Pyrolysis of Propane in Presence of Water Vapor

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A study of the pyrolysis of propane at low partial pressures in the presence of steam was made in which all of the products were determined accurately by fractional distillation and subsequent analysis of the fractions.

Since, up to the temperature of 700° C. with the times of contact used, steam was found to behave substantially as an inert gas, it was utilized to investigate the primary decomposition of propane at partial pressures below atmospheric pressure.

The results show that a bimolecular primary decomposition occurs to an extent which cannot be neglected in the calculation of rate constants; that over the range of temperatures commonly used in the study of primary thermal decompositions, temperature has no effect on the proportions of primary products obtained from propane; and that the proportion of propylene to ethylene in the unsaturated hydrocarbons obtained by the commercial pyrolysis of propane may be increased at higher pressures.

The primary products of the pyrolysis of propane may be accounted for by reactions:

$$C_3H_8 \longrightarrow C_3H_6 + H_2$$
$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$
$$2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4$$

A critical study was made of proposed mechanisms of hydrocarbon pyrolysis, and it is shown that none of the hypotheses currently advanced explains adequately the primary thermal decomposition of propane but that the mechanism may be explained by Nef's dissociation hypothesis.

Apparently the first theoretical study of the products of the thermal decomposition of propane was made in 1928 by Pease (*11*) who reported that the two main reactions were dehydrogenation and demethylation. His analytical procedures, however, were not sufficiently reliable to determine accurately the relative extent of these two reactions. About the same time Frey and Smith (*4*) reported the results of propane decomposition at 575° C., and were the first to give a complete analysis of the products. They also demonstrated that silica has little catalytic effect and that the decomposition is unaffected by an increase in the surface area of the silica. It is important to note that they observed the stoichiometric relations among the products and suggested that these might be accounted for by the following reactions:

$$C_3H_8 \longrightarrow C_2H_4 + CH_4 \tag{1}$$
$$C_3H_8 \longrightarrow C_3H_6 + H_2 \tag{2}$$
$$2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4 \tag{3}$$

These authors observed that reactions 1 and 2 were about equal in velocity and reaction 3 was considerably slower. It was suggested that a study of these reactions at other pressures would prove or disprove the assumption of reaction 3. They did not attempt to show the mechanism of the reactions.

In 1931 Schneider and Frolich (*13*) cracked propane at 725° C. with various contact times, extrapolated their results to zero per cent decomposition, and concluded that the decomposition could be expressed by Equations 1 and 2. The presence of ethane was disregarded in this conclusion, as well as the fact that the greater the percentage of cracking, the less is the average partial pressure of propane. These authors apparently assumed that all products other than those accounted for by the two equations were the result of secondary decompositions and polymerizations. Recently Paul and Marek (*10*) published data on the rate of decomposition of propane, their constants being based on the values obtained by measurement of the olefin content of the exit gases. Their method of determining the time of contact for a flow system is unique and should give reliable results. Here, too, the assumption is made that only monomolecular reactions are involved.

Ebrey and Engelder (*2*) cracked propane in the presence of catalysts and also homogeneously, but the decompositions were allowed to proceed so far that secondary reactions undoubtedly took place.

Materials

Liquid propane obtained from the Carbide and Carbon Chemicals Corporation was used for the experiments. Analysis with the Podbielniak column showed that gases distilling at temperatures lower than propane were present to the extent of only 0.2 per cent and that higher boiling hydrocarbons could not be present to an extent greater than 0.2 per cent. Examination of the propane in the Shepherd apparatus showed that carbon dioxide, oxygen, and unsaturated hydrocarbons were not present in amounts greater than 0.05 per cent. The main impurity in the gas was nitrogen, of which approximately 0.2 per cent was present. Distilled water

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was used for the generation of the steam mixed with the propane, and previous to making an experiment the apparatus was thoroughly flushed out under the conditions of the experiment to eliminate contaminating gases.

Apparatus

A sketch of the apparatus is shown in Figure 1:

The metered propane was admitted to the saturator, *S*, which consisted of a Pyrex suction flask heated by an electric hot plate. In it water was boiled at a rate just sufficient to insure the reflux of the condensate. From the saturator the mixture of propane and water vapor passed through a copper coil, *C*, surrounded by a thermostat which maintained it at the temperature necessary to give the desired vapor pressure of water. The temperature during an experiment did not vary more than ±0.05° C. This arrangement for regulating the proportion of water to propane was entirely satisfactory. At rates of flow considerably higher than those actually used in the experiments, the water vapor content of the mixture, which was determined by measuring the propane in a calibrated wet meter and weighing the water absorbed by calcium chloride, agreed well with that calculated from the vapor pressure curve for water.

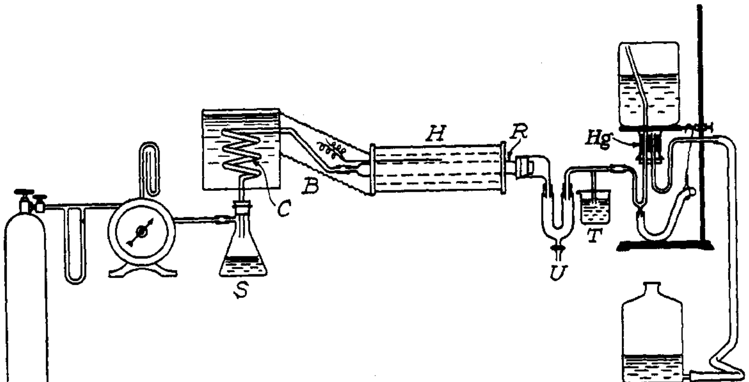


FIG. 1. DIAGRAM OF APPARATUS

The copper tubing extended through the wall of the thermostat and was connected to the silica tube, *R*, which was constricted at this end to the same size as the copper tubing. To prevent condensation of water, the temperature of the gas mixture between the thermostat and the furnace was maintained higher than that of the copper coil by means of an air bath, *B*, heated with an electric lamp. The silica reaction tube was 90 cm. long and had an internal diameter of 2.2 cm. It was heated for a portion of its length in an electric tube furnace, *H*, 60 cm. long and 7.5 cm. in internal diameter. Exploration of the cracking tube in place in the furnace with a small calibrated chromel-alumel thermocouple showed that the temperature in the cracking tube was constant for a portion approximately 20 cm. in length near the center of the furnace, and that this temperature did not differ more than 2° C. from the temperature at a corresponding point on the outside of the tube when the latter temperature was determined with a calibrated fourteen-gage chromel-alumel thermocouple and a high-resistance galvanometer. In the cracking experiments the furnace was maintained at the desired temperature as determined by the fourteen-gage thermocouple with the hot junction touching the outside of the cracking tube at the middle of the furnace. It is believed that these temperatures are correct within 5° C. They represent, however, the highest temperature to which the gas was exposed in passing through the cracking tube and not necessarily the temperature which was attained by the gas.

The exit end of the cracking tube was connected to the tube, *U*, which was air-cooled. This tube trapped most of the water and some of the tars when present. The gas was then led through a tube, *T*, one leg of which was submerged in water to a depth of about 2 mm. This served to maintain the pressure in the reaction tube constant as some of the cracked gases were allowed to bubble out continuously during an experiment. The other leg of *T* was connected to the sampling bottle.

Since it was desirable to take a large sample, the sampling arrangement shown in Figure 1 was used. It consisted of an inverted 2.5-liter acid bottle supported on a ring stand with connections as follows: A gas delivery tube extended through the stopper to the top of the inverted bottle and was bent to a U on the outside. This U-portion of the tube was made into a mercury stopcock by sealing an outlet at the bottom. It connected to a piece of rubber tubing partly filled with mercury. One leg of another U-tube passed through a second hole in the stopper and served as the inlet and outlet for the neutral saturated salt solution used to displace the gas. This tube for the liquid could be moved in and out through the stopper. To form a seal the stopper was covered with mercury to a depth of about 2 cm. and the tube for the liquid was terminated just above the mercury surface.

In collecting a sample, the bottle was filled with the salt solution which was also allowed to fill the gas inlet tube. The gas sample was admitted until the solution was displaced down to the mercury. The liquid outlet tube was next lowered until the U-portion was filled with mercury, and the mercury stopcock on the gas delivery tube was then closed by raising the leveling tube. The gas was thus sealed completely with mercury. It was exposed to the unagitated salt solution for only the comparatively short periods of taking and withdrawing a sample. Partial analyses of city gas sampled in these bottles and withdrawn for analysis by suction showed no measurable change in composition over a period of a week.

The products were separated into suitable fractions by means of a Podbielniak low-temperature distillation column, and the fractions further analyzed with the Shepherd apparatus. The methods used have been described in a separate communication (*6*).

Discussion of Results

The results of the experiments are shown in Table I and Figure 2. The data have been calculated on the basis of hydrocarbon products alone as well as on the basis of the total exit gas. For all the experiments at a given temperature the flow of the entering gaseous mixture was regulated so that the same volume of mixture, calculated to that temperature, passed through the cracking apparatus in unit time. In other words, although it is impossible to calculate what the contact time was, it is known that the contact time at any

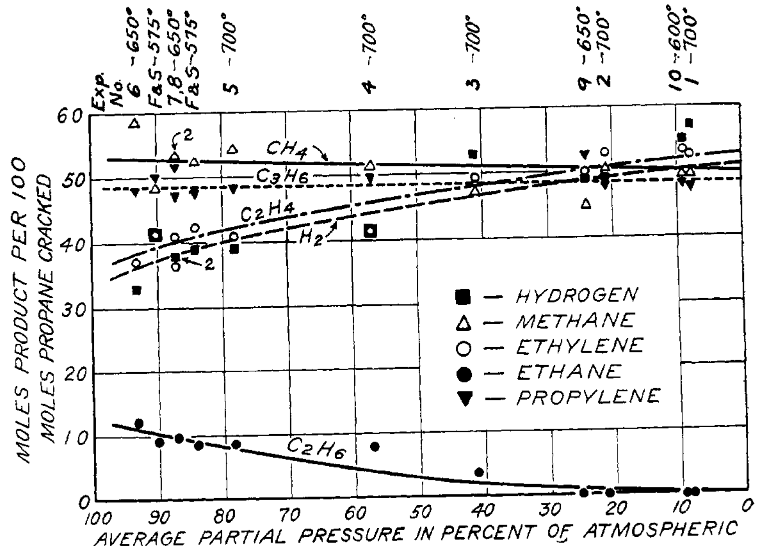


FIGURE 2. EFFECT OF PRESSURE ON PRODUCTS FROM PYROLYSIS OF PROPANE

TABLE I. EXPERIMENTAL DATA

Expt.	1		2		3		4		5		6		7		8		9		10	
Temp., ° C.	700		700		700		700		700		650		650		650		650		600	
Partial pressure propane, mm. Hg	68.8		188.6		377.2		535.2		749.0		751.0		749.0		751.0		187.8		69.0	
Partial pressure water, mm. Hg	687.7		565.8		377.2		229.5		0.0		0.0		0.0		0.0		563.4		691.0	
Av. partial pressure propane during pyrolysis, % of atm.	8.1		21.3		41.1		57.1		78.0		93.2		86.9		86.9		23.8		8.9	
Flow of mixture, at cracking temp., cc./sec.	30.8		30.6		30.6		30.6		30.6		30.5		13.5		13.7		30.7		13.8	
% cracking on total product basis	20.2		24.4		24.9		24.0		25.6		7.6		14.8		14.7		7.6		3.9	
% cracking on olefins in product	19.5		24.5		24.0		21.8		22.6		6.4		13.1		12.9		7.7		3.9	
Analysis	% on products	% on total	% on products	% on total	% on products	% on total	% on products	% on total	% on products	% on total	% on products	% on total	% on products	% on total	% on products	% on total	% on products	% on total	% on products	% on total
CO	0.8	0.3	0.5	0.2	0.5	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO_2	0.7	0.3	0.2	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.1	0.7	0.1
H_2	29.1	10.2	24.8	9.8	26.7	10.8	21.5	8.1	20.3	8.1	17.4	2.3	20.2	5.0	19.5	4.8	26.1	3.7	27.9	2.2
CH_4	22.9	8.0	24.8	9.8	22.9	9.2	26.8	10.1	28.5	11.3	31.3	4.2	28.2	7.0	28.5	7.0	22.1	3.2	23.4	1.8
C_2H_4	24.5	8.6	26.2	10.4	24.1	9.7	21.7	8.2	21.7	8.6	19.7	2.6	19.3	4.8	21.5	5.3	25.0	3.5	25.4	2.0
C_2H_6	0.0	0.0	0.0	0.0	1.7	0.7	4.2	1.6	4.5	1.8	6.2	0.8	5.0	1.2	6.0	1.5	0.0	0.0	0.0	0.0
C_3H_6	22.0	7.7	23.5	9.3	24.0	9.7	25.8	9.7	25.0	9.8	25.4	3.4	27.3	6.8	24.5	6.1	26.0	3.7	22.6	1.8
C_3H_8	..	64.9	..	60.4	..	59.6	..	62.3	..	60.4	..	86.7	..	75.2	..	75.3	..	85.8	..	92.1

given temperature was constant even though the partial pressures were varied. The products at any given experimental temperature of cracking include the products obtained at that temperature as well as the products of the decomposition reactions that occurred at lower temperatures while the gas was being heated up to the temperature reported and while cooling.

An attempt was made to determine the effective heated volume of the cracking tube, from which the time of contact for a given temperature would be calculated. In this attempt nitrous oxide, whose dissociation rate equation is known with a fair degree of accuracy, was utilized. It was found, however, that at the temperatures used for the cracking the rates of flow of nitrous oxide which were necessary to obtain a constant value for the heated volume were far below those used in the experiments with propane. The active heated volume at low rates of flow determined by the dissociation of nitrous oxide approximated those calculated for the uniformly heated portion of the tube as shown by the thermocouple exploration. Since, however, the rates of flow utilized in the cracking experiments were so much greater, no figures for a calculated time of contact are given, since it is felt that they might be misleading.

The partial pressures of propane shown in Table I were calculated not as the arithmetical average of the inlet and outlet pressures, but rather as the partial pressures that would exist at half the decomposition. There is a slight error in this calculated partial pressure caused by the fact that the decomposition reactions are not entirely monomolecular. It is, however, more accurate than the partial pressure calculated as the arithmetical mean.

The percentage decomposition of propane has been calculated on the basis of total unsaturated hydrocarbons alone as well as the decomposition actually found by the complete analysis. It is obvious that rate constants calculated from these two values would differ at partial pressures much above 40 per cent of an atmosphere.

In the data shown on the curves steam has been considered an inert gas. This is not strictly true. In the experiments at 700° C. determinable traces of carbon monoxide and carbon dioxide, which evidently resulted from a steam-hydrocarbon reaction, were obtained (*15*). The values used for the curves have been corrected for the products of these reactions. At 650° C. and lower temperatures there was no evidence of gaseous products of these reactions. Also at the temperatures reported and others at 800° and 900° C., the fuchsin test for aldehydes applied to the condensate from the exit gases gave positive results, indicating that there was some reaction between water and propane or the decomposition products. The extent of these reactions was evidently small, and it is believed that no serious error will be introduced if they are neglected.

Because of the low partial pressures of the products in most of the experiments, it is believed that errors caused by polymerizations have been reduced to a minimum. In regard to errors caused by secondary decompositions, the magnitude of these may be approximately estimated by taking into account the average time of contact compared with that for the less thermally stable propane. It is probable that errors from this source are small.

Interpretation of Results

Figure 2 shows that changes in pressure do affect the products formed by the pyrolysis of propane. It is apparent either that there is a stoichiometric relation between ethane and hydrogen plus ethylene, or, since there are only two remaining products other than ethane, that the ethane, methane, and propylene must be connected. For either case the behavior with variable pressure indicates a bimolecular reaction, such as:

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6$$

or

$$2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4$$

There is also the possibility that an intermediate reaction may account for this bimolecular behavior.

Frey (*3*) has recently reviewed the literature on the pyrolysis of hydrocarbons and the hypotheses relating to the mechanisms proposed to account for the reactions observed. The important mechanisms considered are those sponsored by Rice (*12*), Burk (*1*), and Kassel (*5*).

Of these, only the chain mechanism of Rice accounts for the formation of ethane. The results that should be obtained from the primary dissociation of propane, calculated according to this hypothesis, are as follows:

Temp., ° C.	% Decomposed	H_2	CH_4	C_2H_4	C_3H_6
550	5-10	20.4	29.6	29.6	20.4
600	5-10	20.0	30.0	30.0	20.0
650	5-10	19.5	30.5	30.5	19.5

The hydrogen content is equal to the propylene and that of methane equal to ethylene. According to Rice there should also be small quantities of ethane resulting from the reaction:

$$CH_3CH_2^- + CH_3CH_2CH_3 \longrightarrow C_2H_6 + \text{propyl or isopropyl radical}$$

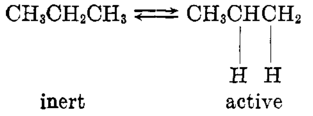
He states, however, that it is not possible to calculate the relative probabilities of the preceding reaction and of the following,

$$CH_3CH_2^- \longrightarrow CH_2CH_2 + H^-$$

but says the prediction can be made that dilution with an inert gas will diminish the bimolecular formation of ethane and leave the unimolecular decomposition unaffected. This prediction that the ethane content of the products should decrease with dilution has been verified.

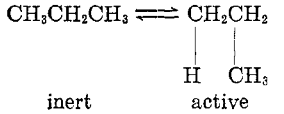
However, at no dilution are the relative quantities of the other products predicted by Rice substantiated by the results of the present work. Where Rice shows that propylene and hydrogen should be present in equal amounts and that the ethylene content should equal the methane, it was found that the methane content equals the propylene and the hydrogen is equal to the ethylene. With a decrease in partial pressure and the accompanying falling off of the ethane content as predicted, there should be some change in the relative quantities of the products other than ethane, but it is believed that there is no combination of equations in the Rice mechanism that will account for the relative quantities of products found in the present experiments.

The use of alkyl radicals, alkylidene radicals, semi-ionization processes, and rearrangements to express the mechanism of hydrocarbon decompositions according to contemporary hypotheses recalls the theoretical speculations of Nef (*7*, *8*). He considered that organic compounds exist in two states, which he called "active" and "inert," and that, although the relative number of active molecules is small, the two exist in a state of dynamic equilibrium. If it is further stipulated that the active valences must be on adjacent carbon atoms, we may write for propane:



$$CH_3CH_2CH_3 \rightleftharpoons CH_3\underset{|\atop H}{CH}\underset{|\atop H}{CH_2}$$

and



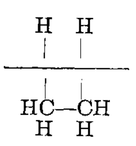
$$CH_3CH_2CH_3 \rightleftharpoons \underset{|\atop H}{CH_2}\underset{|\atop CH_3}{CH_2}$$

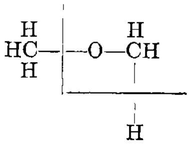
Nef also said that these active molecules may be considered in sort of a state of ionization, or dissociation, although not necessarily in the same category with the ionization of electrolytes.

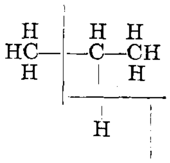
This is in keeping with the observation of Kassel (*5*) that a large number of the known unimolecular reactions may be considered to be of the type:

$$ABC \longrightarrow B + AC$$

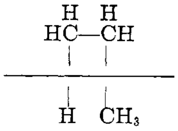
where A, B, and C represent suitably chosen radicals or atoms. He illustrates this statement by the following diagrams:


ethane


dimethyl ether


propane

The diagram for propane might also be written:

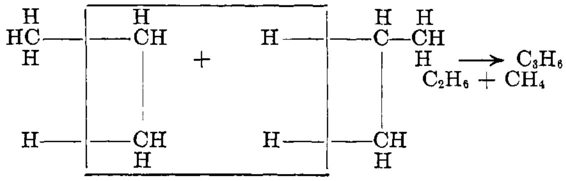


In applying the theoretical deductions of Nef from the behavior of other organic compounds to the thermal decomposition of propane, we may first assume as probable that an increase in temperature will displace the equilibrium toward the formation of more active molecules. It may also be assumed that in more of the active molecules the dissociation will proceed farther until the equilibrium is disturbed by the closing of the bonds on the alkylidene residue and union of the two other radicals from the dissociation of the molecule.

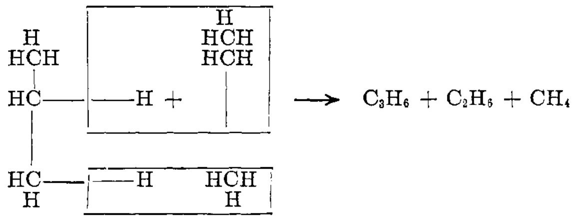
The unimolecular dissociation of propane, which predominates at low partial pressures, is explained by all the mechanisms suggested. However, there is evidence also of a bimolecular reaction which can be explained on the basis of Nef's hypothesis but is difficult to explain by other suggested mechanisms. If we assume that Nef's active molecules are present in sufficient concentration at the decomposition temperatures, they can react to produce the products in the stoichiometrical quantities found in the present experiments as follows:


$\longrightarrow C_3H_6 + H_2$ (1)


$\longrightarrow C_2H_4 + CH_4$ (2)


$\longrightarrow C_3H_6 + C_2H_6 + CH_4$ (3)

The bimolecular reaction may take place also as follows:


$\longrightarrow C_3H_6 + C_2H_6 + CH_4$

This mechanism requires the breaking of one less carbon-hydrogen bond than reaction 3 as shown, and the activation energy would be less for the breaking of three bonds than that required for four. However, a dissociation different from the monomolecular ruptures of reactions 1 and 2 is necessary, and it is assumed in the suggested mechanism of the writers that the bimolecular reaction takes place upon activation sufficient to produce the dissociations of these two monomolecular reactions. In other words, some of the residues of the monomolecular dissociations exist long enough to react as 3.

In any case, the reactions that represent the behavior of propane on pyrolysis may be written:

$$\begin{aligned} C_3H_8 &\longrightarrow C_3H_6 + H_2 \\ C_3H_8 &\longrightarrow C_2H_4 + CH_4 \\ 2C_3H_8 &\longrightarrow C_3H_6 + C_2H_6 + CH_4 \end{aligned}$$

As has already been indicated, it was suggested by Frey and Smith (*4*) that these same equations might account for the results they obtained for the pyrolysis of propane at approximately atmospheric pressure as shown in Figure 2. The present results at different temperatures and pressures confirm this suggestion and show that these equations can be explained by the mechanism of a hypothesis which most workers in the field have overlooked.

Frey and Smith likewise thought that it was improbable for ethylene and hydrogen to react to form ethane at the concentrations existing under the cracking conditions and, in support of their view, used the von Wartenberg equation (*14*) to estimate the equilibrium ratios of these gases. Unless the temperature and the partial pressures of the gases are known quite accurately, this equation cannot be applied with any degree of precision. The hydrogenation reaction is known to proceed much faster than the dehydrogenation reaction and the tendency, therefore, would be in this direction. However, at low percentages of decomposition with correspondingly low partial pressures of ethylene and hydrogen, there should be less ethane formed than with greater degrees of decomposition. This condition does not agree with any of the data published or with the present results, as shown by comparison of the results of experiments 7 and 8 with those of experiments 1 and 2. On the other hand, the ethane content is found to be proportional to the partial pressure of propane.

Calculations based on the free energy equations for the hydrocarbons involved which are given by Parks and Huffman (*9*) show that at 900° K. (627° C.), for instance, the bimolecular reaction, $2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4$, is not only thermodynamically possible but probable as well because at this temperature ΔF, 627° C. = −11,830 calories.

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Removal of Mercaptans from Naphtha by Caustic

The scrubbing of naphtha to remove mercaptans by means of caustic soda solutions finds wide application in the petroleum industry. A method of applying the available data on mercaptans to the design and testing of countercurrent scrubbing systems has been developed. It is believed that this method will also be of general interest as a practical application of the mathematical analyses recently published on this subject.

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THE presence of mercaptans in light petroleum distillates is undesirable because of their disagreeable odor and corrosive nature. Gasoline, solvents, and kerosene are acceptable when sweet according to the doctor test. In order to meet this condition, the mercaptan sulfur content of a distillate must not exceed about 0.001 weight per cent of mercaptan sulfur (*6*).

The use of caustic soda is an effective means of accomplishing reduction in the mercaptan content of naphthas. Because of their weakly acidic nature, mercaptans can be only partially removed by direct caustic washing, and such washing must usually be followed by a sweetening process to remove final traces. It is the purpose of this paper to present data and methods of calculation in typical refinery applications.

Chemistry of Caustic Scrubbing

The two-phase system of naphtha and aqueous caustic solution usually will contain mercaptan in three forms: free (HSR) dissolved in the oil and in the caustic layer (NaSR), and (SR^-) ions (mainly the latter).