2 exchange reaction gave inconclusive results. Both proved to be good catalysts but the fresh catalyst was definitely superior.

It was found that a carbided sample underwent quite rapid particle growth when heated in hydrogen at 360° . The magnetization after such treatment was, at room temperature, over three times greater than it had been on the original freshly reduced sample.

A carbided sample was found to be about as pyrophoric as a freshly reduced sample.

Discussion

Conclusions based on the results presented above will be presented first, after which an attempt will be made to reconcile these conclusions with earlier work.

The magnetic method for determining the number of bonds formed by any adsorbate molecule on nickel has been reviewed earlier.⁷ This review includes a discussion of the assumptions involved. One of these assumptions is that hydrogen adsorbed on nickel does not suffer any kind of progressive change of bond type with time. This possibility is shown to be improbable by the result reported in paragraph A. It will, therefore, continue to be assumed that the isotherm slope of any adsorbate as compared with that of hydrogen under the same conditions gives the number of bonds formed. By this is meant the number of nickel atoms seriously affected by the presence of one adsorbate molecule.

It is shown in paragraph B that the number of bonds formed per molecule of ethylene at 0° is identical with the number formed by a hydrogen molecule under the same conditions. This result is consistent with the view that under these conditions ethylene is held by the associative mechanism.⁸ The grouping $CH_2=CH-$ plus $H-$ is an alternative. This seems less probable because the maximum volume of ethylene chemisorbed under these conditions (in the absence of self-hydrogenation) is only about one-third that of hydrogen. For the dissociative mechanism indicated above to occur it would be necessary that only one-sixth of the sites accessible to $H-$ be accessible to $CH_2=CH-$. There is certainly no obvious reason why this should be true. On the other hand the associative mechanism does have an obvious reason for the $1/3$ C_2H_4/H_2 volume ratio in the large surface-covering capability of any molecule requiring two adjacent sites. The conclusion concerning the associative mechanism is

(7) P. W. Selwood, 2nd International Congress on Catalysis, Paris (1960) Preprint No. 88.

(8) J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

further supported by the presence of ethane in the vapor removed from the surface by hydrogen flowing over the sample and also by the similar and more nearly quantitative results reported below for room temperature adsorption. The absence of significant self-hydrogenation at 0° is established in paragraph B.

Further investigation of the products obtainable by hydrogenating pre-adsorbed ethylene are reported in paragraph C. The adsorption temperature was 28°. Under those circumstances it proved possible to remove 54% of the carbon, and of that removed one-fifth was in the form of methane and four-fifths as ethane. The removal of hydrogenated products under these conditions is notoriously difficult. We may, however, say that somewhat less than half of the ethylene suffered no very serious reaction on the nickel surface. The remainder is held either as carbide ions which resisted hydrogenation or as polymer molecules which would not be desorbed. The number of bonds formed per molecule of ethylene adsorbed at this temperature is about three. This is probably an average caused by some ethylene completely dissociated with carbon-carbon bond rupture and some ethylene possibly polymerized. But the over-all picture is consistent with the view that a substantial fraction of the ethylene is still adsorbed associatively, although dissociative, and more complicated, mechanisms are increasingly important.

It will be noted also that there is still no significantly different effect caused by flowing ethylene over the sample at this temperature.

In paragraph D it is shown that ethylene adsorbed at room temperature may be heated to about 100° without any change in mode of adsorption. But if the pre-adsorbed ethylene is heated to 180° there is a large, irreversible change consisting doubtless of dissociation and perhaps of carbon-carbon bond rupture.

In view of the additional sorption of ethylene reported by Beeck, *et al.*,⁹ on nickel films at room temperature it was thought surprising that nothing of this kind could be found on the nickel-silica systems. A thorough study reported in paragraph E showed that evacuation followed by re-admission at 33.5° caused no additional chemisorption of ethylene, although the slope of the isotherm shows that dissociative adsorption is becoming increasingly important. But if the pre-adsorbed ethylene is heated to 100° then evacuation and re-admission are attended with a substantial increased sorption of ethylene. This result is exactly that reported by Beeck, *et al.*, on nickel film except that the temperature is moderately higher. We see, therefore, that the failure to sorb additional ethylene at room temperature is not directly related to the mode of adsorption of the ethylene but almost certainly to the necessity for desorption of the physically adsorbed ethane formed by self-hydrogenation. It is quite understandable that desorption of ethane from nickel-silica should require a moderately higher temperature than desorption from a

nickel film. The results are, therefore, in very gratifying agreement with those of Beeck, *et al.*

In paragraph F it is shown that adsorbed ethylene shows no progressive change with time at 78°. This is to say that all the changes which occur take place at the instant of adsorption so far as may be ascertained in an experiment of this type. The result is not unexpected because, owing to the large heat of adsorption, the nickel particles become momentarily considerably warmer than the temperature just before the ethylene is admitted.

The several conclusions discussed above are supported by the isotherm obtained at 100° and reported in paragraph G. At this temperature dissociation has become important. The slope of the isotherm, compared with that of hydrogen at the same temperature (paragraph H) is now several times greater than that at 0°. Furthermore, evacuation of the ethane produced by self-hydrogenation permits a very large additional sorption of ethylene. The total volume of ethylene which could be placed on the nickel under these conditions is nearly twice the volume of hydrogen which could be adsorbed to, presumably, complete surface coverage. These conclusions are further supported by the effect of flowing ethylene at 87.6° (paragraph I). Not only does the magnetization loss approach 50%, but the effect of hydrogenating the preadsorbed ethylene is to show that a substantial amount of carbon-carbon bond rupture has taken place.

The final major conclusion is that based on paragraphs J and K. Removal of the ethane formed by using flowing ethylene at 126°, and higher, results not only in surface coverage but in virtually complete conversion of all the nickel present to a non-magnetic substance. This is presumably some form of carbide. This process is reversible in flowing hydrogen, the hydrocarbon liberated being almost pure methane as indicated long ago by Sabatier.¹⁰

Evidence that treatment of the sample with flowing ethylene at 126°, and higher, yields nickel carbide is shown in paragraph M. Hofer, *et al.*,¹¹ found that "fully carburized" Ni₃C had a half-life of 0.26 hr. at 355°, while 95% "carburized" Ni₃C had a half-life of 0.53 hr. not including an induction period. The non-magnetic nickel carbide decomposes at this temperature to ferromagnetic nickel and to carbon. In the experiment reported in paragraph M 70% of the magnetization was regained in 2 hr. at 355°. It may, therefore, be concluded that ethylene, like carbon monoxide, methane and benzene vapor¹⁰ is capable of converting nickel to nickel carbide at a moderately elevated temperature. Heating in hydrogen at 360° is attended with an enhanced rate of sintering, hence a carbided sample may, even after regeneration be less active than before. An attempt at gaining more information concerning the structure of the carbide was frustrated by its pyrophoric nature. The fact that treatment with deuterium yielded principally CD₄ is scarcely proof that car-

(10) P. Sabatier, "Catalysis in Organic Chemistry," trans. by F. F. Reid, D. Van Nostrand and Co., New York, N. Y., 1932, p. 153.

(11) L. J. E. Hofer, E. M. Cohn and W. C. Peebles, *J. Phys. Colloid Chem.*, **54**, 1161 (1950).

(9) O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc. (London)*, **A177**, 62 (1942).

bide ions as such were present, although the rate of exchange of methane over nickel in the presence of excess hydrogen is quite low. It is, further, not surprising that no very large difference in catalytic activity was found for the carbided *versus* the fresh catalyst. Nickel-silica is notoriously difficult to poison for the H₂-D₂ exchange even with hydrogen sulfide as poison. The poisoning effect of pre-adsorbed ethylene, even for the hydrogenation of ethylene, is so well established as to require no further verification.¹²

The widely different conclusion reached by various investigators concerning the mode of adsorption of ethylene on nickel is seen to be due to the peculiar sensitivity of the ethylene molecule to

(12) L. A. Wanninger and J. M. Smith, *Chem. Weekblad*, **56**, 273 (1960).

temperature, to the specific nature of the catalyst surface and to the presence of ethane formed by self-hydrogenation. The poisoning effect of ethylene on films is more than likely due to the carbiding reaction rather than to polymer formation. The only major area of disagreement seems to be with the infrared absorption spectra which demands extensive dissociation at room temperature. Further elucidation of this difficulty must wait for measurements under identical conditions which are now possible through development of the ferromagnetic resonance method for studying chemisorption.¹³

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(13) D. P. Hollis and P. W. Selwood, forthcoming publication.

[CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH, PA.]

Equilibrium between Crystalline and Amorphous Phases in Polyethylene¹

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Crystallization and melting of fractionated linear polyethylenes (Marlex-50 and a specially prepared low pressure polyethylene) have been investigated by dilatometric methods. Crystallization was carried out at the highest feasible temperature (131.3° in most instances) in order to promote growth of a crystalline phase of maximum perfection. Melting of fractions thus crystallized is extraordinarily sharp; for $\bar{M}_v = 490,000$ the degree of crystallinity decreases from *ca.* 50 to 0% from 136.5 to 138.5°; for $\bar{M}_v = 32,000$ from *ca.* 70 to 0% from 134° to 136°. The melting point 138.5° established for the former fraction is the highest yet recorded for polyethylene; it is 1.5° greater than for the unfractionated polymer crystallized under comparable conditions. Melting of binary mixtures of a polyethylene fraction with α -chloronaphthalene has been investigated over the temperature range immediately preceding final disappearance of crystallinity. Results are compared with the relationship of the degree of crystallinity to temperature calculated assuming equilibrium between a pure crystalline phase and a binary phase comprising amorphous polymer and diluent. Agreement with the thermodynamic expression relating temperature to liquid composition (the latter depending directly on the fraction of polymer melted) is excellent up to degrees of crystallinity as high as 50%. Thus, attainment of phase equilibrium in polymer systems is not restricted to very low degrees of crystallinity.

Introduction

Crystallization of a polymer from its melt or concentrated solution invariably yields a composite of crystalline and amorphous regions. The retention of a considerable fraction of residual amorphous material distinguishes the crystalline state in polymers from other polycrystalline materials. Despite exhaustive investigations employing the techniques of X-ray diffraction and electron microscopy, the textural description of the interspersed crystalline and amorphous regions remains incomplete. Results of these investigations, evaluated in light of implications of mechanical properties of semi-crystalline polymers, nevertheless assure that crystalline and amorphous portions exist in intimate association. The two regions doubtless are joined by molecular chains, some of which pass from one of them through the other, and so on.

Whether or not it is warranted to regard the crystalline and the amorphous zones as discrete phases poses a question of long-standing controversy. From a strictly morphological point of view, the answer is to be sought in the sharpness of the boundaries between crystalline and amorphous

zones. Evidence bearing directly on this issue is elusive, however. The low degree of order usually indicated by X-ray diffraction patterns for indiscriminately crystallized samples, the repugnance of sharp boundaries penetrated by continuous molecular chains and the undeniable capability of the macromolecule to assume intermediate states of order have conspired to engender a body of opinion in support of a negative answer to the question raised above. Thus, on the basis of morphological information alone, a continuous gradation of degrees of order ranging from chaos to something approaching the regularity in molecular crystals of organic compounds has been offered as an adequate representation in preference to description in terms of two coexisting phases.³

Phase transformations are characterized by features other than alteration of structure, namely, by discontinuous changes in thermodynamic functions. Description of the zone in question as a phase is legitimate if, and only if, its properties may be uniquely defined by an appropriate set of thermodynamic variables such as temperature, pressure and composition. To the extent that this stipulation is fulfilled for each of two coexisting phases, the transformation from one phase to the other *at*

(1) Presented before the Division of Polymer Chemistry at the 138th meeting of the American Chemical Society, New York, Sept. 12, 1960.

(2) Visiting Fellow from the Chemstrand Corporation, Chemstrand Research Center, Inc., Durham, N. C.

(3) See for example V. A. Kargin, *J. Polymer Sci.*, **30**, 247 (1958) and H. A. Stuart, *Ann. N. Y. Acad. Sci.*, **93**, 3 (1959).