

of hydrocarbons or hydrocarbon free radicals¹⁸ cannot be made because none of the ions in the mass spectra result from collisions after the initial ionization. Thus the characteristic chain reactions are absent.

Summary

The variation of the relative abundances of the

(18) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

ionic dissociation products formed by electron impact in ethane, normal and isobutane are reported as a function of the energy of the bombarding electrons. The critical potentials of a number of the processes have been measured, and their significance is discussed. Certain limitations of the mass spectrometer as an analytical tool are also discussed.

PITTSBURGH, PENNA.

RECEIVED MARCH 20, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE HEBREW UNIVERSITY]

The Mechanism of the Catalytic Conversion of Para-hydrogen on Nickel, Platinum and Palladium

BY A. FARKAS AND L. FARKAS

The catalytic conversion of para-hydrogen on metals was explained by the dissociation of the hydrogen molecules on the surface of the catalyst.¹ This mechanism was later extended to the ortho-para conversion of deuterium and to the reaction $H_2 + D_2 = 2HD$.²

It seemed to receive confirmation when it was found that the rate of ortho-para conversion on palladium was very nearly equal to the rate of the diffusion of hydrogen through palladium.³ From these experiments the conclusion was drawn that in the conversion and in the diffusion process the rate determining step is the dissociation of the hydrogen molecules on the surface of the catalyst.

Roberts questioned the correctness of the suggested mechanism⁴ on the basis of his own experiments.⁵ In these he was able to show that a clean tungsten surface will take up hydrogen molecules with great speed, that the molecules will be dissociated and that the atoms form a very stable layer on the surface of the tungsten. As this layer will give off atoms or molecules only at a very high temperature it was suggested that it is more reasonable to assume that the ortho-para conversion of hydrogen involves a reaction between the atomic layer and the molecules adsorbed or impinging on this layer. A direct proof for this view was brought forward by Eley and Rideal,⁶ who showed that on an evaporated tung-

sten layer which has been in contact with hydrogen, the rate of the para-hydrogen conversion and the rate of exchange of atoms between molecular deuterium and the hydrogen in the tungsten layer are about equal.

The object of the present paper was the examination of the mechanism of the para-hydrogen conversion on typical hydrogenation catalysts such as nickel, palladium and platinum.

Experimental

The reaction vessel was either a bulb or a cylindrical vessel having a volume of 700 to 1100 cc. The pressure in the reaction system was measured by a Pirani gage. The entrance of vapors of grease or mercury into the reaction vessel or into the Pirani gage was prevented by traps cooled by liquid air. The gases were introduced into the reaction vessel by means of locks having a volume of 0.1 to 0.2 cc.

The reaction vessel was equipped with an electrically heated wire. The catalyst was prepared by heating the wire to a temperature at which the evaporation of the metal begins and thus an invisible layer of high activity is formed on the inner surface of the reaction vessel. The active layer thus prepared was, on the average, not more than one or two atoms deep, since the whole of the wire when completely evaporated would have formed a layer about one hundred atoms deep and actually only a small fraction of the wire, certainly not more than one per cent., was evaporated.

The concentration of para-hydrogen and of deuterium was determined according to the micro-thermal conductivity method.^{2,7}

Nickel.—In the first series of experiments a reaction vessel of 730 cc. volume and having an inner surface of 390 sq. cm. was used. This vessel was provided with a nickel wire 11 cm. long, 0.1 mm. in diameter.

Table I shows the dependence of the half-life time of the para-hydrogen conversion on pressure in the presence of an evaporated nickel film.

(7) Farkas, *Z. physik. Chem.*, **B22**, 344 (1933).

(1) Bonhoeffer and Farkas, *Z. physik. Chem.*, **B12**, 231 (1935); Bonhoeffer, Farkas and Rummel, *ibid.*, **B21**, 225 (1933).

(2) Farkas and Farkas, *Proc. Roy. Soc. (London)*, **A144**, 467 (1934).

(3) Farkas, *Trans. Faraday Soc.*, **32**, 1667 (1936).

(4) Roberts, *ibid.*, **35**, 941, 944 (1939).

(5) Roberts, *Proc. Roy. Soc. (London)*, **A152**, 452 (1935).

(6) Eley and Rideal, *Nature*, **146**, 401 (1940); Eley, *Proc. Roy. Soc. (London)*, **A178**, 452 (1941).

TABLE I

EXPT. 1, TEMPERATURE 20°	
Pressure $\times 10^3$ in mm.	Half-life time in minutes
5.2	1.6
10	2.6
26	3.2
76	4.2
26	2.9
Apparent order of reaction.	0.65

In two other series (Expts. 2 and 3), on the same catalyst, but in a less active stage, the order of 0.7 was found in the pressure region 3.4×10^{-3} to 3.4×10^{-2} mm.

In Expt. 4, on a fresh catalyst the para-hydrogen conversion was found to be complete in five minutes. Then (Expt. 5) a sample of pure deuterium was admitted into the reaction vessel at a pressure of 0.013 mm. and the deuterium content of the sample was determined after a four-minute contact with the catalyst. Then after evacuation with a mercury diffusion pump to a pressure of 10^{-6} mm., fresh deuterium was admitted and analyzed and this procedure repeated twice more with deuterium and four times with hydrogen (Expt. 6). In the experiments with hydrogen the pressure was 0.0095 mm. The results obtained are given in Table II. It will be seen that there

TABLE II

Expt.		Change in D-content in %
5	First sample	-26
	Second sample	-8.5
	Third sample	-6.3
	Fourth sample	-4.2
6	First sample	20
	Second sample	14
	Third sample	13
	Fourth sample ^a	10

^a Time of contact nine minutes.

is reversible exchange between the hydrogen adsorbed on the catalyst and the molecular deuterium; *i. e.*, the deuterium introduced by exchange into the catalyst can be recovered by exchange with hydrogen. Furthermore, the extent of the exchange observed indicates that the amount of hydrogen in the catalyst is comparable to the amount of hydrogen (or deuterium) present in the gaseous phase.

By heating the reaction vessel the catalyst was deactivated and neither the conversion of para-hydrogen nor the exchange reaction took place.

The amount of exchangeable hydrogen in the catalyst can be determined by adding up the amount of exchanged hydrogen in a number of consecutive experiments.

Before Expts. 10 and 11 were performed, a fresh deuterium layer was produced on the catalyst by exchange with a

TABLE III
TEMPERATURE 20°

	Expt. 10 %D in sample	Expt. 11 %D in sample
First sample	33	16.4
Second sample	18	12
Third sample	11	8.4
Fourth sample	7	5.9
Fifth sample	4	5.3
Sixth sample		3.7

great excess of deuterium. In Expt. 10 the catalyst was brought into contact five times with fresh hydrogen samples each time, at a pressure of 0.006 mm. for five minutes, after which period the deuterium content of the gas was determined. In Expt. 11 the pressure was 0.0057 mm., the contact time two minutes and the exchange was repeated six times. The results are given in Table III.

Taking the amount of gas present in each experiment in the reaction vessel as unity, the sum of exchanged hydrogen, *a*, is 0.73 in Expt. 10 and 0.52 in Expt. 11. If the amount of exchangeable deuterium is allowed for that which remains in the catalyst layer after the first five or six exchanges, the above figures can be corrected to 0.8 and 0.6, respectively.

Assuming that in equilibrium the concentration of deuterium is equal in the gas and in the catalyst layer the half-life time of the exchange calculated for Expts. 10 and 11 is 2.4 minutes.

Immediately after Expt. 11 the rate of the para-hydrogen conversion was measured at a pressure of 0.006 mm. and a half-life time of two minutes was found. Thus on the nickel catalyst the conversion of para-hydrogen and the exchange reaction proceed at practically identical rates in agreement with the findings of Eley and Rideal on a tungsten catalyst.

In a second series of experiments a Pyrex reaction vessel of cylindrical form (volume 750 cc., surface 550 sq. cm.) was used, equipped with a 34-cm. long nickel wire 0.1 mm. in diameter. This reaction vessel was placed in an electric oven so that it could be baked out at higher temperatures and maintained at any desired temperature.

The first experiments in this reaction were carried out at 64° and again it was found that at pressures of $7-10 \times 10^{-3}$ mm., the para-hydrogen conversion and the exchange reaction proceeded at similar speed, the half-life times being 2.5 and four minutes, respectively. The amount of exchangeable hydrogen was 0.82 if the gas present in the reaction vessel at 0.01 mm. and 64° was taken as unity (Expts. 39 and 40).

As it is known that hydrogen atoms are exchanged between molecular hydrogen and ethylene in the presence of a catalyst,⁸ it was tested whether such an exchange reaction takes place between ethylene and the hydrogen layer. This test was performed by bringing hydrogen into contact with a layer containing about 50% deuterium before and after it had been in contact with ethylene or by saturating the layer with deuterium and continuing the saturation after having exposed the layer to ethylene.

The results of this test (Expts. 41 to 44 at 64°, and Expts. 56 to 59 at 30°) are summarized in Table IV. In Expt. 41 a catalyst layer containing 48% deuterium produced a deuterium content of 17.6% in a hydrogen sample which had been in contact with the catalyst for four minutes. After this experiment a new layer with 49% deuterium was exposed to ethylene and then to a sample of hydrogen. In Expts. 56-57 a hydrogen layer was treated four times with fresh samples of deuterium. After each treatment the loss in the deuterium content of the samples was smaller, showing that the deuterium content of the catalyst layer was increasing. When, however, ethylene

(8) Farkas, Farkas and Rideal, *Proc. Roy. Soc. (London)*, **A145** 630 (1934); Farkas and Farkas, *This Journal*, **60**, 22 (1938).

TABLE IV

Expt.	Pressure in mm.	Gas	Time in min.	D content of sample in %
41	0.0059	H ₂	4	17.6
43	.012	C ₂ H ₄	10	..
44	.0059	H ₂	4	2.5
56	.0094	D ₂	3	20
	.0094	D ₂	3	50
	.0094	D ₂	3	67
	.0094	D ₂	3	79
57	.028	D ₂	5	89
58	.014	C ₂ H ₄	10	..
59	.0093	D ₂	3	39
	.0093	D ₂	3	54

was brought into contact with the deuterated catalyst, the loss in the deuterium content of the deuterium applied subsequently was nearly as large as the loss in the very first treatment in Expt. 56.

Both series of experiments show clearly that fresh exchangeable hydrogen appears on the catalyst layer after the contact with ethylene, indicating that either the hydrogen layer is capable of exchanging with ethylene or that the ethylene is taken up and retained by the catalyst in a form which can subsequently exchange with molecular deuterium. This point requires further investigation but it was proved by special experiments that no measurable amounts of hydrogen are displaced from the catalyst and evolved when the hydrogen layer is brought into contact with ethylene.

Palladium.—In the next series of experiments a reaction vessel having a volume of 1150 cc. and an inner surface of 520 sq. cm., equipped with a palladium wire 10 cm. long, 0.1 mm. in diameter, was used.

The results of Expts. 14 and 15, which were carried out in the same manner as Expts. 5 and 6, are given in Table V. In Expt. 14 deuterium samples and in Expt. 15 hydrogen samples were brought into contact with the catalyst, the pressure being 0.0073 and 0.0082 mm., respectively. Before and after these experiments, the half-life time of the para-hydrogen conversion was found to be fifteen seconds at the reaction temperature of 25°.

TABLE V

Reaction time in min.	Change in D-content in %	Reaction time in min.	Change in D-content in %
Expt. 14		Expt. 15	
1	-53	2	33.7
2	-31.5	2	19.6
2	-21.8	2	9.8
2	-13.0	2	6.5
2	- 9.8	10	5.4
2	- 8.7	20	5.8
90	-16.3	1	2.5
		1	1.4

If the exchange reaction had proceeded at the same speed as the para-hydrogen conversion, equilibrium would have been established in about two minutes. It will be noted, however, that, in the last run, after a reaction time of ninety minutes, the amount of exchange was higher than in the previous run after a reaction time of two minutes. This shows that there is a certain amount of slowly exchangeable hydrogen on the catalyst. The half-life time

calculated with $a = 1.5$ varies between twenty and sixty seconds for the first four runs in Expt. 14, while for the first four runs in Expt. 15 half-life times of fifty-five to one hundred and twenty-five seconds are obtained. In Expt. 15, $a = 1$.

The results of all experiments with palladium layers are summarized in Table VI and it will be seen that the para-hydrogen conversion is up to fifteen times faster than the exchange reaction and that the amount of exchangeable hydrogen is in no direct relation to the rate of the conversion reaction.

TABLE VI

PALLADIUM, TEMPERATURE 20°

Expt.	Gas	a corrected for 0.01 mm.	Half-life time in seconds
13 ^a	<i>p</i> -H ₂	..	20
14	D ₂	1.09	20-60
15	D ₂	0.82	55-125
16	<i>p</i> -H ₂	..	15
21 ^a	<i>p</i> -H ₂	..	15
22	D ₂	0.9	120
23	<i>p</i> -H ₂	..	8
25 ^a	<i>p</i> -H ₂	..	2
26	D ₂	.27	8
29	<i>p</i> -H ₂	..	4
30	D ₂	.22	24

^a Indicates fresh catalyst.

Platinum.—In this series the reaction vessel was a bulb having a volume of 800 cc. and an inner surface of 410 sq. cm., and equipped with a 12 cm. long platinum wire 0.1 mm. in diameter. As shown by the results summarized in Table VII, the conversion of para-hydrogen is five to six times faster on an evaporated layer of platinum than the exchange reaction.

TABLE VII

PLATINUM, TEMPERATURE 20°

Expt.	Pressure in mm.	Gas	a	Half-life time in seconds
31	0.0057	<i>p</i> -H ₂	..	15
32	.0068	D ₂	0.20	45
37	.0057	<i>p</i> -H ₂	..	10
38	.0068	D ₂	.18	60

Discussion

The described experiments with nickel, palladium and platinum catalysts indicate, in accordance with Roberts' conclusions and Eley and Rideal's findings on tungsten, the following points:

1. There is a hydrogen layer on these metals which is not removed by pumping at room temperature and which can exchange atoms readily with molecular hydrogen, and in the case of nickel with ethylene as well.

2. The rate of this exchange reaction with molecular hydrogen is on nickel equal to the rate of the conversion of para-hydrogen, but it is smaller on palladium and on platinum than that of the para-hydrogen conversion.

The explanation of the findings on nickel is that either the mechanisms of the exchange and conversion reactions are the same or the rate determining steps in these two reactions are the same.

Before discussing the various possible reaction mechanisms, the number of exchangeable hydrogen atoms in the stable hydrogen layer will be calculated. This number will be of some importance as it can be taken as the number of the active centers and will indicate that fraction of the catalyst's area which is active.

The difference between the number of exchangeable hydrogen atoms and the number of the hydrogen atoms in the layer on the catalyst is significant. While it is possible to determine the amount of hydrogen in the layer by adsorption measurements, all of these "chemisorbed" hydrogen atoms are not necessarily exchangeable and the whole surface covered by chemisorbed hydrogen is not necessarily catalytically active.

In Expt. 10 the volume of the reaction vessel was 730 cc., its surface 390 sq. cm., the hydrogen pressure 0.006 mm., $a = 0.77$ and the temperature 20° . From these data the number of the hydrogen atoms in the reaction vessel is 2.90×10^{17} and the number of the exchangeable atoms in the layer is 2.22×10^{17} .

If each hydrogen atom is attached to a different nickel atom, 2.22×10^{17} is the number of active centers on the nickel catalyst. The total area of the active catalytic layer is obtained by multiplying the number of active centers by the area covered by each nickel atom. For an unoriented nickel layer the area covered by one nickel atom can be taken as 6.7×10^{-16} sq. cm., being the arithmetic mean of the areas 5.32, 6.15 and 8.7×10^{-16} sq. cm., in the (111), (100) and (110) planes, respectively⁹; thus the total area of 148 sq. cm. As the apparent area of the glass vessel was 390 sq. cm. and the catalyst layer was on the average not deeper than a few atoms it follows that at least one-tenth of the nickel atoms evaporated was catalytically active.

The figure of 2.22×10^{17} corresponds to 5.7×10^{14} active centers per sq. cm. of apparent catalytic area. In other experiments values of the same order were obtained ranging from 1.6 to 16×10^{14} per sq. cm.

These results have significance if considered to-

(9) Beeck, Smith and Wheeler, *Proc. Roy. Soc. (London)*, **A177**, 62 (1940).

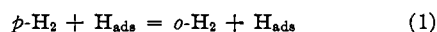
gether with recent experiments of Beeck, Smith and Wheeler.⁹ These authors have found that oriented nickel films of definite crystal structure and reproducible activity for the hydrogenation of ethylene can be prepared by evaporation in an indifferent gas atmosphere at a few millimeters pressure, and that the active regions of the catalyst coincide with a homogeneous, definite crystal lattice, rather than with extra-lattice atoms and related atomic combinations. They have also measured the adsorption of hydrogen on fresh nickel layers up to a thickness of several thousand atoms and have found that an instantaneous, irreversible adsorption, "chemisorption," takes place in agreement with Roberts' results on tungsten.⁵ The chemisorption observed in this case is probably closely related to the chemisorption type A described by Brunauer and Emmett¹⁰ on iron.

There are two different types of reactions which might be operative in the exchange and conversion reactions:

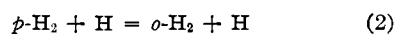
1. Reaction between the stable layer of hydrogen on the catalyst and gas molecules impinging thereon.
2. Reaction between the stable layer of hydrogen on the catalyst and hydrogen adsorbed on places adjacent to those occupied by the stable layer.

According to Roberts and Beeck, Wheeler and Smith, and also to Brunauer and Emmett, the stable layer consists of chemisorbed atoms, but we have no definite information about the hydrogen in the second layer. The hydrogen may be present in the second layer either in the form of more or less deformed molecules or in the form of atoms which can recombine and leave the catalyst in contradistinction to chemisorbed atoms.

The apparent order of a reaction of the first type should be one since the concentration of the hydrogen in the stable layer is independent of the pressure and the number of molecules impinging is proportional to the pressure. Furthermore, one would expect that the collision efficiency of a reaction of this type such as



would be much smaller than that of the homogeneous reaction



(10) Brunauer and Emmett, *THIS JOURNAL*, **62**, 1752 (1940); **69**, 1553 (1937); **67**, 1631 (1935).

because in the latter case the hydrogen atom is free and the molecule can approach the atom in the direction of the line joining the nuclei and thus encounter the least energy of activation.¹¹

Actually, the observed order of reaction (Table I) is definitely below unity and the calculated collision efficiencies for reaction 1 are of the same order as, and in some cases ten to twenty times higher than, the collision efficiencies for reaction 2. For these reasons one might rule out the reaction of type 1 as highly improbable.

On the other hand, it is not possible to decide between the two alternatives of reaction type 2; *i. e.*, whether the reaction with the stable layer involves adsorbed molecules or adsorbed atoms. A close investigation of the conversion of para-hydrogen and of the exchange reaction on palladium and platinum might help to decide between the two mechanisms if it would be possible to ascertain whether the difference in the rates of conversion and exchange is real and not only apparent owing to the existence of centers of various catalytic activity. A renewed comparison of the para-hydrogen conversion on palladium with the diffusion of hydrogen into the metal may also contribute to the solution of the above problem.

In case it is definitely proved that the exchange and para-hydrogen conversion involve adsorbed molecules rather than adsorbed atoms, all conclusions drawn from the assumption that the rate of the para-hydrogen conversion is governed by the rate of dissociation of the molecules, will need revision.

For example, the repeatedly observed parallelism between the rate of the para-hydrogen conversion and the rate of the hydrogenation of ethylene on the same catalyst¹² was explained by the assumption that the dissociation of the hydrogen molecules is the rate determining step in both processes. In case the participation of atoms other than those in the stable layer in the exchange and conversion must be ruled out, another explanation will be needed. The following might be possible. In the exchange reaction between the stable layer and the adsorbed molecules the rate determining step is the adsorption and deformation of the molecules preceding the actual exchange of atoms. In fact this mechanism would not disagree with the general picture of catalytic hydrogenation according to which both hydrogen atoms of the

same molecule are added simultaneously in the act of hydrogenation.¹³

If the dissociation of the hydrogen molecules takes place only in the chemisorbed layer and the recombination of the atoms in this layer is too slow to cause conversion or exchange it is not probable that a dissociation of hydrocarbons into hydrogen atoms and hydrocarbon radicals will contribute to the catalytic exchange of hydrogen atoms between hydrocarbons and molecular hydrogen as postulated by the dissociative theory.^{8,14}

The exchange of hydrogen atoms between hydrocarbons and the stable hydrogen layer is possible according to the experimental results given in Table V. This possibility must be taken into account especially when dealing with exchange of hydrogen atoms between hydrocarbons.¹⁵

Finally, the bearing of the present experiments on two catalytic isomerization reactions will be referred to. Twigg¹⁶ observed that in the catalytic interaction of butene-1 and deuterium the double bond migration was faster than the exchange reaction, while the isomerization was very slow in the absence of hydrogen or deuterium. A similar observation was made by Baxendale and Warhurst¹⁷ in the catalytic hydrogenation of methyl oleate with deuterium when a considerable amount of "light" elaidic ester was formed, indicating that the *cis-trans* conversion proceeded faster than the exchange reaction. Again the isomerization was slow and soon stopped completely when no hydrogen was present.

Both observations can be explained by assuming that the isomerization is caused by an interaction with the stable layer of hydrogen. The effect of hydrogen or deuterium in accelerating the isomerization might be due to the circumstance that the hydrogen in the stable layer is gradually removed by addition to the unsaturated hydrocarbon and gaseous hydrogen is needed for replacing the used-up layer. Since each hydrogen or deuterium atom will cause a number of isomerization processes before it is removed the isomerization will appear to be faster than the exchange.

Summary

The catalytic conversion of para-hydrogen was

(13) Farkas and Farkas, *ibid.*, **33**, 837 (1937).

(14) Farkas and Farkas, *ibid.*, **33**, 678, 827 (1937); **35**, 917 (1939); **36**, 522 (1940).

(15) J. Aman, Thesis, 1941, The Hebrew University, Jerusalem.

(16) Twigg, *Proc. Roy. Soc. (London)*, **A178**, 106 (1941).

(17) Baxendale and Warhurst, *Trans. Faraday Soc.*, **36**, 1161 (1940).

(11) Pelzer and Wigner, *Z. physik. Chem.*, **B15**, 445 (1932).

(12) Farkas, *Trans. Faraday Soc.*, **35**, 909 (1939).

investigated at room temperature and a pressure of about 0.01 mm. on evaporated layers of nickel, palladium and platinum. It was found that there is a stable layer of hydrogen on the catalysts which is not removed by pumping at room temperature and which exchanges readily with molecular hydrogen or deuterium. The rate of this exchange is equal to the rate of the para-hydrogen conversion on nickel, but is smaller on palladium and platinum. It is shown that the amount of ex-

changeable hydrogen in the stable layer can be taken as an indication of the number of active centers on the catalyst. This number is 10^{14} to 10^{15} cm.⁻² and shows that a great fraction of the apparent catalytic surface is active. The various possible mechanisms for the conversion of para-hydrogen and the exchange are discussed and their bearing on other exchange, hydrogenation and isomerization reactions considered.

JERUSALEM, PALESTINE

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Fluorochlorobromomethane

BY KENNETH L. BERRY^{1,2} AND JULIAN M. STURTEVANT

In connection with recent theories of optical activity,³ an optically active pentatomic molecule would be of considerable interest. Attempts have therefore been made to resolve fluorochlorobromomethane, perhaps the most readily obtainable of the few such substances having potential optical activity. During this work several physical properties of this substance have been determined.

Swarts⁴ attempted to resolve this substance by fractional crystallization of the complex it forms with salicylide, but without success. He was also unsuccessful⁵ in attempts to decarboxylate optically active fluorochlorobromoacetic acid to yield the active substituted methane.

Preparation and Purification.—Ethyl chloroacetal was prepared by the addition of chlorine to vinyl acetate in alcohol solution according to the method of Filachione.⁶ Bromination⁷ of the chloroacetal, followed by hydrolysis, yielded chlorodibromomethane. This latter halide on treatment with antimony trifluoride and bromine gave fluorochlorobromomethane⁴ in fair yield, though contaminated with considerable amounts of higher and lower boiling halides. The crude product was washed at 0° with very dilute alkali followed by water, dried over calcium chloride,

and fractionated from phosphorus pentoxide through a 48-cm. vacuum-jacketed column packed with glass helices. The main fraction was collected between 36.3 and 36.8°, and was stored in sealed ampoules in the dark. Over-all yields of approximately 25% were obtained.

Anal. 0.2097 g. gave 0.4693 g. AgCl + AgBr; calcd. 0.4711 g. AgCl + AgBr.

One hundred and forty grams of material boiling at 36.3–36.8° was refractionated, and the middle cut of 65 g. was again fractionated to give a 37 g. fraction boiling at 36.11–36.18° (cor.) (756.0–756.2 mm.). This sample was used for the determination of physical properties. It remained perfectly colorless when sealed in an ampoule and stored in the dark.

Physical Properties.—The fusion curve of fluorochlorobromomethane, which was observed in an apparatus similar to that described by Skau,⁸ showed the 36.11–36.18° fraction to be quite pure. The melting point was found to be –115° (cor.).

The density was determined dilatometrically from 0 to 25°, and can be represented in this range by the equation ($t = ^\circ\text{C.}$)

$$d_t = 1.9771 - 2.51 \times 10^{-3}t - 2.03 \times 10^{-6}t^2 + 3.3 \times 10^{-7}t^3 \quad (1)$$

A Pulfrich refractometer was employed to determine the refractive dispersion of fluorochlorobromomethane in the visible spectrum at 0.5, 10.0 and 20.0°. The data were fitted to an equation of the form recommended by Tilton⁹ ($\lambda =$ wave length in microns)

$$n^2 = a^2 - k\lambda^2 + \frac{m}{\lambda^2 - l^2} \quad (2)$$

(1) The material in this communication constitutes part of a dissertation submitted by Kenneth L. Berry to Yale University in partial fulfillment of the requirements for the Ph.D. degree, June, 1940.

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(3) Kuhn, *Z. physik. Chem.*, **B31**, 23 (1936); Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); Condon, Altar and Eyring, *ibid.*, **5**, 753 (1937).

(4) Swarts, *Bull. acad. roy. Belg.*, [3] **26**, 102 (1893).

(5) Swarts, *ibid.*, [3] **31**, 28 (1896); *ibid.*, *Memoirs Couronnes*, **54**, 54 (1896).

(6) Filachione, *THIS JOURNAL*, **61**, 1705 (1939).

(7) Jacobsen and Neumeister, *Ber.*, **15**, 601 (1882).

(8) Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

(9) Tilton, *Bur. Standards J. Research*, **17**, 646 (1936).