vs)
ζ mv.
35
48
69
34
69
39
48

graphite; the total amount present in the cell was only about 0.5 mg., and of this only a small fraction was deposited because of the incompleteness of the cataphoretic motion. From the writer's study<sup>7</sup> on diffusion of tridecanoic acid in oil, a figure of 0.2 milliequivalent of acid adsorbed per g. graphite can be derived. From this a = 0.04, and from Equation 4 with B = 40,  $D = 10^{-4}$  g. follows. This means that about 20% of the graphite was deposited by cataphoresis. While this figure could not be determined experimentally, it appears of the right order of magnitude, judging from the microscopic observations.

The amphoteric nature of carbon, as found in

(7) Andrew Gemant, THIS JOURNAL, 54, 569 (1950).



Fig. 8.—Counts/min. vs. time for labeled graphite in oil; acid, 0.01 normal; field, 950 v./cm.

this study, is in agreement with corresponding observations from aqueous systems.

# STUDY OF THE FISCHER–TROPSCH REACTION USING DEUTERIUM GAS<sup>1</sup>

BY SYDNEY O. THOMPSON, JOHN TURKEVICH AND A. P. IRSA

Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, New York

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A description is given of an apparatus for the production of deutero carbons from deuterium and carbon monoxide. The various deutero carbons and waxes are examined for their mass spectrum patterns and infrared spectra.

### Introduction

The Fischer–Tropsch reaction is important not only from an industrial point of view but also from the scientific viewpoint in that it offers in its complex but flexible features a challenge to the theory of heterogeneous catalysis.

In this paper we shall present the study of the interaction of deuterium and carbon monoxide over a Fischer-Tropsch cobalt catalyst and the infrared and mass spectral data of the deuterated products.

Apparatus.—The apparatus (Fig. 1) was designed to study the reaction both under straight flow conditions and under conditions in which the exit gas was recycled. The latter procedure was used in the work with deuterium in order to conserve this gas. For the flow experiments the apparatus consisted of a gas mixing section (not shown in the figure), a reactor (1), a series of traps (2), (3), (5) and a circulating system consisting of a pump (7) and ballast chamber (6) and (8).

For the recycle experiments the gas mixture was introduced from the storage bulb (9) and recycled by the pump (7) using ballast chambers (6) and (8). The pressure was determined by mercury manometers, the flow rate by ro-tameters; and the temperature was monitored by thermo-couples placed in the heating jacket and in the catalyst bed.

The reactor was a glass tube 35 mm. diameter and about 30 cm. long. Two wells extending from the top to the midpoint of the catalyst bed were used for a bimetallic thermoregulator and a chromel-alumel thermocouple. The reactor was charged with 20.5 g. of catalyst and occupied a space of 65 cc., the actual volume of the catalyst being 42 cc.

cc. The trap system consisted of one at  $0^{\circ}$  (2), another at Dry Ice temperature (3), and a third one (5) at liquid air temperature. The first two were constructed so that one could syphon off the liquid products without opening the system to air. The contents of the liquid air trap, when brought to room temperature, were stored over water in a gas reservoir. A gas pipet (4) was used for intermittent sampling of the recycled gas. The recycling pump was constructed of bronze sylphon bellows and valves of stainless steel ball bearings.<sup>2</sup> The

The recycling pump was constructed of bronze sylphon bellows and valves of stainless steel ball bearings.<sup>2</sup> The pump was driven by a 0.1 horsepower Boston Ratio Motor Type MB and gave a displacement of approximately 90 liters per hour. A 5-liter ballast bulb before the pump and the 3-liter bulb after the pump was used to increase the gas capacity of the system and to even out the pressure variations during the pumping cycle. An 18-liter reservoir tank

<sup>(1)</sup> Research carried out under the auspices of the Atomic Energy Commission. Presented at symposium on the Use of Tracers in the Petroleum Industry at the Chicago Meeting of the ACS, September, 1950.

<sup>(2)</sup> B. B. Corson and W. J. Cerveny, Ind. Eng. Chem., Anal. Ed., 14, 899 (1942).



Fig. 1.—Apparatus used in the Fischer-Tropsch process.

was used to introduce the synthesis gas through a bleeder valve into the recycling system to maintain atmospheric pressure within the system. The drop in pressure of the tank was used as a measure of the progress of the reaction.

Materials.—Tank hydrogen and tank carbon monoxide were used directly. The carbon monoxide gas has the following impurities: 0.36% CO<sub>2</sub>, 0.97% H<sub>2</sub>, 1.0% N<sub>2</sub>, 0.9% saturated hydrocarbons, 1.9 mg. per liter of iron and 0.32 mg. per liter of sulfur. The deuterium gas was ob-

tained from the Atomic Energy Commission and its deuterium value fluctuated from 98.5 to 99.4% D2.

The catalyst was the standard cobalt-thoria-magnesia kieselguhr material.<sup>3</sup>

In the initial stages of the investigation the deuterium gas was generated by electrolysis of heavy water.

Procedure .- The reduction schedule-used to activate the catalyst was identical to that described by the Bureau of Mines group.<sup>3</sup> For the deuterium work the reduction was carried out with deuterium on a catalyst that had been previously evacuated at 250°.

For the operating conditions a space velocity of 150 per hour and a temperature of 200° was used with protium synthesis. For deuterium synthesis two temperatures, 192 and 227°, were used, and products were discarded until the analysis of the water produced indicated a light hydrogen impurity of less than 2%. A typical run consisted of eight hours of synthesis followed by 16 hours of standing in deuterium gas at the synthesis temperature. When the rate of product formation fell off, the catalyst was purged with deuterium at a space velocity of 2000 per hour for eight hours. The products obtained from the various traps were dis-

tilled either through a Podbielniak low temperature column or a highly efficient high temperature fractionation column. The gaseous products were examined in a General Electric Mass Spectrometer. Infrared spectra were obtained on all products with the Baird Double Beam Recording Infrared Spectrometer.

#### Results

Typical data on the process are given in Table I. while Table II gives the distribution of the converted deuterium between the liquid, gaseous and aqueous phases.

The gas phase was analyzed during the course of reaction by an Orsat apparatus. Typical results

FISCHER-TROPSCH	Data	FOR DEUTERIUM	and Carbon	Monoxide (2:1	Vol.) on	COBALT (	Catalyst
Time T	amn	No. of moles <sup>4</sup>	No	of moles of produc	t	Inp	ut,

TABLE I

Run no.	Time, hr.	Temp., °C.	No. of moles <sup>a</sup> of synthesis gas used	] Water	No. of moles of proc Deutero- carbon	luct Gas	Input, moles deuterium	Output, moles, deuterium
1	36.5	190.2	3.11	1.26	0.045	0.22	1.97	2.20
2	57.	192.	1.78	0.69	.036	.06	1.07	2.21
3	45	192.	1.32	.56	.027	.035	0.79	0.93
4	42	192	1.37	.52	.038	.085	0.85	1.09
5	63	227	2.48	.96	.045	.20	1.65	1.86
6	20	227	1.67	.58	.031	.13	1.1	1.17
7	24	225	1.62	,47	.030	. 20	1.1	1.20
8	30	225	1.64	.48	.033	.13	1.1	1.1
9	20	227	1.64	.19	.035	.17	1.1	0,91
10	53	227	1.63	.36	.014	.32	1.1	1.15
11	56	232	1.64	.42	.029	.13	1.1	1.0

<sup>a</sup> Synthesis gas is deuterium and carbon monoxide (2:1 vol.).

#### TABLE II

Yields <sup>a</sup>	OF	FISCHER-TROPSCH	Products	FOR	DEUTERIUM
		AND CARBON MO	NOXIDE INF	UT	

Run	Liquid, %	Gas, %	Aqueous, %
1	23	20	57
<b>2</b>	33	10	57
3	38	7	55
4	53	30	17
5	27	22	52
6	28	22	49
7	28	33	39
8	30	24	46
9	42	37	21
10	13	55	32
11	32	26	42
	—		
<sup>a</sup> Based on	input D <sub>2</sub> .		

are presented in Table III. The residual gas from the Orsat was dried, examined in the infrared spectrometer and found to be primarily deuteromethane. Gases obtained from run to run were collected and separated into  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  cuts by

### TABLE III

#### ANALYSIS OF GAS PRODUCTS

Temp., °C.	CO2, %	со, %	Deutero carbon	D2, %	Sat., %	Unsat., %
190	7.0	11.5	81.5	1.0	75.5	6.0
192	14.9	25.0	59.9		54.0	5.9
1 <b>92</b>	11.5	25.7	61.8	2.0	58.0	3.8
227	9.2	26.4	61.6	1.9	57.2	4.6
227	13.4	21.1	63.2	2.3	63.2	6.0
227	9.2	27.8	62.5	<b>0.2</b>	54.5	8.0

(3) R. B. Anderson, A. Krieg, B. Seligman and W. O'Neill, Ind. Eng. Chem., 39, 1548 (1948).



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distillation in a Podbielniak column. The degree of unsaturation was determined either by catalytic deuteration or by absorption in fuming sulfuric acid. Table IV gives typical analyses. It is seen that methane is the main gaseous product and the per cent. unsaturated in the C<sub>2</sub> and C<sub>3</sub> fractions is between 20-30%.

	TTT
LABLE	

ANALYSIS	OF THE DEUTE	rocarbon Gas	PRODUCTS
C1, %	C2, %	C:, %	C4, %
87.5	5.5	6.7	0.3
94.5	2.4	2.8	0.3
90.0	4.8	4.7	0.5
90.5	3.8	3.8	2.4

DEGREE OF UNSATURATION IN FISCHER-TROPSCH PRODUCT C1 Sat., % Unsat., % Sat., % C: Unsat., % 79 21 69 31

The infrared spectrum of deuterated methane is given in Fig. 2 and Table V. The mass spectrum is substantially the same as that of CH<sub>4</sub> after due

\* 7

1 ABLE	v
INFRARED ABSORPTION DA	TA FOR METHANE-d4
Sample Wave length in cm1	Literature reference <sup>a</sup>
2250 strong	2258.2
2215 weak	
2095 weak	
995 strong	995.6
968 weak	
960 weak	

<sup>e</sup>G. Herzberg "Molecular Spectra," Vol. II, D. Van Nos-trand Co., New York, N. Y., p. 307.

allowance is made for the change in masses. The sample contained 5.4% CD<sub>3</sub>H indicating a 1.3%protium impurity in the product.

#### TABLE VI

#### MASS SPECTRUM OF METHANE

m/e	Methane-d <sub>1</sub>	m/e	Methane-d4	Methane				
20	100.0	16	7.8	100.0				
19	5.4	15	0.3	80.9				
18	81.5	14	3.5	10.3				
		13	•••	4.7				
17	2.4	12	1.3	1.5				

### TABLE VII

INFRARED ABSORPTION DATA (WAVE LENTGH, CM.<sup>-1</sup>) FOR ETHYLENE-d4 AND ETHANE-d6

Ethane-d and ethylene-d	Ethane- $d$	Ethylene- $d$	Ethane- $d^b$	Ethyl- ene-d <sup>b</sup>
2345 shoulder		2345 shoulder		2345
2200 strong	2200 strong	2200 strong	2236	2200
			2110	
2080 medium	2080 medium		2087	
2060 medium	2060 medium			
			1907 weak	
			1654 weak	
				1595
1510 weak		1510 weak		1510
1480 weak		1480 weak		1495
1470 weak		1470 weak		1480
1090 medium	1095 medium		1102	
1080 strong	1073 strong	1080 strong	1072	1079
1045 medium	1045 medium			
993 strong <sup>a</sup>	993 strong <sup>a</sup>			
718 strong		718 strong		723
-		-		720
			601	

<sup>a</sup> Absorption wave length for methane-d. <sup>b</sup>G. Hertzberg, "Infrared and Raman Spectra," p. 344, ethane-de; p. 326, ethylene-d,.





The infrared spectra of the deuteroethane-ethylene, deuteroethane and protium ethane are presented in Fig. 3 and in Table VII. The agreement with published data is satisfactory. The mass spectrum of the deuterated ethane is given in Table VIII. The light ethane is given for comparison. It is seen that there is about 8.2% C<sub>2</sub>D<sub>5</sub>H in the product corresponding to 1.3% protium impurity.

### TABLE VIII

# MASS SPECTRUM OF ETHANE AND DEUTEROETHANE

m/e	Deuteroethane	m/e	Deuteroethane	Ethane
36	100.0	30	147.9	100 0
35	8.2	<b>29</b>	11.9	<b>92</b> .4
34	88.6	28	95.8	441.8
33	16.3	27	11.1	143.6
<b>32</b>	561.3	26	27.0	95.8
31	25.2	<b>25</b>	0.1	19.2
		24	0.3	4.1

The agreement between the  $C_2D_6$  spectrum and the  $C_2H_6$  spectrum after due allowance is made for mass changes, is satisfactory except for the case of the removal of two hydrogen atoms giving ions of masses 32 and 28, respectively.

The deuterated propane-propylene mixture, the deuterated propane and ordinary propane infrared spectra are given in Fig. 4 and Table IX. It is seen that the completely deuterated propane has two bands in the 2–16  $\mu$  region, one at 4.6  $\mu$  and another at 9.3  $\mu$ , both corresponding to an isotopic shift from 3.4 and 6.8  $\mu$ , respectively. The completely deuterated propylene spectrum is characterized in part by a band at 6.3  $\mu$  and a broad band from 13 to  $15 \mu$  which definitely disappear on bromine treatment and distillation of the deuterated propane-propylene mixture. The mass spectrum of the deuterated propane is given in Table X. The concordance betwen the mass spectra of the  $C_3D_8$ and  $C_3H_8$  is not as good as in the case of the ethanes





	668	weak		-	
<sup>a</sup> Absorption frequency for m	frequencies	for	ethane- $d_6$ .	<sup>b</sup> Absorption	

705 strong

705

and methanes, particularly for the positive ions of masses 34, 32 and 28. This is undoubtedly due to either an air contribution to masses 32 and 28 or to  $C_2D_6$  and  $C_4D_{10}$  components not completely removed by fractional distillation.

The deuterated butane was recovered by the stabilization of the liquid product to give a gas boiling -9 to 0°. The butenes were separated by bromine treatment. The infrared spectrum shows three bands at 4.6, 4.8 and 9.5  $\mu$  as shown in Fig. 5 and Table XI. The mass spectra are given in Table XII. The concordance between the protium and deuterium spectra is reasonably good among the C<sub>4</sub> fragments. However, in the C3 and C2 region the deuterium compound shows considerably higher

NFRARED	ABSORPTION	DATA	(WAVE	LENGTH,	см)	FOR
	PROPANE	-ds AND	PROPY	LENE- $d_6$		
Propan propy	e-d and lene-d	Propa	ane-d	Propyler (partial spec	ne-d ctrum)	

propylene-d

2860 weak 2320 shoulder		
2180 strong	2220 strong	
2070 medium	2094 medium	
	2085 medium	
	2070 medium	
590 strong		
1580 strong		1580°
450 medium		
430 medium		
1380 weak		
175 medium	1 <b>200</b> weak	
145 medium		
1055 strong <sup>e</sup>	1073 medium	
043 strong <sup>e</sup>	_	
	992 weak <sup>6</sup>	
868 medium		868



currents which may be due either to impurities or greater ease of fragmentation of the deuterated butane. The infrared spectra of the liquid phase deutero

carbons before stabilization, after stabilization at

room temperature to remove dissolved gaseous products, and after catalytic deuterization are given in Fig. 6. Figure 7 gives the spectra of the hydrocarbons for comparison. It is seen that removal of dissolved gases clears up the spectrum considerably

800 625 5000 2000 1500 WAVE NUMBERS IN cmrl 1000 100 PERCENT TRANSMISSION. 80 60 40 HYDROCARBON LIQUID 20 HYDROGENATED 7/20/48 0 PERCENT TRANSMISSION. INFRA-RED SPECTRUM OF HYDROCARBON LIQUID PRODUC TROPSCH PROC 0<u>L.</u> 2.0 15.0 16.0 12.0 13.0 14.0 8.0 9.0 10.0 11.0 30 40 5.0 6.0 7.0 WAVE LENGTH IN MIGRONS. Fig. 6.-Infrared spectra of liquid hydrocarbon product.



146.5

33.0

4.6

1.0

2.5

9.5

1.4

3.2

0.4

23.9

2.9

12.7

. . .

Mass	Spectra (Genera	of Deutera l Electric	TED PI Mass S	ROPANE AND PECTROMETE	Propane r)
m/e	Deuterated propane	Propane	m/e	Deuterated propane	Propane
52	100.0		33	30.4	

27

26

25

24

20

19

18

17

16

100.0

102.0

17.9

55.1

9.2

67.1

20.7

13.6

46

45

44

43

42

41

40

39

38

87

47.1

1.8

19.6

3.0

52.7

2.6

14.3

1.0

8.3

• • •

9± '	414.1		10		1	.0
			12	2.6	0	.8
		TABL	e XI			
FRARED	ABSORPTION	Data	(WAVE	LENGTH	см. <sup>1</sup> )	FOR
	BUTANE-0	dio and	ISOBUT.	ANE- $d_{10}$		

Butane-d and isobutane-da	Butane-d and isobutane-d <sup>a</sup>
2230 shoulder	1210 weak
<b>2200</b> strong	1180 weak
2150 weak	1150 weak
2115 shoulder	1095 shoulder
2090 strong	1065 medium strong
2050 shoulder	

" Product is mixture of butane and isobutane.

while deuterization removes the bands at 6.3  $\mu$  and 14.2  $\mu$  due to deutero unsaturateds.

The wax products obtained both as solids during synthesis and from distillation of the liquid were

		TABL	z XII		
MA	SS SPECTRU	IM OF DEUT	EROBUT.	ANE AND B	UTANE
m/e	Deutero- butane	Butane	m/e	Deutero- butane	Butane
68	100.0		43	8.0	905.0
67	10.9		42	214.0	134.0
66	16.3		41	7.3	321.8
65	1.5		40	48.1	16.2
64	4.6		39	1.9	126.2
63	0.4		38	27.2	21.4
6 <b>2</b>	4.5		37	35.2	14.5
61			36	4.0	1.3
60	0.4		35	26.4	
59			34	1162.0	
58	4.0	100.0	33	78.6	
57		19.2	32	994.0	
56	0.9	6.8	31	51.9	
55	0.8	8.9	30	741.0	9.4
<b>54</b>	4.6	1.6	29	26.2	457.0
53	4.0	6.7	<b>28</b>	180.0	291.6
52	19.7	2.3	27	7.3	310.0
51	59.0	10.5	<b>2</b> 6	25.0	54.3
50	1521.0	13.9	<b>25</b>		5.2
49	111.2	3.9	<b>24</b>	4.0	0.8

\_\_\_\_

48	235.4	0.5	20	10.5
47	29.8		19	3.4
46	501.0	0.8	18	59.8
45	21.8		17	
44	12.8	28.7	16	

white in color and amounted to about 5-6% of the liquid product. Their infrared spectrum showed bands at 4.6, 4.8, 9.15 and 9.4 and the spectrum was similar to that of the catalytically deuterated liquid deutero carbons. This is taken to indicate that they were relatively free of unsaturation.

Density determinations on the aqueous phase indicated 98% deuterium, and about 1% organic constituents. The latter were partially identified by distillation of the liquid between 60–100°, extraction of the various fractions with carbon tetrachloride and examination of the infrared spectra of the extract. Indications were obtained of the presence of OD and C=O bands.

Acknowledgments.—We wish to express our appreciation to Dr. Richard Dodson and Dr. Lewis Friedman for advice during the course of this investigation.

# APPLICATION OF THE CATHODE-RAY OSCILLOSCOPE TO POLAROGRAPHIC PHENOMENA. I. DIFFERENTIAL CAPACITY OF THE ELECTRICAL DOUBLE LAYER

## BY J. WEST LOVELAND AND PHILIP J. ELVING

### Department of Chemistry, The Pennsylvania State College, State College, Pennsylvania

#### Received February 2, 1951

A detailed description of an electronic circuit has been given whereby the differential capacity vs. potential curve may be obtained on the screen of an oscilloscope. The capacity current pattern consists of a charging current trace and a discharging current trace. Comparison of calculated capacity values with known values agree favorably for the five solutions investigated. The potentials of certain distinguishing points on the curves likewise are in agreement with known values. The time required is a fraction of that needed with other methods. The application of the circuit is useful for studying charging currents at a streaming mercury electrode. Adsorption phenomena can be easily followed by the technique.

The application of the cathode-ray oscilloscope (CRO) to the measurement of polarographic phenomena has been reported by many investigators. A few have shown how the CRO may be used to study capacity phenomena at the mercury capillary electrode. Heyrovsky<sup>1</sup> employed a sine wave voltage alternately to charge and discharge negatively a mercury capillary electrode. The voltage output from the polarographic cell was placed on the vertical deflection plates of a CRO. The horizontal sweep was synchronized with the frequency of the applied potential to give on the face of the oscilloscope a potential-time trace consisting of the charging and discharging branches. Reversible depolarization processes are accom-panied by definite kinks or time-lags situated symmetrically on the two arms of the potential-time curve. Similar kinks result when various nonelectrolytes are adsorbed and desorbed at the electrode. On adsorption of the non-electrolyte film the capacity of the film-electrode layer be-

(1) J. Heyrovsky, F. Sorm and J. Forejt, Collection Czechoslov. Chem. Commun., 12, 11 (1947). comes smaller than that of the aqueous double layer, whereas, on desorption the film suddenly breaks up at a certain charge density of the polarized electrode.

Delahay<sup>2</sup> developed an electronic saw-tooth voltage sweep for the purpose of studying reduction processes at the dropping electrode. The horizontal sweep of the CRO is proportional to the applied potential; the vertical deflection is proportional to the current flowing at the electrode. Because of the high rate of voltage change, ca. 20 volts per second, a considerable capacity current flows. Delahay measured the capacity currents of a 0.5 molar sodium sulfate solution on both the positive and negative branches of the electrocapillary curve, the observed and calculated values of which differed by 12 and 17%, respectively.

Bieber and Trumpler<sup>3</sup> described a method for studying polarographic phenomena using an isosceles triangular voltage sweep to polarize the dropping mercury electrode (D.M.E.) alternately,

(2) P. Delahay, THIS JOURNAL, 53, 1279 (1949).

(3) R. Bieber and G. Trumpler, Helv. Chim. Acta, 30, 971 (1947).