$30\,^\circ$ C., upon the performance of process 7A are shown in Table XI, and a comparison is also made with a combination of process 4B producing syngenite, and 4A using this syngenite to yield potassium sulfate as the only final product.

The use of a two-stage crystallization reduces the loss of potassium sulfate in the syngenite mother liquor. This decreased loss is due to the fact that almost all of the magnesium sulfate appears in the waste liquors after the syngenite formation, and the concentration of potassium sulfate in this solution is almost independent of the concentration of magnesium sulfate. Therefore, for a given amount of magnesium sulfate in process there will be less end solution the higher the concentration of magnesium sulfate and, hence, less potassium sulfate discarded with this solution. The effects of variations in the procedure are shown because it is difficult to predict the most economical operating conditions which might prevail at the treating plant. Future variations in the markets for schönite, syngenite, or potassium sulfate may make it desirable to alter the method of treatment to meet these demands.

The modification of Bureau of Mines process 4B presented here as process 7A offers several advantages over the former method of treatment:

1. As indicated in Table XI, the evaporation necessary in the earlier method is eliminated if part of the potassium sulfate is to be marketed as syngenite, or greatly reduced if the product is to be potassium sulfate alone. Even with no evaporation, as high as 67 per cent of the total potassium sulfate can be pro-duced in the form of potassium sulfate, a high-grade product for which there is a well-established market (6).

2. An additional product, dehydrated schönite or kali-magnesia, is available if desired.

3. The hot extraction of polyhalite may be conducted most advantageously at temperatures below the boiling points of the solutions used, thus not only effecting heat economies but also decreasing the difficulties of material handling inherent in the use of boiling solutions.

4. A procedure for extracting comparatively coarse poly-halite has been devised which may eliminate the necessity for filtering large quantities of hot solutions and allow the use of settling and decantation or of classification in the separation of the solid residue from the hot extract liquors.

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Bromination of Saturated Aliphatic Hydrocarbon Gases

W. J. PERELIS, Box 323, Berkeley, Calif.

'N ENDEAVORING to utilize the constituents of natural gas for the manufacture of alcohols and other chemical compounds, the writer considered the halogenation of the gaseous aliphatic hydrocarbons as a preliminary step.

Scientific chemical literature did not give sufficient information on this point. Patent literature recites methods by which mixtures of halogenated products can be obtained. Some of the patents claim the production of pure monohalides (5, 6, 9). Egloff, Schaad, and Lowry (3) described the situation as follows: "Considerable difficulties are encountered in halogenating hydrocarbons * * * chief among these are * * * the production of undesired polysubstitution products where monosubstitution is desired." Frohlich and Wiezewich (4) state, "The main objection seems to be the difficulty of limiting the reaction to the introduction of only one chlorine atom per molecule of hydrocarbon." Bedford (1) explains why pure monohalides are not produced by stating that the chlorine has more affinity towards chloromethanes than towards methane itself.

However, one record claimed that a lower halogen concentration produces a larger proportionate amount of the lower halogenated compounds (7). From this it is assumed that a sufficiently low halogen concentration could lead to pure

monohalides; also, that the failure to produce the desired monohalogenated products was partly caused by not working with an unchanging halogen concentration.

At first, the method indicated by Schroeter (9) was used, but it was found impracticable for large-scale operation. The method worked out is as follows:

Dry the bromine and the hydrocarbon gas. Bubble the dried gas through a layer of dried liquid bromine. Use a sufficiently high bromine layer to produce a saturated bromine solution in the gas. Vary the temperature of the gas and the bromine ac-cording to the products or product desired.

By varying the temperatures, any bromine concentration can be produced; to each bromine concentration correspond certain products. For pure monohalides, therefore, the proper bromine concentration must be used.

Commercial products were used for all the experiments, and the following compounds were isolated: methyl bromide, methylene bromide, ethyl bromide, ethylene bromide, ethylidene bromide, N-propyl bromide, sec-propyl bromide, Nbutyl bromide, sec-butyl bromide.

Table IA shows that a bromine concentration of 6.6 per cent will produce pure butyl bromide; Table IB, bromine concentration of 5.6 per cent gives propyl bromide.

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In Table IC, group 2 shows that an increase in the bromine layer, with a temperature of 22° to 23° C., does not appreciably alter results because the lowest level used was high enough to produce a saturated solution of bromine in the gas. The bromine concentration varied little in all four cases, and the halide composition was much the same. Group 3 shows that a higher bromine concentration reduces the yield of monohalides.

Table I, C and D, gives some instances of high percentage

yields of ethyl and methyl bromides.

Butane and propane brominations were carried on without drying the reactants. When brominating ethane, superior results could be obtained by the use of dried materials (Table IC, group 2).

Figure 1 shows the apparatus used. Approximately 1.5 liters of dried gas per hour were used, bubbled through a layer of dried liquid bromine. The gas-bromine vapor produced was heated in the presence of an iron powder catalyst and the products separated after cooling. For large-scale operations the bromine can be recovered by the use of chlorine, air oxidation, or electrolysis.

Conclusions

(1) A sufficiently low halogen concentration in a mixture of an aliphatic saturated hydrocarbon gas and bromine vapor leads, when heated in the presence of an iron catalyst, to the



FIGURE 1. BROMINATION APPARATUS

formation of pure monohalides.

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(2) Increased halogen concentration leads to the formation of a mixture of halogen substitution products.

(3) With increased halogen concentration, an increased proportion of highly halogenated products are formed.

(4) A method is given for continuous production of a mixture of saturated aliphatic hvdrocarbon gas and bromine vapor of unchanging composition, suitable for large-scale operation.

(5) Up to a certain point of bromine con-

centration, the affinity of bromine is greater toward hydrocarbons than toward brominated hydrocarbons; otherwise no pure monohalides would be formed.

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TABLE I. BROMINATION OF HYDROCARBONS

	BROWINE	BEACTION	Moxo-		CONVERSION	BROMINE	BROMINE
Run	LAYER	TEMP.	BROMIDES	DIBROMIDES	PASSAGE	Concn.	TEMP.
	Mm	° C.	Mole %	Mole %	%	9%	° C.
			A. BROMINATIO	N OF BUTANE	•		
1	8.5-9.5	290	93.3	6.7	7.4	7.28	23
$\overline{2}$	8.5	290	95.23	4.77			23
3	9.0	295	96.19	3.81	7.6	7.30	23
4	9.0 8 5.0 K	290	90.0	4.7	8.U 7.9	7.7	23
6	8.5-9.5	295	100.0	0.0	7.17	6.6	23
-			B. BROMINATION	OF PROPANE		0,0	
14	9.0	315	95.5	4.5			23
2	8.5-9.0	325	94.88	5.12	4.4	4.55	23
3	8.5-9.0	320 - 325	93.7	6.3	3.78	3.4	23
4	8.5-9.0	325	100.0	0.00	5.94	5.6	23
2	8.5- 9.0	345	97.6	2.4	8.7	8.2	23
0 7	9.5	345 345	95.00	0.40 2.57	9 73	9.43	23
•	0.0	010	C. BROMINATION	VOF ETHANE	0.10	5.07	20
			Group	10			
0	9.5	350	81.2	18.8			23
0'	8.5-9.5	350	88.3	11.7	10.0	10.0	22
0″	8.5	350	88.89	11,11	6.89	7.11	23
	0 5 10 5	850	Group	20			
1	9.5-10.5	350	92.94	7.06	14.4	10.1	23
2	16.5	350	94.00	0.12 8 3	14.7	13.4	23
4	22.5	350	92.3	7.7	15.03	14.0	20
		••••	Group	3d	20100	11.0	
5	22	350	89.1	10.9	21.2	19.06	30
6	22	350	85.59	14.41	23,2	21.02	35
7	22	350	84.5	15.5	23.61	21.40	40
		070	D. BROMINATION	OF METHANE¢			
1	21	370	59.6	40.4 .	17.28	19.53	35
3	19	375	00.0 70.2	44.4 20.9	$\frac{17.17}{17.9}$	19.8	30
4	19	370	96.15	3.85	15.02	13.5	22
^a In runs 1 to	3 no solid carbon dioxi	de cooling was used;	in runs 4 to 7	c Ethane and brom	ine dried; bromine	at room temperat	ure.
lid <u>ca</u> rbon dio	xide cooling was used.	-		d Ethane and brom	ine dried; bromine	heated.	
Ethane and	i bromine not dried.			 Methane and bro 	mine dried.		