THE CONDENSATION OF HYDROCARBONS BY ELECTRICAL DISCHARGE. VIII. THE CONDENSATION AS A FUNCTION OF TIME AND PRESSURE[1]

BY S. C. LIND[2] AND GEO. R. SCHULTZE[3]

In one of the former papers[4] results have been reported of some attempts to get information about the mechanism of condensation of hydrocarbons under the influence of electrical discharge. Since all the products of the initial reaction are in turn subjected to the influence of the discharge and, except hydrogen, are condensed in a similar manner and in some cases even more readily than the initial hydrocarbon, it is not surprising that the final products are of extreme complexity. Two factors are especially responsible for such complexity. (a) The long duration of the runs obviously must complicate the condensation by further action of discharge upon the primary products. (b) The numbers of collisions of molecules at the pressures employed (atmospheric) are so great that almost every conceivably possible reaction probably does take place. These two factors necessitate a study of the condensation at lower pressures and shorter times than have been used before. Such investigations have been carried out and will be reported in this paper. Other results of a more complete study of the methane reaction, concerning the influence of pressure and length of time of the runs, also will be communicated.

The Experimental Procedure.—A detailed description of the apparatus employed and the methods of analysis used has been given in another paper appearing in the *Transactions of the American Electrochemical Society*. For the sake of clearness, the following facts may be repeated. The Siemens ozonizer in series with a Liebig condenser represented a circulation system in which the gaseous hydrocarbons were exposed to the electrical field (primary circuit, 6 amp., 89 volts; secondary circuit, 16,200 volts).

The initial gases were taken from industrial tanks and purified by repeated low temperature distillation.

The final gases were analyzed for unsaturated compounds by means of alkaline mercuric cyanide[5] (C_2H_2) and half-saturated bromine water (C_2H_4),

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[4] S. C. Lind and George Glockler, THIS JOURNAL, **52**, 4460 (1930).

[5] Treadwell and Tauber, *Helv. Chim. Acta*, **2**, 601 (1919).

the saturates being separated by low temperature distillation and identified by their vapor pressures as well as by combustion.

The pressure changes during the run were measured and reduced to normal conditions according to the method described in the paper appearing in the *Trans. Am. Electrochem. Soc.* (Preprint 59–16–1931).
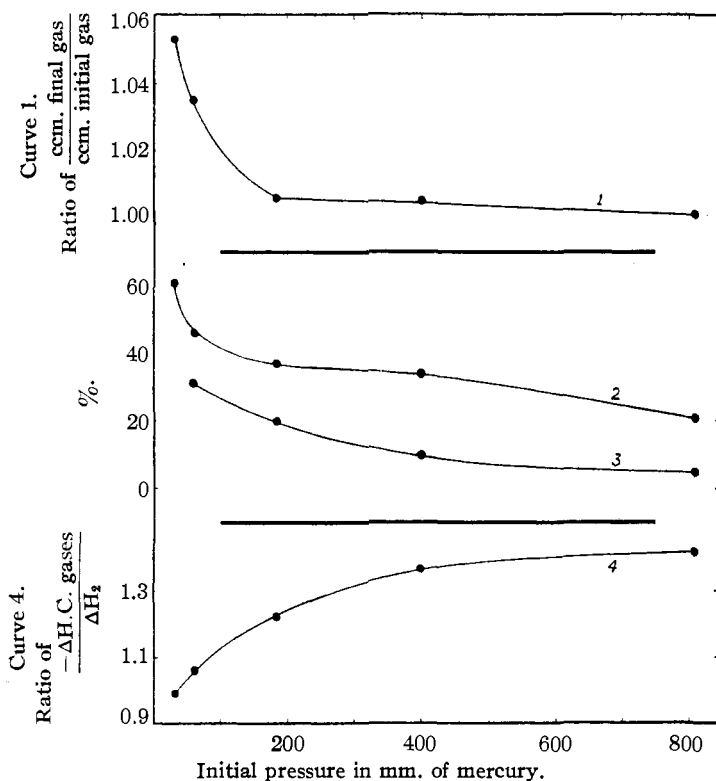
Curve 2, % of methane which reacted. Curve 3, % of methane converted to liquids.

Fig. 1.—Results of five different one-hour methane runs made at various pressures.

The Results

Runs of Different Pressures.—In order to get a general conception of the condensation as a function of the pressure, the simplest hydrocarbon, methane, was studied first. Five different runs made at different pressures under comparable conditions are summarized in Table I and plotted in Fig. 1. The important principle which can be learned from the pressure changes during the runs is demonstrated most clearly by plotting as a function of time the quotient $(P - P_0)/P_0$ as in Fig. 2.

Table I and Fig. 1 need some interpretation. We do not believe that,

TABLE I

ONE-HOUR METHANE RUNS MADE AT DIFFERENT PRESSURES IN THE SAME TUBE UNDER COMPARABLE CONDITIONS

		Run 1	Run 2	Run 3	Run 4	Run 5
Initial gas taken, cc., N. T. P.		395.4	199.5	88.3	28.5	15.13
Init. press. for given room temp., °C. ozonizer		811.1 (29.6) (32.5)	400.5 (19.2) (..)	182.5 (23.6) (23.2)	59.3 (22.5) (22.8)	32.0 (22.4) (22.4)
Time of the run		60.5	60	62	61	61
Final press., for given room temp., °C. ozonizer		820.3 (28.2) (44.3)	401.0 (19.0) (..)	185.3 (23.9) (30.3)	61.0 (22.5) (26.6)	34.0 (23.7) (27.8)
Final gas left, cc., N. T. P.		396.0	200.9	88.9	29.5	15.95
Final analysis:	C_2H_4	1.0 (0.25)	4.0 (1.9)	0.7 (0.8)	...	...
in cc. of gas	CH_4	314.6 (79.5)	132.5 (63.5)	55.9 (62.8)	15.2 (51.5)	5.96 (37.4)
In parentheses are	H_2	57.4 (14.5)	49.1 (23.5)	26.4 (29.7)	12.4 (42.0)	9.28 (58.1)
given the percentages	C_2H_6	13.2 (3.3)	8.0 (3.8)	3.3 (3.7)	0.7 (2.4)	The rest
	C_3H_8	6.8 (1.7)	4.6 (2.2)	1.5 (2.0)	0.5 (1.7)	(0.73 cc.)
	C_4H_{10}	3.0 (0.8)	1.8 (0.9)	Traces	Traces	Not analyzed
Ratio of $\dfrac{\text{Cc. of final gas}}{\text{Cc. of initial gas}}$		1.001	1.005	1.006	1.035	1.053
$\Delta H_2 / -\Delta$ Hydrocarbon		0.71	0.73	0.83	0.93	1.01
Empirical formula of the liquid calculated from an atomic balance sheet		$C_nH_{2.04n}$	$C_nH_{2.32n}$	$C_nH_{2.12n}$	$C_nH_{1.93n}$	...
Liquid production in %		4.4	9.85	19.9	31.6	...
Total hydrocarbon reacted, %		20.4	33.6	36.7	46.5	60.6

for example, the small differences found in the empirical composition of the liquid have any real meaning since this formula is very much dependent upon small limits of error.   The essential data and general principles which may be recognized are as follows.   (1) The total amount of methane which has reacted increases rapidly as the pressure is lowered. That should be expected from the enormous increase in the ionization at lower pressures. Therefore, from the standpoint of efficiency, it is better to work at lower pressures although the difficulties of the analysis of such small absolute amounts of gases and liquids increase.   (2) The same principle holds for
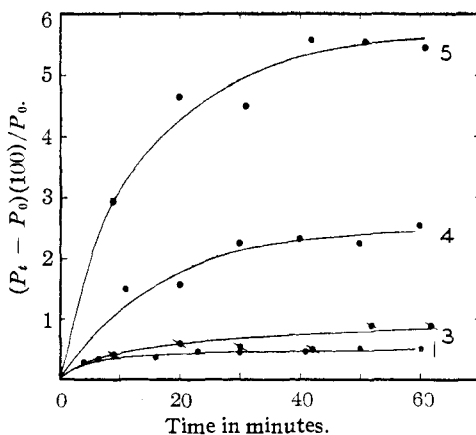

Fig. 2.—One-hour methane runs. Curve numbers refer to runs in Table I. Pressure increases during the run, the more the initial pressure is lowered.

the liquid conversion factor. This seems to be self-understandable, since one would expect the appearance of liquid to go parallel with the disappearance of initial gas in the course of the condensation. However, it will be shown later that in the first stage of the reaction, *i. e.*, for a short time of the runs, the decomposition of the initial gas has no immediate relation to the formation of the liquid phase. (3) The percentage of free hydrogen increases rapidly for lower pressures. (4) Small amounts of unsaturated compounds were detected only for pressures of about 200 mm. This is an interesting point, for it was formerly believed that the presence of unsaturated compounds in the gas phase might account for the maximum in the pressure–time curves which had been found in the earlier work for runs made at normal pressures. It was later proved that the maximum for normal pressure runs disappears completely when the pressure is properly reduced, taking into account all temperature effects.[6]

Since the maximum disappears with proper temperature correction, the presence of unsaturates, if such compounds should be found, would require a further explanation. When the normal pressure runs were stopped at the "apparent" maximum, no unsaturated hydrocarbons could be detected.[7]

However, in all the cases where a real increase in pressure was found with respect to the initial pressure, *i. e.*, for methane runs made at lower than atmospheric pressures, small traces of unsaturates were proved to be present. Thus, ethylene was among the final gaseous products for runs of intermediate pressures where a real pressure increase was found.

At still lower pressures no unsaturates were found although there was a real pressure increase. The absence of unsaturates may here be easily explained by the overwhelming amount of free hydrogen developed, which may hydrogenate any unsaturated compounds formed.

The absolute amount of hydrogen, *i. e.*, the absolute concentration, of course, is decreasing for lower pressure, but the chances for ionization of the hydrogen molecule as well as for the formation of atomic hydrogen are very much increased. The assumption of atomic hydrogen would be satisfactory to explain hydrogenation since Wartenberg and Schultze[8] have shown that C_2H_4 is hydrogenated by atomic hydrogen even at pressures of 0.1 mm. of total gas pressure.

The ratio of the amount of final gas left after the run to the amount of initial gas taken increases as the pressure is decreased. This increase is due mostly to the increasing liberation of free hydrogen.

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[6] The method of pressure reduction by means of a blank run with an inert gas is described in the paper already mentioned in the *Trans. Am. Electrochemical Soc.*

[7] For the higher saturated hydrocarbons the maximum is a real one. In accordance with this fact also unsaturates were found when the runs were stopped at the maximum.

[8] Wartenberg and Schultze, *Z. physik. Chem.*, **B2**, 1 (1929).

The result, of course, is still more evident when the time of the run is not so short as one hour. Therefore, the results of five different methane runs of the length of 440–465 minutes are plotted in Fig. 3. In order to confirm the statement of point (3) the change in percentage of free hydrogen formed during these runs is also shown.

The changes in the gas phase must, of course, reappear in some way in the liquid phase. However, neither calculations from the atomic balance sheets nor direct combustions showed any pronounced difference in the constitution of the liquid phase. But one must remember that the formula obtained from an atomic balance sheet is influenced very much by slight changes in the final analysis, so that small errors of analysis are greatly increased by such a calculation. On the other hand, the amount of liquid product one has available for a direct combustion is so extremely small and volatile and furthermore rather much influenced by air as well as by light that the combustion furnishes little

Fig. 3a.—450-minute methane runs at different pressures.

Fig. 3b.—450-minute methane runs at different pressures.

knowledge as to the true composition of these droplets. In general, the liquid obtained from low pressure runs seems to be more volatile and more easily attacked by light and air than that yielded by high pressure runs.

Runs of Different Lengths of Time.—After obtaining this information about the influence of the pressure on the condensation, a series of runs was carried out at constant initial pressure and with different durations. Furthermore, the investigation was extended to include similar experiments on ethylene and acetylene.

A series of twenty-minute runs was made under comparable conditions and compared with a series of sixty-minute runs. The experimental results are given in Tables II–IV.
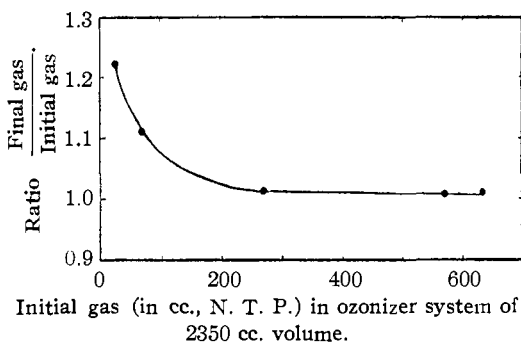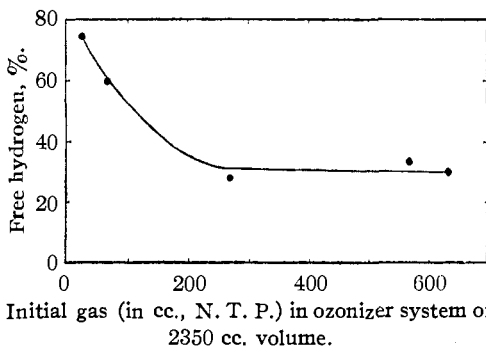
TABLE II

METHANE RUNS, TWENTY AND SIXTY MINUTES

	Run a	Run b	Run c	Run a	Run b	Run c
Initial gas taken, cc., N. T. P.	264.6	265.5	267.4	264.0	266.0	267.8
Initial pressure for given	557.9	554.0	556.6	552.5	553.8	554.9
Room ⎱ Temp., °C.	30.0	25.5	25.9	29.3	26.2	23.7
Ozonizer ⎰	30.5	25.5	25.0	31.0	25.2	24.1
Time of run	20	20	20	61	60	60
Final pressure for given	562.2	558.3	559.5	561.9	562.3	562.4
Room ⎱ Temp., °C.	30.0	25.9	26.6	32.3	26.9	23.7
Ozonizer ⎰	37.0	32.0	31.6	42.0	37.0	36.3
Final gas, cc., N. T. P.	264.1	266.0	267.6	266.0	266.0	269.1
Final gases, cc., N. T. P. CH_4	240.6	245.5	248.7	209.6	205.3	198.5
H_2	13.4	13.5	10.0	40.4	45.0	51.4
C_2H_2	...	...	...	...	...	...
C_2H_4	Doubtful	...	3.0?	0.5?	...	...
C_2H_6	6.1	5.3	2.3	8.8	11.9	12.5
C_3H_8	2.8	1.5	1.0	2.9	2.9	3.4
C_4H_{10}	0.2	0.6	0.2	2.2	0.6	1.6
C_5H_2 and higher	Traces	Traces	Traces	0.3	Traces	0.4
Impurities	...	...	...	...	...	...
Ratio $\dfrac{\text{Cc. of final gas}}{\text{Cc. of initial gas}}$	0.999	1.005	1.001	1.008	1.000	1.004
$- \Delta$ Hydrocarbon/ΔH_2	1.05	1.49	1.87	1.34	1.35	1.35
Formula of liquid, calculated from atomic balance sheet	...	...	...	$C_nH_{1.98n}$	$C_nH_{2.02n}$	$C_nH_{2.0n}$
Liquid conversion, %	0.9	0.7	1.6	5.6	8.5	8.4
Percentage of hydrocarbon reacted	9.1	7.5	7.0	20.6	22.8	25.9

The set of twenty-minute runs is the same as was used for the determination of the M/N ratio in the paper appearing in the *Transactions of the American Electrochemical Society* previously cited.

Concerning Tables II, III and IV, one may recognize the following facts: (A) for methane—(1) the action on methane is, at least for the first hour, proportional to the time; for twenty minutes 7.9% of the initial gas has, on the average, reacted, and for sixty minutes, 23.1%.

(2) The limits of error confine any definite assertion about the formula of the liquid formed to runs not shorter than one hour. The empirical formula seems to be the same for a short run as for a long run, although it has been proved (see later) that the discharge acts on the liquid phase. No discrepancy is included in these results if one assumes that the composition of the liquid is dependent upon a certain state of equilibrium with the composition of the gas phase. A support for this assumption is furnished by (3).

(3) The absolute amounts of higher hydrocarbons in the gas phase do

TABLE III

ETHYLENE RUNS, TWENTY AND SIXTY MINUTES

	Run a	Run b	Run c	Run a	Run b	Run c
Initial gas taken, cc., N. T. P.	267.0	266.0	262.3	265.0	264.2	267.2
Initial pressure for given	556.1	554.8	548.4	553.0	550.7	549.2
Room ⎰ Temp., °C.	25.0	25.8	27.2	29.3	27.6	21.8
Ozonizer ⎱	26.0	24.5	26.5	31.0	30.0	22.5
Time of run	20	20	20	60	60	60
Final pressure for given	468.7	460.6	450.4	286.8	261.1	244.0
Room ⎰ Temp., °C.	24.8	26.1	27.2	30.3	28.2	22.9
Ozonizer ⎱	32.1	33.0	34.0	44.5	41.0	37.5
Final gas, cc., N. T. P.	221.5	214.5	211.4	130.8	118.9	113.9
Final gases, cc., N. T. P. CH_4	3.0	3.2	3.9	8.4	14.1	7.5
H_2	16.0	15.3	16.8	36.3	40.4	42.5
C_2H_2	15.0	12.1	10.8	14.1	9.5	8.7
C_2H_4	116.5	160.1	157.8	45.3	38.3	26.8
C_2H_6	8.4	8.0	5.7	4.8	3.6	4.9
C_3H_8	8.0	9.2	7.1	9.6	6.0	7.9
C_4H_{10}	2.6	3.2	3.5	8.6	4.9	5.1
	2.0	1.3	1.0	1.1	1.2	1.5
C_5H_{12} and higher	...	...	2.8	...	...	1.0
Ratio of $\dfrac{\text{Cc. of final gas}}{\text{Cc. of initial gas}}$	0.829	0.806	0.805	0.493	0.449	0.426
$\Delta H_2/\Delta(CH_4 + H_2)$	0.843	0.826	0.813	0.814	0.742	0.851
$-\Delta$Hydrocarbon$/\Delta H_2$	6.58	6.92	6.21	6.05	5.59	5.66
Formula of liquid calculated from atomic balance sheet	$C_nH_{1.42n}$	$C_nH_{1.54n}$	$C_nH_{1.59n}$	$C_nH_{1.66n}$	$C_nH_{1.67n}$	$C_nH_{1.69n}$
Liquid conversion, %	24.5	22.1	24.3	59.7?	71.3	71.6
Percentage of hydrocarbons reacted	39.3	39.7	39.8	82.9	85.4	90.1

not change appreciably between twenty minutes and eight hours after starting the run.

(4) In the earlier state of reaction, less liquid is produced than later; the state of equilibrium is not reached yet.

(5) The ratio $-\Delta$H.C.$/\Delta H_2$ does not change appreciably for different length of the runs, but it does change for differences in pressure. Therefore the action on methane may be generally characterized by the following stages.

(a) Induction period (about first twenty minutes). The action of the discharge results in building up an equilibrium, whereby the same amounts of each hydrocarbon are decomposed as are formed. The assumption of an induction period which in this paper has been proved for the ozonizer system is in full agreement with the results obtained in the semi-corona type of discharge [THIS JOURNAL, 51, 2814 (1929)] where, for a flow system, an increasing amount of liquid was formed for each trap until the gas reached the third. From the rate of flow and the dimensions of the ap-

TABLE IV

ACETYLENE RUNS, TWENTY AND SIXTY MINUTES

	Run a	Run b	Run c	Run d	Run e
Initial gas taken, cc., N. T. P.	261.7	264.2	263.1	268.0	262.5
Initial pressure for given	551.7	553.7	553.2	547.2	549.6
Room ⎫ Temp., °C.	33.2	28.1	29.4	20.5	31.3
Ozonizer ⎭	34.0	29.0	29.5	22.0	33.2
Time of the run	20	20	20	20	60
Final pressure for given	201.1	138.6	165.5	179.9	11.0
Room ⎫ Temp., °C.	33.1	28.6	29.6	21.6	31.9
Ozonizer ⎭	40.5	36.0	36.0	28.8	40.3
Final gas, cc., N. T. P.	84.0	56.4?	74.6	76.5	4.25
Final gases, cc., N. T. P. H_2		5.5	6.6	6.5	3.44
C_2H_2	76.6	48.9	65.4	68.0	0.18
C_2H_4	Analysis	. . .	1.5?	. . .	. . .
C_2H_6	of rest	1.1	Traces	1.0	0.28
Impurities	spoiled	0.8	0.7	1.0	0.26
Ratio of $\dfrac{\text{Cc. of final gas}}{\text{Cc. of initial gas}}$	0.321	0.213	0.283	0.285	0.016
Total hydrocarbon reacted, %	70.9	81.4	75.2	74.6	100

paratus in those experiments a computation shows that an induction period of about twenty-five minutes is required before the equilibrium stage is reached.

(b) The main state of reaction. Further action on the methane can only give rise to an increase in the amount of liquid formed and of free hydrogen developed. The formation of liquid and liberation of hydrogen per minute must reach a constant value.

(c) The last state of reaction. A slow decomposition of the liquid phase is the only essential change in the system.

(B) For ethylene: (1) the ratio $\Delta H_2 / \Delta(CH_4 + H_2)$ is the same for the sixty-minute runs as for the twenty-minute runs. This is proof of Lind and Bardwell's assumption of such a constant proportionality for these values, under which the separate values of CH_4 and H_2 have been calculated in the alpha-ray work.[9]

(2) In agreement with the methane runs the ratio of hydrocarbon disappearing over the hydrogen appearing is not changed when the time of the run is changed from twenty to sixty minutes.

(3) The formula of the liquid formed shows no appreciable change for different lengths of runs, just as was found for methane. On account of the greater reaction, i. e., greater value of the M/N ratio than was found for methane, a formula can be calculated even for the twenty-minute runs.

(4) For the ethylene runs a time of twenty minutes is so long that the influence of an induction period, if there is any, is completely covered up.

[9] Lind and Bardwell, THIS JOURNAL, **48**, 1563 (1926).

Neither the liquid conversion factors nor the amounts of hydrocarbon reacted allow any conclusion in this connection, for the conversion factor proportionality with the time seems to hold, although one value (59.7) is far off.

(5)   The reaction velocity is already so diminished in one hour that no simple assertion can be made about the relationship between the velocity of reaction and the time.

(C)   For acetylene: (1) the earlier alpha-ray work seemed to indicate that the free hydrogen is mostly developed by further action of the discharge from the solid cuprene which has been formed.   This does not seem to be true for the action of electrical discharge since the proportion of free hydrogen which has been formed in twenty minutes is certainly not smaller than that formed in sixty minutes.   When the discharge was allowed to act on the wall skin for many hours alone after the gas phase had been removed, no hydrogen was developed by further action.

(2)   In addition to the development of free hydrogen during the condensation, traces of a hydrocarbon appear to be present, the formula of which checks best for ethane.   But the decision may be left open whether it is ethane or ethylene.   In every case its presence indicates that even for acetylene some side reactions occur during the condensation.

Reaction Mechanism

The question which remains to be answered is: what is the mechanism of these reactions?

After the investigations given had shown how many different factors must be taken care of by a satisfactory assertion about the mechanism, the question of how the condensation takes place seemed to be more complicated than ever.   The acetylene condensation, of course, seems to be the simplest one and, thus, to promise most success.   In the meantime a more detailed study of this reaction has been made but as yet no satisfactory reaction has been found.   Therefore, we prefer to postpone the discussion to a later date when still more analytical data have been procured.

Single Facts which Ought to be Mentioned.—Some other facts which have been discovered in the course of these investigations ought to be mentioned although they have no immediate connection with the problem involved.

(1)   One cannot say what the actual behavior of the liquid in presence of the gas phase might be during the run, but it is evident that if no action of the discharge on the liquid is found after having completely removed the gas phase, one can be sure that there is no action which developed gas, during the time of the run.   (Polymerization, of course, may occur.) The reverse conclusion is not valid;   one can only find out from the results of an action in the absence of the original gas phase, what the chief products of such action, if there are any, may be.

After the run the gas phase was pumped off, and the discharge was switched on again for further action on the liquid.

For the liquid produced from *methane* only the fact of reaction was established by measuring the increase of the pressure.

For the liquid produced from *ethylene*, where a larger absolute amount of condensation product was present, the gas developed from the liquid phase with one hour of exposure to the discharge was pumped off and analyzed. Of 5 cc. of gas obtained 80.3% was hydrogen. The rest appeared to be a mixture of ethylene and methane, although the presence of ethylene seemed to be rather doubtful.

For *acetylene*, 2.5 mm. of gas pressure (400 cc. volume of the system) was developed in less than one hour, and after more than twenty-four hours no further increase in pressure was detected. One is prone to assume that the gas primarily developed was gas occluded and absorbed during the condensation of the wall skin at the time of the main run, and now knocked off by electron impact.

(2)   In order to get evidence as to whether it is an ionized free radical which acts as clustering center, a special run was made: the current was alternatingly switched on for five minutes and off for one minute until the exposure to the discharge amounted to twenty minutes, in order to give a chance for the dissociated molecules to recombine in another way than they would under the influence of the discharge. No decisive difference between this and the other acetylene runs was detected. The run seems to prove that the formation of the cuprene molecule is a very quick process if the primarily ionized molecule is once provided.

(3)   It may be noted that throughout all ethylene runs, the amount of propane formed is greater than that of ethane. If one considers that the stopping power for propane is much higher than that of ethane, one has only the explanation available that the formation of propane by some step of reaction is especially favored over a simple hydrogenation of the ethylene. This is a new indication that ethylene under these conditions shows little or no tendency for a reaction leading to the nearest saturated compound.[10]

Contrary to the results obtained by Lind and Bardwell,[11] with alpha-rays acetylene is hydrogenated under influence of electrical discharge. Table V shows the results of a run made with a mixture of acetylene and hydrogen in almost equal proportions. In addition to the formation of the yellow cuprene, one obtains a hydrogenation effect, resulting in the formation of paraffins and liquids as may be seen from the empirical formula of the liquid plus solid. One-third of this hydrogen which is used up for hydrogenation reappears in the gas phase, while the remaining two-thirds goes into the liquid plus solid phase. The hydrogenation effects may also be

[10] Lind, "The Chemical Effects of Alpha Particles and Electrons," 1928, p. 178.
[11] Lind and Bardwell, THIS JOURNAL, 48, 1556 (1926).

seen from the fact that the wall skin in this case is attacked even by cold cleaning solution.   Furthermore, the final pressure after the run indicates that some hydrogen is used up for hydrogenation.   The velocity of condensation is somewhat slower than in the case of pure acetylene.

TABLE V
HYDROGENATION OF ACETYLENE (360 MIN.)

Initial acetylene taken, cc., N. T. P.		145.6
Initial hydrogen taken, cc., N. T. P.		140.6
Total initial pressure for given		568.0
Room Ozonizer } Temp., °C.		{ 21.6 { 23.0
Time of the run		36.0
Final pressure for given		209.0
Room Ozonizer } Temp., °C.		{ 21.3 { 30.0
Final gas, cc., N. T. P.		101.4
Final gases, cc., N. T. P. C_2H_2		1.6
C_2H_4		...
CH_4		9.4
H_2		89.0
C_2H_6		1.1
C_3H_8		0.3
Ratio of cc. of final gas/cc. of initial gas		0.354
Ratio of cc. of final gases/cc. of initial hydrogen		0.721
Empirical formula for (liquid and solid) produced		$C_nH_{1.25n}$
Hydrogen used up for hydrogenation		36.7%
Total hydrocarbon reacted		99.0%

(4)   As to the condensation of methane it may be noted that the ratio of cc. of final gas/cc. of initial gas fluctuates about the value of 1.000, if the reaction is complete (after about eight hours).   It was proved that for normal pressures of gas the value of 0.980 can be reached if the initial gas is extremely pure.   Even traces of impurities result in raising the value of the ratio to 1.000.   Small traces of higher hydrocarbons present in the initial gas account for this fact.   Thus the value of this ratio can be used as a measure of the purity of the initial methane if the total initial pressure is about one atmosphere.   For lower pressures, of course, the ratio increases according to the principles which have been given in this paper.

The authors wish to thank Mr. John L. Wilson, who has assisted in this work as American Petroleum Institute Research assistant.

Summary

A large series of general principles has been described which shows the influence of pressure and time on the condensation of methane, ethylene and acetylene.

The effect of the electrical discharge on the liquid products has been studied.

In contrast to the reaction under influence of alpha-radiation, acetylene is hydrogenated in the electrical discharge to some extent.

MINNEAPOLIS, MINNESOTA

THE SODIUM COULOMETER

BY OLUS J. STEWART

Several years ago R. C. Burt[1] effected the electro-deposition of elementary sodium within incandescent lamp bulbs lowered into baths of molten sodium nitrate. Investigation showed that the bulbs were not appreciably attacked by the bath and that the process followed Faraday's law with an accuracy of at least 0.2%. Burt urged the use of the instrument as a voltameter which he[2] later modified "by using metal contact with glass instead of thermoionic emission." Further description of the instrument was omitted except for the statement that "the process yields results which are certainly correct to 1:2000 and probably to 1:6000."

Advantages uniquely held by the sodium voltameter made it desirable to investigate its accuracy further.

The work began with Burt's original voltameter, which was soon abandoned in favor of an instrument containing mercury in contact with ordinary glass. The quantity of sodium deposited was determined either by weighing or by dismantling the instrument and titrating the alkali with standard acid. Numerous objectionable features, such as the high density of mercury, the low solubility of sodium in mercury, the proneness of mercury to "bump" and the low electrolytic conductivity of ordinary glass led to the production of a superior type of instrument.
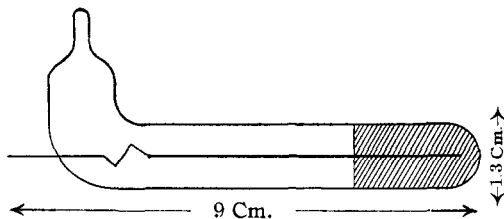

Fig. 1.

This coulometer, Fig. 1, is made of glass (about 1.4 mm. thick) designated by the Corning Glass Works, "Corning clear, soft lime tubing, No. 015." The platinum wire, sealed through the glass and coiled for flexibility, is brazed to a stout nickel wire extending to the bottom of the tube. Each electrode contained 15 g. of cadmium but the anode also contained 0.5 g. of sodium. Evacuation,

[1] R. C. Burt, *J. Opt. Soc. Am.*, 11, 87 (1925).

[2] R. C. Burt, *Phys. Rev.*, 27, 813 (1926).