

Nov. 7, 1950

A. P. LIEN ET AL
XYLENES SEPARATION

2,528,892

Filed Aug. 25, 1948

3 Sheets-Sheet 1

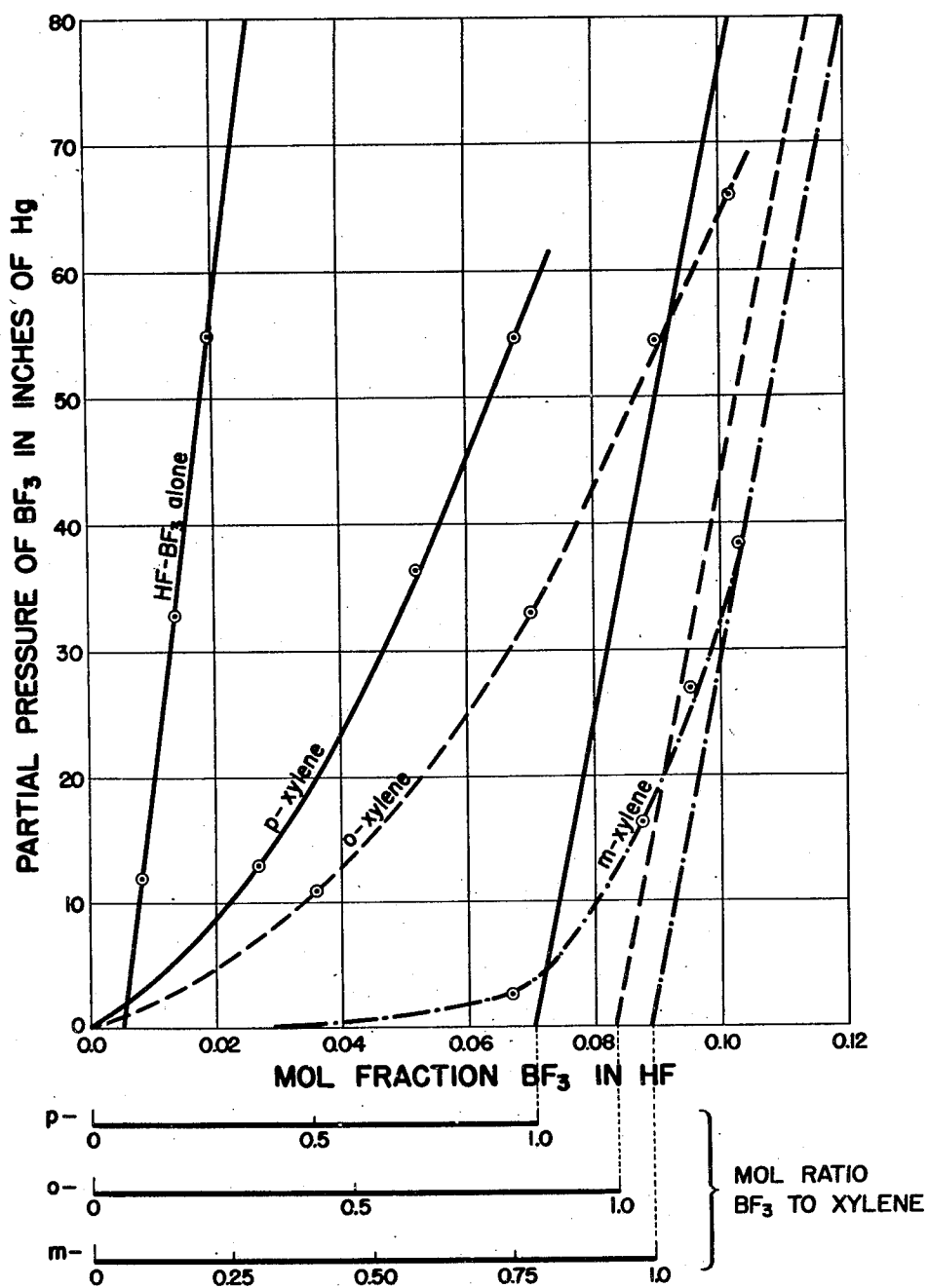


FIG. 1.

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3 Sheets-Sheet 2

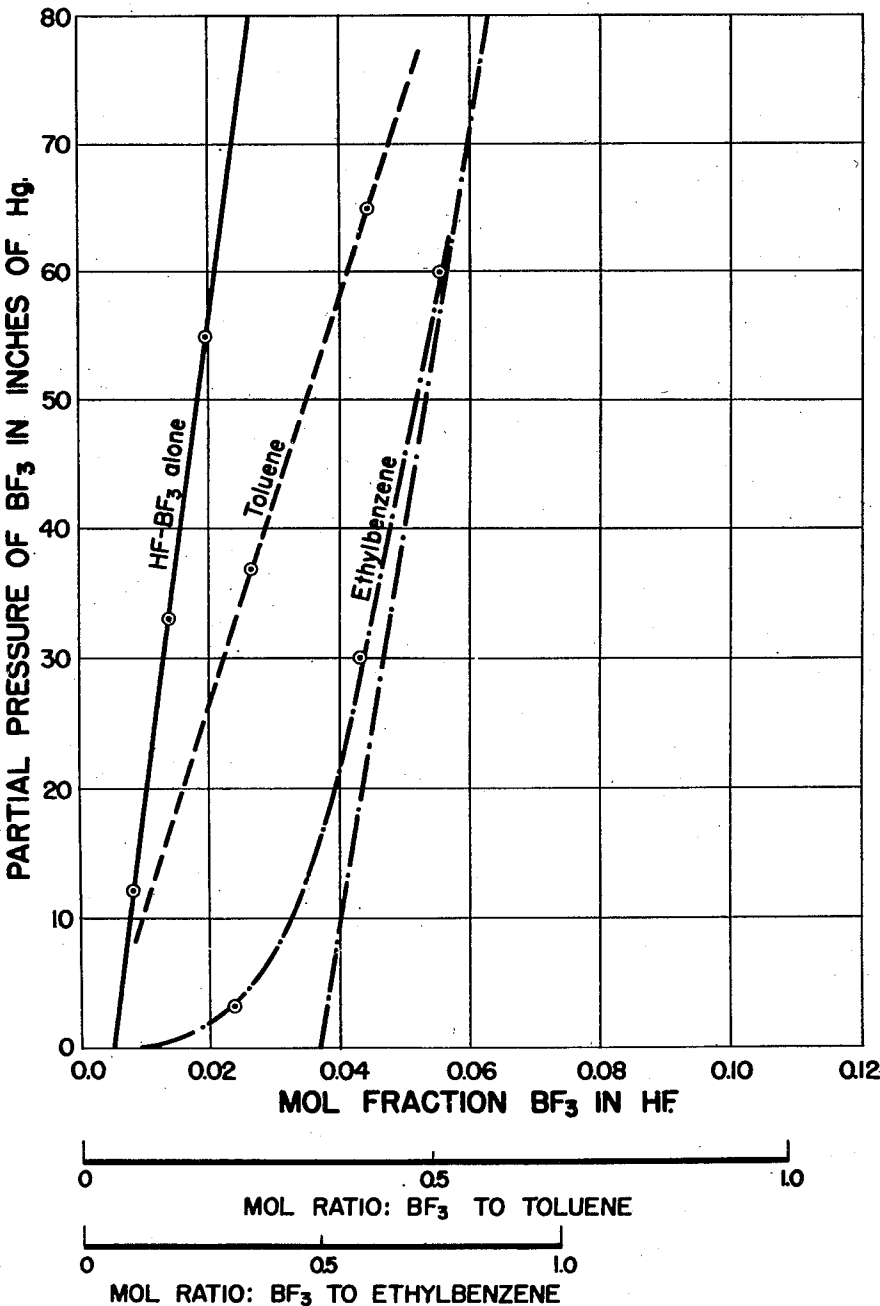


FIG. 2.

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3 Sheets-Sheet 3

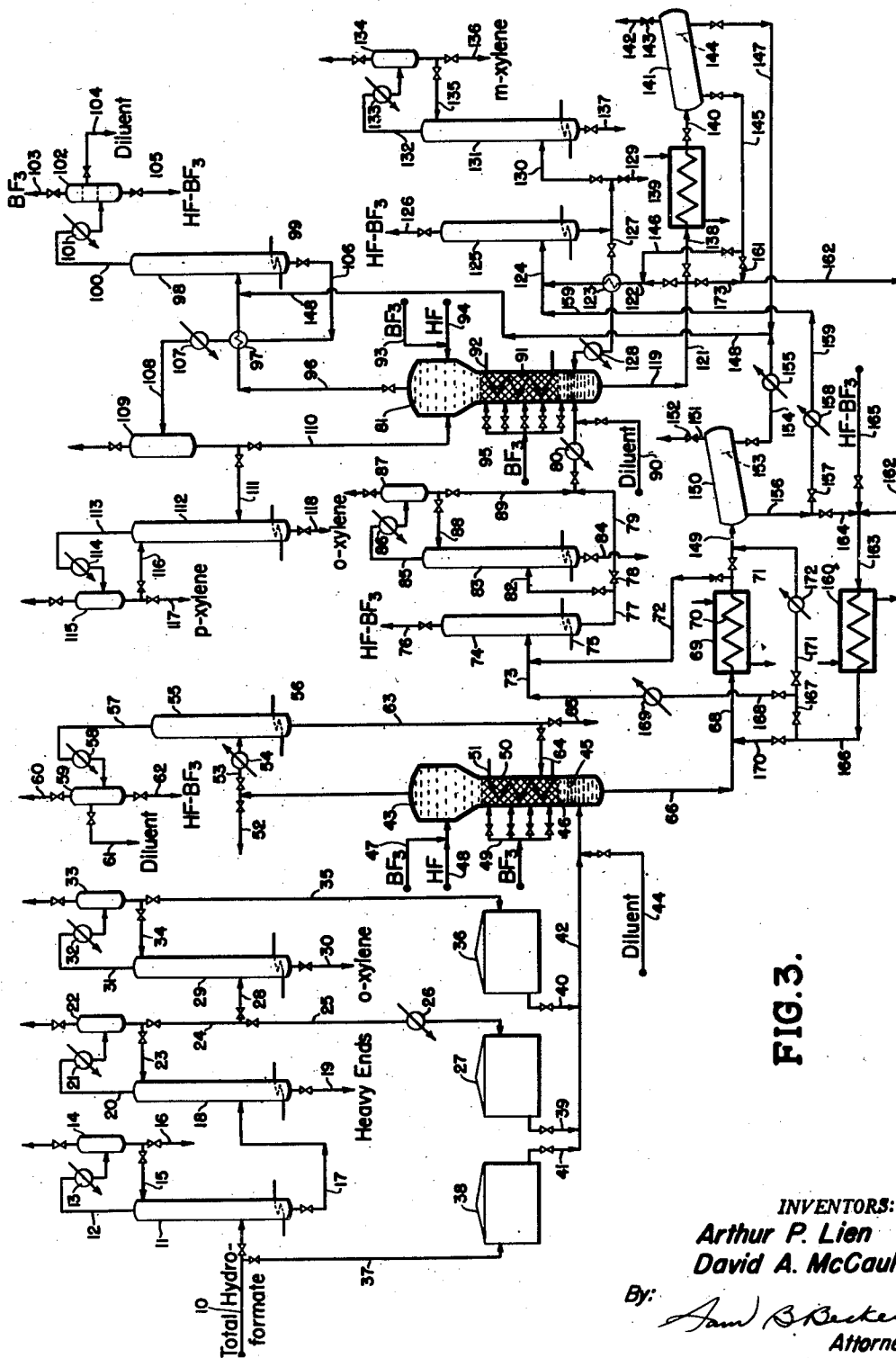


FIG. 3.

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UNITED STATES PATENT OFFICE

2,528,892

XYLENES SEPARATION

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Application August 25, 1948, Serial No. 46,136

8 Claims. (Cl. 260-674)

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This invention relates to a process for the selective separation or concentration and recovery of certain dialkylbenzenes from their mixtures with other dialkylbenzenes, which mixtures may also contain monoalkyl benzenes, benzene and saturated hydrocarbons. In one specific form, this invention relates to a process for the selective separation or concentration and recovery of individual xylene isomers from narrow boiling range aromatic hydrocarbon fractions containing the same. This invention relates more particularly to a process for the selective separation or concentration of meta-xylene from narrow boiling range aromatic hydrocarbon fractions containing meta-xylene, para-xylene, ethylbenzene and saturated hydrocarbons boiling in the boiling range of the xylene fraction and normally associated with said xylenes as produced by hydrocarbon conversion processes; the aromatic hydrocarbon fractions may also contain ortho-xylene.

In accordance with this invention, we have observed that by the joint employment of liquid HF and BF₃ as a selective reaction solvent under appropriately selected operating conditions, it is possible to achieve the selective extraction of certain meta-dialkylbenzenes from other dialkylbenzenes and less-alkylated benzene hydrocarbons.

We have also made the surprising observation that ethylbenzene, which is usually associated with xylenes as produced in hydrocarbon conversion processes, undergoes disproportionation with surprising ease in the presence of liquid HF and BF₃ to produce chiefly benzene and diethylbenzenes and, in the presence of xylenes, ethylxylenes. The disproportionation of ethylbenzene is of immense value in simplifying its separation from xylenes and makes it possible thereafter to separate selectively or to concentrate individual xylene isomers from each other by means of liquid HF and BF₃, without interference by ethylbenzene.

It has been appreciated heretofore that liquid HF and BF₃ function jointly as a solvent or "solvent-catalyst" for aromatic hydrocarbons generally, presumably by the formation of complex compounds wherein HF, BF₃ and an aromatic hydrocarbon are joined and dissolved in excess HF and BF₃ (U. S. Patents 2,343,744; 2,343,841 and 2,405,995, for example). However, it was not heretofore appreciated that liquid HF in combination with BF₃ could be employed in such a manner as to exert selective solvent characteristics for certain aromatic hydrocarbons in

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admixture with other aromatic hydrocarbons. It was very surprising therefore, to observe that liquid HF and BF₃ could be employed selectively to concentrate individual aromatic hydrocarbon isomers, e. g., individual xylene isomers, from mixtures thereof. Moreover, although it was postulated that HF-BF₃-aromatic hydrocarbon complexes might exist, these were not heretofore actually isolated or characterized, nor were any comparisons extant of the complex compounds formed by various aromatic hydrocarbons with liquid HF and BF₃. Thus, the molecular composition of HF-BF₃-aromatic complexes had not heretofore been revealed nor has any publication been devoted to the relative stability of the various aromatic hydrocarbon complexes with liquid HF-BF₃. It appears to have been known with certainty only that if the postulated complexes of HF and BF₃ with aromatic hydrocarbons did exist, they all appeared to be uniformly and highly soluble in excess HF or HF-BF₃, so that HF and BF₃ appeared to offer no promise as a selective solvent for the extraction of one aromatic hydrocarbon from another.

We have made observations which lend weight to the postulations concerning aromatic hydrocarbon complexes with BF₃ and have studied the composition and properties, especially the relative stabilities of various such complexes. Surprising variations were observed in the stabilities of BF₃-isomeric xylene complexes which were unexpected because of the close chemical and physical similarities of the xylene isomers. We have also observed that the relative stabilities of aromatic hydrocarbon complexes containing BF₃ can be substantially correlated with the actual extractabilities of the individual aromatic hydrocarbons by liquid HF and BF₃.

Although benzene and toluene have been stated to form complexes with liquid HF and BF₃, we have observed that such complexes, if they are formed at all, are completely dissociated (i. e. they do not exist as such) at temperatures as low as 0° C.

We have also found that isomeric xylenes may be substantially completely extracted from mixtures containing the same and saturated hydrocarbons of close boiling range by contacting said mixtures with a molar excess of liquid hydrogen fluoride and with BF₃ in at least an equimolar ratio, based upon the aromatic hydrocarbon content of said mixture. As has been pointed out above benzene and toluene do not appear to form complexes with HF and BF₃, with the result that xylenes may be selectively ex-

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tracted from mixtures thereof with benzene and toluene (as well as saturated hydrocarbons) by the employment of liquid HF and BF₃ in an amount which is at least equimolar with respect to the xylenes present in said mixture.

Also, when a solution of xylenes in liquid HF and BF₃ is treated to withdraw sufficient BF₃ to reduce its concentration below 1 mol per mol of aromatic hydrocarbons contained in said solution, the solution can be readily separated into two layers by conventional means such as settling, centrifuging or the like. Analysis of the two resultant layers indicates that the xylene isomers are distributed in different proportions in the two layers, viz., the "raffinate" layer which is characterized by containing only small amounts of HF and BF₃ and which consists essentially of complex-free xylene isomers and the "extract" layer which consists of BF₃-HF-xylene isomers dissolved in excess liquid HF. The distribution of xylene isomers in the "raffinate" and "extract" layers is essentially the same as would be produced by initially contacting the xylenes with a molar excess of liquid HF and with BF₃ in an amount less than 1 mol per mol of xylenes. The withdrawal of BF₃ from the solution containing xylenes can be effected by various methods which will be pointed out in some detail hereinafter.

One object of our invention is to provide processes for the selective separation or concentration of individual xylene isomers from mixtures of xylene isomers. An additional object of our invention is to provide processes for the selective separation or concentration and recovery of meta-xylene from mixtures thereof with para-xylene or ortho-xylene or from mixtures containing all three isomeric xylenes. Yet another object of our invention is to provide a process for the separation of a mixture of xylenes or concentrates of individual xylene isomers from ethylbenzene.

A further object of our invention is to provide a process for the separation of xylenes from mixtures thereof with benzene and monoalkylbenzenes, particularly toluene and ethylbenzene. Still another object of our invention is to provide a process for the separation of a mixture of isomeric xylenes from associated, close boiling saturated hydrocarbons, following which individual xylene concentrates are produced by the process of this invention.

Another important object of our invention is to provide a practical process for the concentration of individual xylene isomers from xylene fractions such as are normally produced by hydrocarbon conversion operations or by the extraction of petroleum fractions. The above and other objects of our invention are achieved by the process whose details are set forth below.

Since the extraction processes involved in our invention appear to function through the formation of BF₃-HF-aromatic hydrocarbon complexes, detailed consideration will be given to the identities and properties, especially the relative stabilities of such complexes. In order to prepare and study the complexes in question, a BF₃ storage cylinder, a BF₃ metering flask and a reaction flask were valved to a manifold of copper tubing which was suitably attached to an evacuation pump. A pressure gage was also attached to the copper manifold line.

A weighed amount of HF and aromatic hydrocarbon (usually about 5 moles of HF and about 0.4 mol of alkylbenzene) were introduced into the reaction flask. The flask was then attached to

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a vacuum system, its contents frozen with liquid nitrogen, the whole system evacuated and the valve to the vacuum pump closed. Boron trifluoride was then passed into the system from the storage cylinder and allowed to fill the metering flask. The valve of the reaction flask was then opened and increments of BF₃ were condensed in the flask. The valve of the metering flask was then closed and the reaction flask allowed to warm to 0° C. in a water-ice bath. The flask was agitated at 5-minute intervals at this temperature until a constant pressure was reached; this usually required from one to two hours. After the pressure reading was taken, the process was repeated, i. e., the contents of the flask were again frozen down in liquid air and another increment of BF₃ was added and the pressure was read again when the system came to equilibrium.

The following data were obtained employing the above procedure at 0° C., on the liquid HF-BF₃-system (containing no hydrocarbons).

TABLE 1
BF₃-HF system

g. BF ₃ in liq. phase	g. HF	BF ₃ Mol Fraction	Partial Press. of BF ₃ (in. Hg)	Press. HF (in. Hg)
0	106	0	0	15
2.8	106	.0079	11.5	15
5.0	106	.0141	33	15
7.2	106	.0200	54.5	15

The above data are plotted in Figure 1. It will be noted that when the partial pressure of BF₃ is plotted against the mol fraction of BF₃ in solution in HF, a straight line results. This straight line intersects the abscissa at about a mol fraction of 0.005, which could be caused by the presence of about 0.25% water in the HF. Neglecting this small deviation it is seen that BF₃ in HF obeys Henry's law, which at 0° C. may be expressed as $P_{BF_3} = 3530N_{BF_3}$, where P_{BF_3} is the partial pressure of BF₃ in inches of mercury and N_{BF_3} is the mol fraction of BF₃ in solution in liquid HF.

These results show that the solubility of BF₃ in liquid HF is relatively low. At atmospheric pressure and at 0° C. about 3.5 g. of BF₃ will dissolve in 100 g. of HF. There is very little tendency for HF and BF₃ in a binary system to combine to form the often postulated compound HBF₄.

The following data were obtained in a study of the system BF₃-HF-meta-xylene at 0° C., employing 44 g. (0.415 mol) of meta-xylene and 93.5 g. (4.675 mols) of liquid HF in the reaction flask.

TABLE 2
BF₃-HF-meta-xylene system

Mols BF ₃ in Liq. Phase	Mol fraction BF ₃ in HF soln.	Total Press. (in. Hg)	Partial Press. of HF (in. Hg)	Partial Press. of BF ₃ (in. Hg)
0.0	0.0	14	14	0.0
0.155	0.0332	16.5	13.5	3
0.315	0.0674	15.5	13	2.5
0.404	0.0864	29.5	13	16.5
0.446	0.0954	39.5	12.5	27
0.489	0.1024	51	12.5	38.5

The partial pressure of BF₃ was plotted against the mol fraction of BF₃ in the HF as shown in Figure 1. A comparison of the partial pressure of BF₃ over the HF-BF₃-meta-xylene system with the HF-BF₃ system shows that the inclusion of meta-xylene has resulted in a tremendous reduction of the vapor pressure of BF₃, clearly indicating the formation of a BF₃-HF-meta-xylene

complex which has a relatively low vapor pressure compared to HF-BF₃. It will be noted that the P_{BF₃} curve approaches an asymptote which is almost parallel to the P_{BF₃} curve of the HF-BF₃ system. Extrapolating the asymptote to P_{BF₃}=0 indicates the composition of BF₃-HF-meta-xylene complex, which can be read off the scale indicating the mol ratio of BF₃-meta-xylene. It will thus be seen that the meta-xylene complex contains one mol of BF₃ per mol of meta-xylene. This complex of meta-xylene probably also contains one mol of HF and the complex is dissolved by the excess liquid HF which is present in the reaction flask. It appears that the following reaction takes place in the reaction flask:



The equilibrium constant for this reaction can be defined as follows:

$$K_{eq} = \frac{N_{\text{complex}}}{P_{\text{BF}_3} N_x N_{\text{HF}}}$$

where,

N_{complex}=mol fraction of the complex in the acid phase;

N_x=mol fraction of free xylene in the acid phase;

N_{HF}=mol fraction of HF;

P_{BF₃}=partial pressure of the BF₃ in inches of Hg.

From the standpoint of calculating equilibrium constants from the data, a more practical expression of the above equation is K_{eq}=mols HF

$$\frac{(N_{\text{TBFB}_3} - N_{\text{BF}_3}) / P_{\text{BF}_3} [\text{mols xylene-mols HF} (N_{\text{TBFB}_3} - N_{\text{BF}_3})] N_{\text{HF}}}{\text{wherein } N_{\text{TBFB}_3} \text{ is the total mol fraction of BF}_3 \text{ in the liquid phase, including both free BF}_3 \text{ and BF}_3 \text{ combined in the hydrocarbon complex. } N_{\text{TBFB}_3} \text{ can be determined from the } P_{\text{BF}_3} \text{ vs. BF}_3 \text{ mol fraction curve (Figure 1). } N_{\text{BF}_3} \text{ is determined from the Henry's law expression (supra). } N_{\text{HF}} \text{ can be approximated by subtracting } N_{\text{TBFB}_3} \text{ from one.}$$

A study of the vapor pressure of the system meta-xylene-BF₃-HF over the range of 0° C. to 25° C. showed that the following equation defines the variation in the magnitude of the equilibrium constant with temperature.

$$\log K_{eq} = \frac{642}{T} - 2.434$$

From this equation it is seen that, for the reaction BF₃ (gas) + meta-xylene (1) + HF (1) → BF₃·meta-xylene·HF (1), ΔH=(2.303 R) (642) = -2.9 K cal. This value of ΔH is approximately the same as the heat of condensation of BF₃.

The following data were obtained in a study of the system BF₃-HF-ortho-xylene at 0° C., employing 44 g. (0.415 mol) of ortho-xylene and 99.5 g. (4.975 mols) of liquid HF.

TABLE 3

BF₃-HF-ortho-xylene-system

Wt. BF ₃ added (g.)	Mols BF ₃ in Liq. Phase	Mol fraction BF ₃ in Liq.	Total Press. (in. of Hg)	Partial Press. of BF ₃ (in. of Hg)
0	0	0	14	0
12.5	.178	.0358	24.5	11
25.0	.346	.0696	46	33
33.3	.448	.0901	67.5	54.5
37.5	.506	.1017	78.5	66

The partial pressure of BF₃ was plotted against the mol fraction of BF₃ in the HF, as was done in the case of the meta-xylene complex (shown in Figure 1) and a curve was obtained which shows that ortho-xylene likewise formed a complex containing 1 mol of BF₃ per mol of ortho-xylene. However, a comparison of the partial pressure of BF₃ over the meta-xylene and ortho-xylene complexes shows that the ortho-xylene complex is much less stable than the meta-xylene as evidenced by the far greater P_{BF₃} over the ortho-xylene complex.

The following data were obtained in a study of the system BF₃-HF-para-xylene at 0° C. employing 41 g. (0.387 mol) of para-xylene and 109.5 g. (5.475 mols) of liquid HF.

TABLE 4

BF₃-HF-para-xylene

Wt. BF ₃ added (g.)	Mols BF ₃ in liq.	Mol fraction BF ₃ in liq.	Total Press. (inches of Hg)	Partial Press. of BF ₃ (in. Hg)
0	0	0	14	0
10.7	.147	.0269	26.5	13
21.4	.285	.0521	49.5	36.5
24.5	.374	.0680	68	55

A much longer time was required to reach equilibrium with the para-xylene than was necessary with the other xylenes, probably because the para-xylene was a solid at the temperature of measurement.

The results were plotted as before (Figure 1) and a curve was obtained which showed that the para-xylene also formed a complex with HF and BF₃ containing one mol of BF₃ per mol of para-xylene. However, this complex is less stable even than the ortho-xylene complex.

From the data supplied above the following equilibrium constants (at 0° C.) can be calculated:

	K _{eq}	Ratios
meta-xylene.....	0.83	20
ortho-xylene.....	0.084	2
para-xylene.....	0.044	1

The relative stabilities of the meta-, ortho- and para-xylene complexes are in the ratio of their equilibrium constants and are, therefore, 20:2:1.

The following data were obtained employing 43 g. (0.468 mol) of toluene and 86.5 g. (4.325 mols) of liquid HF.

TABLE 5

BF₃-HF-toluene system at 0° C.

Wt. BF ₃ added (g.)	Mols BF ₃ in liquid	Mol fraction BF ₃ in liq.	Total Press. (in. Hg)	Partial Press. of BF ₃ (in. of Hg)
9.9	.114	.0264	51	37
16.5	.189	.0437	79	65

When the mol fraction was plotted against the partial pressure of BF₃ (Figure 2) a straight line drawn through the points passed close to the origin and had a slope almost as steep as the line for HF-BF₃ system. This means that HF, BF₃, and toluene have very little, if any, tendency toward complex formation even under high BF₃ pressures. It follows, therefore, that liquid HF and BF₃ can be used as a solvent for the selective extraction of the xylenes from toluene.

It was expected that all monoalkylbenzenes would behave similarly to toluene; consequently, the results for ethylbenzene were surprising. They indicated that a stable complex was formed containing only one-half mol of BF_3 per mol of ethylbenzene.

The ethylbenzene employed in the ethylbenzene-HF- BF_3 study was derived by fractionation of technical ethylbenzene in a column packed with wire gauze equivalent to 20 theoretical plates, and a 500 cc. heart cut (7 to 70% on charge) was collected and employed. This fraction had the following properties: $n_D^{20}=1.4954$, B. P.=136° C. A portion of this material was used in the vapor pressure measurements, employing 44 g. (0.415 mol) and 114.5 g. (5.725 mols) of HF.

TABLE 6

Wt. BF_3 added (g.)	Total Press. at 0° C. (in. of Hg)	Mols BF_3 in liq.	Mol fraction BF_3 in liq.	Partial Press. of BF_3 (in. Hg)
9.4	17.5	0.135	.0236	3.5
18.8	44	0.252	.0440	30
25.0	74	0.318	.0556	60

¹ Pressure was 55" Hg at start. On shaking for 15 minutes at 0° C. it gradually fell to 17.5" Hg.

The mol fraction of BF_3 was plotted against its partial pressure (Figure 2). The plot showed that a complex was formed having the same order of stability as the BF_3 -HF-meta-xylene complex. However, the plot also showed that only 0.207 mol of BF_3 were required to form the complex, which is exactly $\frac{1}{2}$ the number of mols of ethylbenzene present. This suggests that ethylbenzene disproportionates according to the following equation:



and forms a diethylbenzene, which forms a complex with BF_3 and HF, and benzene which does not form a complex with BF_3 and HF.

A fractionation analysis of the hydrocarbon recovered from the experiment showed it to have the following composition:

	Vol. Per Cent	Mol Per Cent
Benzene.....	28	40
Ethylbenzene.....	5	5
Diethylbenzene.....	67	55

Evidently, under the conditions of the experiment, the ethylbenzene disproportionated almost quantitatively into equimolar amounts of benzene and diethylbenzene, and it was the latter which formed a monomolecular complex with the BF_3 and HF.

Suitable feed stocks for our selective extraction process are mixtures of xylenes. The boiling points and freezing points of the xylenes, and of ethylbenzene which boils within the same range, are

	B. P., °F.	F. P., °F.
ortho-xylene.....	291.95	-13.32
meta-xylene.....	282.38	-54.17
para-xylene.....	281.03	+55.87
ethylbenzene.....	277.14	-138.96

("Selected Values of Properties of Hydrocarbons"—Nat. Bur. Stds.—C461—Nov. 1947—p. 67).

From the above boiling point data it will be apparent that a mixture of meta- and para-

xylenes cannot be resolved by fractional distillation and this is essentially true also of a mixture of either meta- or para-xylene with ethylbenzene. Although ortho-xylene can be separated by superfractionation from the isomeric xylenes and ethylbenzene, such a process entails extremely expensive and large equipment which, because of the high reflux ratios which are necessary, has only a low throughput. Also, it is practically impossible to obtain an ortho-xylene concentrate containing more than about 70% ortho-xylene by superfractionation from xylene fractions containing saturated hydrocarbons boiling in the same range, due to the formation of azeotropes of overlapping boiling ranges of the various xylenes with the saturated hydrocarbons. Para-xylene has been separated from mixtures thereof with meta-xylene by fractional freezing, which is an expensive and laborious procedure compared with the process of the present invention. Fractional freezing or melting is severely handicapped, even disregarding economic considerations, by the fact that para- and meta-xylenes form a eutectic mixture containing about 88 weight percent meta- and 12 weight percent para-xylene (M. P., -73° F.) and para-xylene can not be selectively frozen from mixtures containing less than about 16% para-xylene (U. S. Patents, 1,940,065 and 2,398,526 and British Patent 585,076).

Aromatic hydrocarbon charging stocks suitable for employment as feed stocks in the process of this invention can be prepared by a variety of processes, probably the most important of which is the catalytic hydroforming process. For the preparation of xylene-rich products, a desirable charge to hydroforming is a light naphthenic naphtha rich in dimethylcyclohexanes (boiling range about 230 to 280 F.). In this process a petroleum naphtha, which may be a virgin or cracked naphtha or mixture of both, is converted to aromatic hydrocarbons by contact with a solid, porous dehydrogenation catalyst at a temperature in the range of about 850° F. to about 1050° F., preferably in the presence of hydrogen. Suitable catalysts are oxides of metals of groups 2 to 6 of the periodic system, particularly oxides of 6th group metals such as chromium and molybdenum, preferably supported by alumina or magnesia. Excellent catalysts can be prepared by depositing about 4 to about 10% of molybdenum oxide upon an activated alumina. Suitable space velocities for hydroforming fall within the range of about 0.2 to about 4 volumes of the liquid charge per hour per volume of catalyst space. About 0.5 to about 8 mols of hydrogen can be charged to the process with each mol of naphtha feed stock. Note also, G. Armistead, Jr., Oil & Gas J. 45, 17 (Aug. 31, 1946) pp. 85-7 and 100; L. R. Hill et al., Trans. Am. Inst. Chem. Eng. 42, 4 (Aug. 25, 1946) pp. 611-637.)

Other sources of xylenes and other aromatic hydrocarbon charging stocks for our selective solvent extraction process are catalytic cracking, catalytic dehydrogenation of naphthenes over dehydrogenation catalysts such as NiS-WS_2 or the like, thermal cracking at high temperatures, preferably in the presence of steam, for example as in the Forward process; the extraction or extractive distillation of virgin naphthas and kerosenes with selective solvents such as phenol, furfural, methanol, ethylene glycol, SO_2 and the like; the coking of coal, which yields a light aromatic oil from which it is conventional practice to produce nitration grade xylenes, etc.

We may also employ mixtures of isomeric xylenes obtained by the isomerization of xylenes with liquid HF-BF₃, various Friedel-Crafts type catalysts, clays and the like. The above-mentioned processes for the preparation of aromatic hydrocarbons suitable as charging stocks for our selective solvent extraction process are illustrative only, and it should be understood that our process is generally applicable to the selective extraction of meta-dialkylbenzenes from isomeric dialkylbenzenes regardless of the specific method by which the charging stock was prepared.

Suitable xylene mixtures which can be used as charging stocks in our process have been analyzed by A. D. Streiff and F. D. Rossini. These investigators have reported the results of analysis, by measurements of freezing points of appropriate mixtures, supplemented by analytical distillation, of the four individual C₈ alkylbenzenes (ethylbenzene, ortho-xylene, meta-xylene and para-xylene) occurring in the product from the following five different catalytic petroleum refining processes: (1) "Hydroforming," (2) "Two-pass Fixed Bed" catalytic cracking, (3) "Three-pass Fixed Bed" catalytic cracking, (4) "Low-temperature Fluid" catalytic cracking, and (5) "High-temperature Fluid" catalytic cracking. The data indicate that the relative amounts by volume of the four C₈ alkylbenzenes are not greatly different in the five different products, being, on the average, as follows: ethylbenzene, 12; ortho-xylene, 21; meta-xylene, 48; para-xylene 19%. These amounts correspond substantially to those called for in chemical thermodynamic equilibrium for the operating temperatures involved. The naphthenic plus paraffinic hydrocarbon content of the samples varied from about 7 to about 45 percent by volume. ("Alkylbenzenes in the

stood that this example is merely an illustrative embodiment carried out on a small scale through a single extraction stage.

Example

A batch extraction experiment was carried out in a 1570 cc. carbon steel autoclave fitted with a 1725 R. P. M. mechanical stirrer. A sample of a C-8 cut of hydroformer xylenes was introduced into the reactor along with liquid HF. Next, BF₃ was admitted from a small weighing cylinder and the mixture was stirred for one-half hour at 68-77° F. The initial reactor pressure was 350 p. s. i. g., but when stirring was started the pressure immediately fell to 0 p. s. i. g., showing that the BF₃ was absorbed. At the end of the stirring period the mixture was allowed to settle, and the two phases were separated. The HF and BF₃ were removed from the extract phase by vacuum distillation and the composition of the extract, as well as the composition of the raffinate and the feed were determined by fractionation followed by ultra-violet absorption analysis. The results of the experiment are shown in Table 7. The difference in composition between the raffinate and extract shows that meta-xylene was selectively extracted by the HF-BF₃.

TABLE 7

Batch extraction of hydroformer xylenes with HF-BF₃

Reactor charge

- Hydroformer xylenes 239 g. (2.25 mols)
BF₃ 93 g. (1.4 mols)
HF 354 g. (17.7 mols)

Results

- Total hydrocarbon recovery=94 wt. %.

	Wt. (g.)	Wt. Per Cent	Ultra-violet Absorption Analysis, Wt. Per Cent				
			Ortho-Xylene	Meta-Xylene	Para-Xylene	Ethylbenzene	Total
Feed.....	239	100	19.6	41.2	16.7	19.7	97.2
Raffinate.....	95.3	42.5	26.1	17.7	23.3	26.1	93.2
Extract.....	128.6	57.5	19.4	60.7	12.5	0.1	92.7

	Individual Hydrocarbon Balance, Wt. Per Cent			
	Ortho-Xylene	Meta-Xylene	Para-Xylene	Ethylbenzene
Feed.....	19.6	41.2	16.7	19.7
Raffinate plus extract.....	22.3	43.2	17.6	11.2
Balance.....	+2.7	+2.0	+0.3	-8.5

	Fractionation Analysis of Products, Volume Per Cent	
	Raffinate	Extract
Benzene.....	2	0
C-8 Aromatics.....	98	83
C-10 Aromatics.....	0	17
	100	100

C₈ Fraction from Five Different Catalytic Petroleum Refining Processes", J. Res. Nat. Bur. Standards 39 (Oct. 1947) pp. 303-308.)

The following example represents one practical application of the principles of this invention which were set forth above. It should be under-

- 70 From the data presented in Table 7 it will be noted that 57.5% of the feed, which is equivalent to 1.3 mols of xylenes, dissolved in the HF-BF₃ and that 93 g. or 1.4 mols of BF₃ were used, which within experimental error is equal to the mols of
75 xylenes present in the extract phase.

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The fact that a mol of BF_3 causes one mol of xylenes to pass into solution in liquid hydrogen fluoride presents a means of treating the extraction of xylenes as a fractional distillation problem, so that engineering calculations of the extraction process can be readily made.

The single stage separation (enrichment) factor, α , is

$$\alpha = \frac{1-N'}{N'} \bigg/ \frac{1-N}{N} = \frac{1-.177}{.177} \bigg/ \frac{1-.607}{.607} = 7.2$$

where N' and N are the mol fractions of meta-xylene in the raffinate and extract respectively. The α corresponds, in vapor-liquid distillation terminology, to the relative volatility. This is a very high separation factor and it can be calculated by the use of a McCabe-Thiele graphical analysis that a system of only four stages is needed to separate the hydroformer xylenes into an overhead product comprising 95% o- and p-xylenes and a bottoms product containing 95% m-xylene. The distribution of ortho- and para-xylenes obtained in the present extraction are consistent with α values of 0.69 and 0.47. The α ratios of meta-, ortho- and para-xylenes are, therefore, 15.3:1.47:1, which is considered to be in good agreement with their stability equilibria ratios of 20:2:1 (supra) as determined by vapor pressure measurements.

The individual hydrocarbon balance in Table 7 shows, within experimental error, that all three xylenes remained unchanged during the run; i. e., they neither isomerized nor disproportionated. However, there is a net disappearance of ethylbenzene and the results of the fractionation analyses of the products shows that the ethylbenzene tended to disproportionate to form benzene plus either diethylbenzenes or ethylxylenes. This disproportionation reaction simplifies immensely the xylene separation problem since ethylbenzene is thereby removed far from the boiling range of the xylenes. It will be noted that benzene was insoluble in the HF-BF_3 mixture and appeared in the raffinate phase, whereas the C_{10} aromatic hydrocarbon disproportionation product was extracted by the HF-BF_3 .

An illustrative flow diagram concerning the extraction processes of this invention is presented in Figure 3. The operation of the flow diagram will be described with reference specifically to the separation or concentration of a mixture of isomeric xylenes, although it will readily be understood that the equipment is adaptable for the separation or concentration of other dialkylbenzenes. We may charge, for example, an aromatic fraction obtained by catalytic hydroforming of naphthas or the like (hydroformate). The aromatic fraction from hydroforming may include not only the xylenes and ethylbenzene but also benzene, toluene and associated saturated hydrocarbons, i. e., paraffinic and cycloparaffinic hydrocarbons boiling in the same range. The aromatic fraction may also contain small proportions, e. g., up to about 10 percent by volume, of C_9 aromatics, predominantly isopropylbenzene. The boiling range of the aromatic fraction from hydroforming may be about 170 to about 325° F.

The aromatic fraction from hydroforming is passed through valved line 10 into a fractionator 11 wherein light ends boiling between about 170° F. and about 270° F., principally benzene, toluene and saturated hydrocarbons are removed overhead through line 12, thence to condenser 13 and accumulator drum 14, from which a portion may

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be recycled to the upper portion of tower 11 through valved line 15 and the remainder removed from the system through valved line 16. A xylene fraction boiling in the range of about 270° F. to about 325° F. is removed from tower 11 through valved line 17 and is passed into fractionating tower 18, from which a heavy hydroformate fraction boiling above about 310° F. is discharged through valved line 19. The overhead from fractionating tower 18 consisting essentially of the isomeric xylenes and associated saturated hydrocarbons, boiling in the range of about 270 to about 300° F. is passed through line 20 and condenser 21 to reflux accumulator drum 22, whence a portion is recycled to the upper portion of tower 18 through valved line 23 and the remainder is passed through line 24 and either through valved line 25 and cooler 26 into storage tank 27, or through valved line 28 into fractionating tower 29. Tower 29 is a superfractionator, of which one or more may be used, wherein an ortho-xylene concentrate is separated as a bottoms cut and discharged through valved line 30. A mixture of meta- and para-xylenes, together with ethylbenzene and saturated hydrocarbons boiling in the range of about 275° F. to about 285° F. passes overhead from tower 29 through line 31 and condenser 32 into reflux accumulator drum 33, whence a portion is recycled to the top of tower 29 as reflux through valved line 34 and the remainder is passed through valved line 35 to storage tank 36. If it is not desired to effect fractional distillation of the hydroformate prior to extraction with liquid HF and BF_3 , it may be diverted from line 10 through valved line 37 into storage tank 38.

Charging stocks for the initial extraction operation may be passed from any of storage tanks 27, 36 and 38 through valved lines 39, 40 or 41, respectively, into manifold 42 which leads to the lower portion of extraction tower 43.

The feed stocks to the initial extraction operation should be substantially free of water, since water is tenaciously retained by both HF and BF_3 . Conventional drying procedures may be used to treat the feed stocks.

Various specific extraction cases will be discussed hereinafter.

Case 1

[Total aromatic cut from hydroforming charged]

In this case the aromatic fraction is passed from storage tank 38 through valved line 41 and manifold 42 into the lower portion of extraction tower 43. We prefer to employ a feed containing substantially no components boiling above about 310° F. If desired, a low boiling diluent may be introduced into manifold 42 through valved line 44 in amounts between about 0.1 and about 5 volumes (preferably about 0.8 to 1.5 volumes) per volume of charging stock. Suitable diluents comprise low boiling saturated hydrocarbons such as n- or isobutane, pentanes, hexanes, heptanes, octanes; low boiling cycloparaffinic hydrocarbons such as cyclopentane, methyl- and dimethylcyclopentanes, cyclohexane, methyl-cyclohexane; and the like. The extraction in tower 43 is conducted in such a manner that two immiscible phases are present therein, viz., a lower extract phase whose upper surface is indicated by meniscus 45 and a supernatant raffinate phase 46 above meniscus 45. Boron trifluoride and liquid hydrogen fluoride are introduced into the upper portion of the extraction tower through valved

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lines 47 and 48, respectively. Part or all of the diluent may be introduced (by lines not shown) directly into the extract phase below meniscus 45 in tower 43.

Although we prefer to employ essentially anhydrous hydrogen fluoride, i. e., HF containing not more than 1 to 2 weight percent of water, we may employ HF containing up to about 5 to 10 weight percent of water. By HF as used herein we intend to denote the molecular species having the molecular weight of 20, which weight is employed in the necessary calculations.

Extraction tower 43 is provided with a manifold 49 to permit the introduction of BF₃ at various levels in the extraction tower. All or a portion of the HF and/or BF₃ may also be added to the charging stock at a point or points in advance of the extraction tower 43 and additional HF or BF₃ can then be added as described above.

The extraction operations in tower 43 are conducted in such a manner as to effect the removal of substantially all the xylenes from the charging stock into the extract phase. In order to secure this result it is necessary to contact the charging stock with a molar excess of liquid hydrogen fluoride (usually between about 5 and about 100 mols or even more of liquid hydrogen fluoride per mol of xylenes contained in the charging stock) and BF₃ in the amount of at least 1 mol per mol of xylenes contained in the charging stock. Usually we employ about 1.25 to 2 mols or even more, e. g. 3 or 5 mols, of BF₃ per mol of xylenes contained in the charging stock in order to insure complete removal of xylenes from the charging stock into the extract phase. Where the charging stock contains ethylbenzene in addition to the xylenes and where it is desired to remove diethylbenzenes and ethylxylenes formed by the disproportionation of ethylbenzene into the extract phase, an additional quantity of BF₃ over the amount required simply for the extraction of xylenes is necessary. This additional quantity of BF₃ is at least 0.5 mol per mol of ethylbenzenes contained in the charging stock.

The temperature employed in extraction tower 43 will ordinarily be maintained between about 0 and about 150° F., preferably 40 to 100° F.; the pressure will be at least sufficient to maintain liquid phase operating conditions.

The charging stock passes upwardly through tower 43 against a counterflow of liquid hydrogen fluoride and BF₃, traversing a bed of packing material 50 comprising shaped solid fragments resistant to the action of HF and BF₃, for example, carbon, copper or monel metal. Since the extraction is accompanied by considerable release of heat, as pointed out above, a cooling coil 51 is provided to remove all or at least a substantial part of the heat of extraction (heat due to complex formation). If desired the cooling in the extraction operation may be so conducted as to provide an ascending temperature gradient, for example about 10° F. to 25° F. or even as much as 50° F. across the length of the extraction zone.

In the extraction operation a raffinate is formed which consists essentially of the diluent which was introduced through line 44, saturated hydrocarbons derived from the charging stock, benzene and toluene present in the charging stock, benzene derived by disproportionation of some of the ethylbenzene or higher monoalkylbenzenes such as isopropylbenzene, and traces of ethylbenzene which was present in the charging stock and which escaped disproportionation.

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The raffinate may be discharged from the extraction tower and from the system through valved line 52; however, it is usually desirable to pass all or at least a substantial proportion of the raffinate through valved line 53 and heater 54 into stripping tower 55 provided with reboiler coil 56. Tower 55 is ordinarily operated at a top temperature between about 150° F. and about 250° F. and a bottom temperature between about 250° F. and about 400° F. and a pressure between about 0 and about 100 p. s. i. g. to effect stripping of HF, BF₃ and low boiling saturated hydrocarbons. The HF, BF₃ and low boiling diluent passes overhead through line 57 and condenser 58 into a settling and accumulating drum 59, whence BF₃ is discharged as a gas through valved line 60, diluent is removed through valved side-line 61 and liquid HF saturated with BF₃ is removed through valved line 62. The BF₃ and HF solution of BF₃ are recycled to the extraction operation, and all or part of the diluent leaving drum 59 through line 61 may likewise be recycled to the extraction operation. When a charging stock containing saturated hydrocarbons is employed, as where a crude hydroformate fraction is employed, saturated hydrocarbons from the raffinate phase may be passed through line 63 to valved line 64 back to the extraction zone to operate as a diluent and stripping medium. In this mode of operation, saturated hydrocarbons tend to accumulate in the raffinate and to do away with the necessity of adding a separate diluent through valved line 44. Part or all of the raffinate hydrocarbons may be discharged from the system through valved line 65.

Benzene and toluene can be recovered from saturated hydrocarbons by extraction or extractive distillation with various solvents such as phenol, ethylene glycol, methanol, nitrobenzene, furfural, nitromethane, liquid sulfur dioxide, and the like. Also, benzene can be separated from other raffinate hydrocarbons by fractional freezing.

The primary extract phase is withdrawn from the bottom of tower 43 through line 66 and is passed through line 68 into a heater 69 represented in the form of a coil 70 within a shell 71 through which a heating medium such as steam or other hot gases or liquids may be circulated.

After passing through heater 69, the extract may be treated in either of two ways, viz., all the HF and BF₃ may be stripped therefrom and the extracted hydrocarbons may then be subjected to selective extraction with liquid HF and BF₃ to separate individual xylene concentrates, or only a part of the BF₃ may be removed from the extract phase, sufficient to lower the BF₃ concentration thereof to less than 1 mol per mol of contained xylenes, thus permitting the formation of a second extract phase and a second raffinate phase upon settling, centrifuging or the like. Each processing method will be described in detail hereinafter, taking first the alternative of stripping substantially all of the HF and BF₃ from the primary extract phase.

The primary extract phase is passed through valved line 72 into manifold 73 and thence to stripping tower 74 provided with reboiler coil 75.

Stripping tower 74 is operated at a temperature between about 100 and about 160° F. and a pressure between about 0 and about 20 p. s. i. g. Low-boiling saturated hydrocarbons capable of forming azeotropes with HF, e. g., propane, butanes, pentanes, etc., may be introduced into stripper 74 to facilitate the stripping operation. Suf-

cient heat is applied to the charge to tower 74 by heater and reboiler 75 to effect substantially complete removal of HF and BF₃ overhead through valved line 76, whence these materials may be recycled to the extraction system.

The stripped, extracted aromatic hydrocarbons leave tower 74 through line 77, whence they may be passed through valve 78, line 79 and heat exchanger 80 into selective extraction tower 81. Since ethylbenzene contained in the charging stock disproportionates to produce C₁₀ aromatic hydrocarbons which are preferentially soluble in liquid hydrogen fluoride and BF₃ and since it is usually undesirable to burden the selective extraction carried out in tower 81 with these C₁₀ aromatic hydrocarbons, it is ordinarily desired to divert all or at least a substantial proportion of the stripped extracted aromatic hydrocarbons from line 77 through valved line 82 into fractionating tower 83, whence C₁₀ aromatics are removed as a bottoms cut through valved line 84 and a mixture of xylenes is taken overhead through line 85 and condenser 86 to an accumulator drum 87, whence a portion may be recycled to fractionating tower 83 through valved line 89 and the remainder passed through valved line 89 and heat exchanger 80 into selective extraction tower 81. A controlled amount of a low boiling saturated hydrocarbon diluent may be introduced with the charge to extraction tower 81 through valved line 90.

The extraction operation in tower 81 is conducted with a molar excess of liquid hydrogen fluoride, as in the operation of tower 43, but less than 1 mol of BF₃ is employed per mol of xylenes charged to tower 81, resulting in selective extraction of the isomeric xylenes as demonstrated by the different individual xylene distributions in the raffinate and extract phases produced in tower 81. Tower 81, like tower 43, is provided with a bed of packing materials 91, a cooling coil 92, lines 93 and 94 for the introduction of BF₃ and HF, respectively, into the upper portion of the tower and a BF₃ manifold 95 for introducing BF₃ at various points along the length of the tower.

In the extraction tower the xylene charging stock is contacted with a counterflow of a molar excess of liquid hydrogen fluoride (between about 5 and about 50 mols or even more per mol of xylenes contained in said charging stock) and BF₃ (in an amount between about 0.2 and about 0.8 mol per mol of xylenes contained in said charging stock) at a temperature between about 0 and about 150° F. under pressure sufficient at least to maintain the liquid phase, for a period of time sufficient to effect selective extraction, usually between about 1 and about 30 minutes. Preferred operating conditions involve the use of about 7 to 15 mols of liquid hydrogen fluoride per mol of xylenes, about 0.4 to 0.7 mols of BF₃ per mol of xylenes, a temperature between about 60° F. and about 100° F. and an extraction period varying from about 5 to about 15 minutes.

The raffinate phase derived from the selective extraction operation is characterized by a greatly reduced content of meta-xylene as compared with the meta-xylene content of the charging stock entering tower 81. The raffinate is taken overhead from selective extraction tower 81 through valved line 96 and heat exchanger 97 into stripping tower 98 provided with a reboiler coil 99. Stripping tower 98 is operated at a top temperature between about 150° F. and about 250° F. and a bottom temperature between about

250° F. and about 400° F. and a pressure between about 0 and about 100 p. s. i. g. to remove substantially all of the relatively small amounts of HF and BF₃ carried from tower 81 by the raffinate phase. When a diluent is employed in tower 81, it, too, will be stripped from the raffinate in tower 98. The distillate passes overhead through line 100 and partial condenser 101 into an accumulator and settling drum 102, from which BF₃ is discharged overhead through valved line 103. A stratum of diluent is withdrawn through valved side line 104 and liquid hydrogen fluoride saturated with BF₃ is discharged through valved line 105. It will be obvious that all the effluents of drum 102 may be reemployed in the various extraction operations.

Stripped raffinate hydrocarbons are discharged from tower 98 through valved line 106 whence they pass through heat exchanger 97, cooler 107 and line 108 to an accumulator drum 109. A portion of the raffinate xylenes may be recycled to extraction tower 81 through valved line 110 and the remainder is passed through valved line 111 into fractionating tower 112.

A para-xylene concentrate is removed from tower 112 as a distillate through line 113 and condenser 114 to an accumulator drum 115 whence a portion may be recycled to the upper section of tower 112 as reflux through valved line 116 and the remainder discharged from the system through valved line 117. An ortho-xylene concentrate is removed as a bottoms fraction from tower 112 through valved line 118.

We prefer to employ a sufficient number of selective extraction stages to be able to produce ortho-, meta- and para-xylene concentrates, respectively, of at least about 80 mol percent concentration.

An extract phase which is greatly enriched in meta-xylene, based on the distribution of xylenes in the charging stock, is withdrawn from tower 81 through line 119 and is passed through valved lines 121 and 122, heat exchanger 123 and line 124 into stripping tower 125. This tower may be operated under substantially the same conditions as raffinate stripper 98. Hydrogen fluoride and BF₃ vapors are removed overhead from stripper 125 through valved line 126 for reuse in our process as desired. A portion of the stripped extracted xylenes (essentially a meta-xylene concentrate) is withdrawn from stripper 125 through valved line 127, heat exchanger 123 and cooler 128 for recycle to the lower portion of extraction tower 81 to serve as a backwash or "reflux." The meta-xylene backwash exerts a stripping effect on the extract phase, apparently by selectively displacing ortho- and para-xylenes from their complexes with BF₃ and HF, resulting in the rejection of ortho- and para-xylenes to the raffinate phase in tower 81. All or the remainder of the meta-xylene concentrate may be withdrawn from the system through valved line 129.

If C₁₀ aromatic hydrocarbons were not removed from the charging stock to tower 81 in fractionating tower 83, a predominant proportion of these will be retained in the meta-xylene concentrate derived from the selective extraction process and may be removed, if desired, by diverting the concentrate from stripper 125 through valved line 130 into fractionating tower 131. By the appropriate choice of operating conditions in tower 131 a meta-xylene concentrate is removed as the distillate through line 132, whence it is passed through condenser 133 into an accumu-

lator drum 134. A portion of the meta-xylene concentrate may be employed to reflux tower 131 by passage through valved line 135 and the remainder may be discharged through valved line 136. Ten carbon atom aromatic hydrocarbons (ethylxylenes and diethylbenzenes) are removed as a bottoms fraction from tower 131 through valved line 137.

If it is desired to remove small proportions of ortho- and para-xylenes which are present in the extract phase, at least part of the extract phase in line 121 is diverted into valved line 138, whence it passes through a heater 139 of the same type as heater 69, which was described above. In heater 139, sufficient heat is imparted to the extract phase to render possible the vaporization of part of the BF_3 contained therein. The heated extract phase is passed through valved line 140 into a settling drum 141 provided with a line 142 and a pressure control valve 143 for the removal of BF_3 . Sufficient BF_3 is released through valve 143 to reduce its amount in the solution charged to the settling drum to less than 1 mol per mol of contained xylenes, preferably to reduce the BF_3 content of said solution to a value between about 0.75 and about 0.9 mol per mol of contained xylenes. Following the removal of BF_3 , the solution in settling drum 141 stratifies into two immiscible liquid layers, viz., a raffinate which flows over weir 144 and a secondary extract layer which collects in the lower portion of settler 141, whence it is withdrawn through valved line 145, following which it may be passed through valved line 146 through heat exchanger 123 and line 124 into stripper 125, whose operation has previously been described, in order to complete the removal of HF and BF_3 from the extract phase. The raffinate layer which accumulates in drum 141 is discharged through valved line 147 into line 148 and thence into stripper 98 (whose operation has previously been described) to effect the removal of small amounts of occluded HF and BF_3 , following which the stripped raffinate is treated in the same equipment and manner as the raffinate which leaves extraction tower 81 through line 96, in order to effect its separation into ortho- and para-xylene concentrates, respectively.

The above description has been concerned with the method of operation in which a solution of xylenes and other aromatics in liquid hydrogen fluoride and BF_3 derived from the extraction, for example, of a hydroformate is stripped of its entire content of HF and BF_3 , following which the extracted aromatic hydrocarbons are subjected to selective extraction with liquid hydrogen fluoride and BF_3 to produce individual xylene concentrates.

Consideration will be given at this point to a second method of operation in which the primary solution of xylenes and other aromatics in liquid hydrogen fluoride and BF_3 derived from the extraction, for example, of a hydroformate is treated to withdraw only a portion of the BF_3 therefrom in order to reduce the concentration of BF_3 in the solution to a value between about 0.5 and about 0.9 mol per mol of contained aromatics, preferably to a value between about 0.6 and about 0.75 mol per mol of contained aromatics in order to produce secondary raffinate and extract phases.

Upon the partial withdrawal of BF_3 from the solution of xylenes and other aromatics in liquid HF and BF_3 , the solution separates into two immiscible liquid layers, viz., a secondary raffi-

nate and a secondary extract, of which the former is relatively rich in ortho- and para-xylenes and the latter is essentially a concentrate of meta-xylene in liquid hydrogen fluoride and BF_3 . It appears thus, that partial withdrawal of BF_3 from a homogeneous solution of xylenes in liquid HF and BF_3 produces an effect which is substantially identical with that obtained upon the extraction of a mixture of isomeric xylenes with liquid hydrogen fluoride and an amount of BF_3 which is less than 1 mol per mol of xylenes charged to the extraction process.

In the second method of operation, the solution of xylenes and other aromatic hydrocarbons in liquid hydrogen fluoride and BF_3 prepared in extraction tower 43 is removed from the lower end of said tower through line 66, thence through valved line 68 and heater 69, through valved line 149 into a settling and separating drum 150 provided with line 151 and valve 152 for the withdrawal of BF_3 . Generally, temperatures between about 100 and about 160° F. and pressures between about 0 and about 75 p. s. i. g. are maintained in drum 150. Preferred operating conditions in drum 150 are temperatures between about 120 F. and about 150° F. and pressures between about 15 and about 60 p. s. i. g. Sufficient BF_3 is withdrawn through line 151 and valve 152 to reduce the BF_3 concentration in the solution charged to drum 150 to a value substantially below 1 mol per mol of aromatics contained in said solution, for example, to 0.5 to about 0.9 mol BF_3 , preferably to 0.6 to 0.8 mol BF_3 , per mol of aromatic hydrocarbons. Following the withdrawal of BF_3 from the solution, it separates into a secondary raffinate phase which is relatively rich in ortho- and para-xylenes; the secondary raffinate phase flows over weir 153 and is removed from drum 150 through valved line 154, whence it is passed through heater 155 into line 148, thence into stripper 98 (whose operation has been described above) in order to strip HF , BF_3 and any low boiling saturated hydrocarbons contained in said secondary raffinate. A low boiling saturated hydrocarbon diluent, e. g., a pentane, may be introduced into drum 150 (by a line not shown) to facilitate the separation process therein. Thereafter the stripped secondary raffinate is processed in the equipment and by the method described in detail for the treatment of the raffinate passing overhead from selective extraction tower 81 through valved line 96, resulting finally in the separation of said secondary raffinate into ortho- and para-xylene concentrates, respectively.

The secondary extract layer formed in the lower portion of drum 150 is discharged through valved line 156, whence it may be passed through valved line 157, heater 158 and line 159 into line 124 and HF - BF_3 stripper 125, to be processed in the same equipment and manner as heretofore described for the stripping and fractionation (in tower 131) of the extract phase produced in tower 81, resulting in the production of a meta-xylene concentrate (preferably having a concentration of at least about 80 volume percent) which may be discharged from the system through valved lines 129 or 136 and a C_{10} aromatic fraction which may be discharged from the system through valved line 137. If desired, at least a portion of the meta-xylene concentrate may be recycled from lines 129 and/or 136 to the lower portion of drum 150 to serve as a backwash.

It will be noted that each of the above-described processes, when applied to the treatment

of a mixture of aromatic and saturated hydrocarbons boiling between about 170 and about 300° F., such as may be produced by the catalytic hydroforming of naphtha fractions, results in the separation of the charging stock into a fraction containing benzene and/or toluene, and saturated hydrocarbons; individual concentrates of ortho-, meta- and para-xylenes, respectively; a C₁₀ aromatic hydrocarbon fraction consisting essentially of diethylbenzenes and ethylxylenes, (predominantly of meta-configuration) produced by disproportionation of ethylbenzene contained in the charging stock.

Case 2

[Ortho-, meta- and para-xylene charged]

The method of operation with this charging stock is essentially the same as in Case 1. However, the charging stock (from tank 21) in this case has been prefractionated to remove benzene, toluene and other hydrocarbons boiling below about 270° F. The raffinate phase passing overhead from tower 43 through valved line 53 will, therefore, not contain these low boiling hydrocarbons and the stripping operation in tower 55 will, therefore, yield a bottoms fraction, passing through line 63, consisting essentially of saturated hydrocarbons boiling between about 270 and about 300 or 325° F. The composition of the extract phase in tower 43 will be essentially the same as in Case 1 and can be treated in the same fashion to resolve it into its constituents.

Case 3

[Meta- and para-xylenes charged]

The charging stock is removed from storage tank 36 through valved line 40 into manifold 42 and thence to extraction tower 43 for treatment in the same manner as the charging stocks in Cases 1 and 2. The ortho-xylene concentration in the charging stock is reduced to a relatively low value by prefractionation in one or more superfractionators 29. However, especially where saturated hydrocarbons are also present in the charging stock, some ortho-xylene will be present in the meta-para-xylene concentrate in storage tank 36. The method of treatment of this charging stock is essentially the same as in Cases 1 and 2 except that it may not be considered worthwhile to fractionate a small amount of ortho-xylene from the para-xylene concentrate, produced in the selective extraction or partial BF₃ withdrawal operations, by the use of tower 112.

A great many chemical reactions, uses and possible applications of the isomeric xylenes have been studied more or less extensively ("Xylene Technical Review," published by Oronite Chemical Co., 1947). At the present time it appears that the largest scale demand for orthoxylene is for its employment as a charging stock for vapor phase catalytic oxidation processes for the production of phthalic anhydride (I. E. Levine, Trans. Am. Inst. Chem. Eng. (Chem. Eng. Progress) 43, 4 (April, 1947), pp. 168-171).

Para-xylene is desirable as a high octane aviation gasoline component. Another outlet of potentially greater commercial significance for para-xylene lies in its oxidation to terephthalic acid which reacts with ethylene glycol to produce synthetic resins (Terylenes) which can be used for the production of synthetic textile fibers (Oil and Gas J., Feb. 5, 1948, page 99).

Of the individual xylene isomers, the meta-

xylene does not have as attractive commercial outlets as the other two xylene isomers. Any process by which meta-xylene or a meta-xylene concentrate could be converted in high yield into ortho- and para-xylenes would be of substantial economic significance.

We have observed that liquid hydrogen fluoride and BF₃ function as highly desirable catalysts to isomerize meta-xylene to equilibrium proportions of the three isomeric xylenes. The isomate or equilibrium mixture of the isomeric xylenes may be subjected to selective extraction with liquid hydrogen fluoride and BF₃ by the methods described above to produce concentrates of the individual xylene isomers. By the combination of HF-BF₃ catalyzed isomerization of meta-xylene concentrates and the selective separation or concentration of individual xylene isomers by the employment of liquid HF and BF₃, it is possible to convert meta-xylene essentially quantitatively into ortho- and para-xylenes.

Sufficiently severe meta-xylene isomerization conditions can be selected to induce also the disproportionation of a substantial proportion of meta-xylene to produce toluene and trimethylbenzenes, both of which are in very great demand, so that their production from meta-xylene would yield a substantial profit.

The following is an example which is adduced for illustrative purposes only. The apparatus employed was a 1570 cc. carbon steel autoclave fitted with a 1725 r. p. m. mechanical stirrer. A 258 g. sample of a meta-xylene concentrate, 290 cc. of liquid hydrogen fluoride and 47 g. of BF₃ were stirred in the reactor at 250° F. for 25 minutes. At this temperature the reactor pressure was 270 p. s. i. g. The reactor was then cooled to 75° F. and the HF and BF₃ were removed from the reaction mixture by vacuum distillation. The hydrocarbon product, which amounted to 96 percent by weight of the charging stock, was fractionated in a column packed with wire gauze equivalent to 30 theoretical plates and was found to have the following composition:

	Vol. Per Cent	Mol Per Cent
Toluene.....	22	26
Xylenes.....	47	47
Trimethylbenzenes.....	31	27

It is evident that under the conditions of the experiment, which were intentionally made severe to insure equilibrium isomerization, about 50% of the xylene was converted to toluene and to a trimethylbenzene which has been identified by its physical properties and ultraviolet spectrum as mesitylene. In the following tabulation, the ultraviolet analysis of the C-8 cut is compared with the composition of the feed and with the thermodynamic equilibrium composition:

	Mol Per Cent		
	Feed	Product (C-8 Cut)	Equilibrium ¹
ortho-xylene.....	1.3	17.8	17
meta-xylene.....	82.3	56.3	58
para-xylene.....	13.8	22.3	23
Ethylbenzene.....	2.4	2.4	2

¹ F. D. Rossini, Report on Chemical Thermodynamic Properties of Hydrocarbons, A. P. I. Research Project 44, Mar. 31, 1947; Fig. 35.

The above results show that isomerization equilibrium is readily reached and that it is possible by combining the HF-BF₃ extraction and isomerization operations to reach as near to 100 percent ultimate yield of ortho- and para-xylenes as is desired.

Reference will be made once more to Figure 3 to describe in more detail the meta-xylene isomerization and extraction process. Isomerization zone 160 is schematically represented as a tubular reactor surrounded by shell through which a thermophoric medium may be circulated to maintain the desired temperature. It will be obvious that other batch or continuous reactors such as autoclaves, towers, etc. such as are well known in the art of hydrocarbon conversion can be employed in lieu of the tubular reactor. The charging stock is meta-xylene or a meta-xylene concentrate, for example, the material passing through valved lines 129 or 136, which may be passed to isomerization zone 160 (by lines not shown) or meta-xylene concentrates dissolved in liquid hydrogen fluoride and BF₃ which may be passed from selective extraction tower 81 through valved lines 119, 121, 173, 162 and 163 into isomerization zone 160; a meta-xylene concentrate dissolved in liquid HF and BF₃ from settler 141 through valved lines 145, 161 and 162 to manifold 163, thence to isomerization zone 160; a meta-xylene concentrate dissolved in liquid hydrogen fluoride and BF₃ from settling drum 150, which may be passed through valved lines 156 and 164 into manifold 163 and isomerization zone 160. Additional HF and BF₃ catalyst may be supplied to isomerization zone 160 through valved line 165 or (by means of lines not shown) at various points along the length of the tubular reactor.

In isomerization zone 160 the meta-xylene concentrate is contacted with liquid hydrogen fluoride in an amount between about 3 and about 20 mols per mol of xylene and BF₃ in an amount between about 0.05 and about 0.3 mol per mol of xylene at temperatures between about 160 and about 600° F., preferably at temperatures between about 175° F. and about 300° F. for a period of time sufficient to effect substantial isomerization of meta-xylene, usually between about 2 minutes and about 4 hours to allow the isomerization of meta-xylene to equilibrium proportions of ortho-, meta- and para-xylenes. The isomerization reaction mixture is discharged from isomerization zone 160 through valved line 166 to be treated to separate concentrates of ortho-, meta- and para-xylenes, respectively, and such incidental products as toluene, trimethylbenzenes, ethylbenzenes and ethylxylenes.

One method of effecting the desired separation of the isomerization reaction products involves passing the isomerization product stream from valved line 166 into line 167, thence through valved line 168, heater 169 into manifold 73 and stripper 74 (whose operation has previously been described). Hydrogen fluoride and BF₃ are substantially completely removed from the isomerization product stream, which is discharged from stripper 74 through line 77 and may be passed through line 79 to extraction tower 81 wherein selective extraction of the mixture of isomeric xylene is conducted as has been described above. If desired, the mixture in line 166 may be passed (by a line not shown) directly into extractor 81. Alternatively, the mixture of xylene isomers may pass from stripper 74 through lines 77 and 82 into fractionator 83 to remove C₈ and C₁₀ aromatic hydrocarbons as a bottoms fraction

through line 84 and to distill xylenes in admixture with some toluene and, possibly, some benzene overhead through line 85 and condenser 86 into accumulator drum 87. The mixture in accumulator drum 87 may be further fractionated (in a tower not shown) to separate a xylenes heart cut which may be subjected to extraction with liquid hydrogen fluoride and BF₃ in tower 81, or the entire product in the accumulator drum may be passed into extraction tower 81. When appreciable amounts of benzene and toluene are present in the xylene charging stock to tower 81 they will pass overhead as raffinate through line 96 into stripper 98, in which the operating conditions may be adjusted so as to take HF, BF₃, low boiling saturated hydrocarbon diluent, benzene and toluene overhead and a xylenes bottom fraction will be discharged through valved line 106 for treatment as hereinbefore described. There are obvious alternative methods for fractionating the raffinate from tower 81 which will, no doubt, suggest themselves to one skilled in the art and need not, therefore, be detailed here.

Another method of treating the isomerization reaction products involves passing them from valved line 166 through valved line 170, thence through line 68, heater 69 and valved line 149 into settling and separating drum 150. If desired, part or all of the isomerization product stream may be diverted from line 166 through line 167, valved line 171 and heat exchanger 172 into line 149 and settling and separating drum 150. The operation of drum 150 has previously been described. In this drum a portion of the BF₃ is withdrawn from the solution containing xylenes, HF and BF₃, resulting in separation of the solution into a raffinate phase relatively enriched in ortho- and para-xylenes and an extract phase relatively rich in meta-xylene which can be withdrawn through valved lines 156, 164 and 163 for recycle to isomerization zone 160 to effect the ultimate conversion of substantially all the meta-xylene to ortho- and para-xylenes.

Although Figure 3 describes a continuous extraction operation, the process of our invention can be operated batchwise. It can also be operated in a plurality of stages employing either batch or continuous extraction equipment. Various contacting equipment may be used in lieu of the packed towers shown in Figure 3, for example, agitated autoclaves or the like in combination with settling drums, or a pipe coil wherein the HF, BF₃ and charging stock are concurrently contacted at high velocity and discharged into a settling chamber. The extraction and phase separation may be conducted in a centrifuge. The above and other known means of contacting employed in solvent extraction processes and in processes wherein liquid catalysts are contacted with hydrocarbons may be employed to practice the process of our invention.

In order to produce a meta-xylene concentrate having the highest proportion of meta-xylene, we prefer, in one-stage batch operation, to add an amount of BF₃ just sufficient to cause the formation of two liquid phases. This amount of BF₃ will be less than 1 mol per mol of meta-xylene contained in the feed stock.

Although HF and especially BF₃ are relatively expensive reagents and would of necessity be recovered in any large commercial application of the process of this invention, in small scale operations the recovery of these reagents might be considered immaterial. When the recovery of

HF and BF_3 as such is not required, the distillation and stripping operations illustrated in Figure 3 may be dispensed with. As an alternative to distillation of the extract phase, said phase may be mixed with water, alkaline or acid solutions, or the like which dissolve the HF and BF_3 , leaving a supernatant hydrocarbon phase which may then be recovered. A desirable acidic solution with which to treat the extract phase is the azeotropic HF- H_2O solution, which becomes enriched in HF upon contact with the extract phase and from which the HF in excess of the azeotropic amount can thereafter be readily recovered by distillation. An alternative would be to distill free HF from the extract phase, following which the residual firmly bound BF_3 -HF-xylene complex could be treated with water or aqueous alkaline or acidic solutions to liberate xylenes bound in said complex. In place of the aqueous solutions mentioned above, one may employ organic compounds capable of forming complexes with HF and BF_3 and which are capable of displacing xylenes, especially meta-xylene from its complexes with HF and BF_3 , e. g., organic compounds having a more basic (greater electron-donating) capacity than the xylenes, especially meta-xylene. Such organic compounds include various amines, sulfur compounds, e. g., alkyl bithioethers, and oxygenated organic compounds such as phenol, alkyl ethers, ketones, aldehydes, etc.

Having thus described our invention, what we claim is:

1. A process for the concentration of individual xylene isomers from a solution of at least two isomeric xylenes in liquid hydrogen fluoride and BF_3 , said solution containing at least 1 mol of BF_3 per mol of contained xylenes, which process comprises withdrawing BF_3 from said solution in an amount sufficient to reduce the concentration of BF_3 in said solution to a value between about 0.5 and about 0.9 mol per mol of aromatic hydrocarbons originally present in said solution and to convert said solution into two immiscible liquid layers, one liquid layer consisting essentially of xylenes in a ratio different from their ratio in said solution and the other liquid layer consisting essentially of a second solution of xylenes in liquid hydrogen fluoride and BF_3 , the ratio of xylenes in said second solution being different from the ratio of xylenes in the original solution, and separating said liquid layers from each other.

2. A process for the concentration of individual xylene isomers from a solution of meta-xylene and at least one additional isomeric xylene in liquid HF and BF_3 , said solution containing at least 1 mol of BF_3 per mol of contained xylenes, which process comprises withdrawing BF_3 from said solution in an amount sufficient to reduce the concentration of BF_3 in said solution to a value between about 0.5 and about 0.9 mol per mol of aromatic hydrocarbons originally present in said solution and to convert said solution into two immiscible liquid layers, one liquid layer consisting essentially of xylenes of substantially reduced meta-xylene content, and the other liquid layer consisting essentially of a second solution of xylenes in liquid hydrogen fluoride and BF_3 , said second solution being substantially enriched in meta-xylene in comparison with the original solution, and separating said liquid layers from each other.

3. A process for the concentration of individual xylene isomers from a solution of meta-

xylene and at least one additional isomeric xylene in liquid HF and BF_3 , said solution containing at least 1 mol of BF_3 per mol of contained xylenes, which process comprises withdrawing BF_3 from said solution in an amount sufficient to reduce the concentration of BF_3 in said solution to a value between about 0.6 and about 0.75 mol per mol of aromatic hydrocarbons originally present in said solution and to convert said solution into two immiscible liquid layers, one liquid layer consisting essentially of xylenes of substantially reduced meta-xylene content, and the other liquid layer consisting essentially of a second solution of xylenes in liquid hydrogen fluoride and BF_3 , said second solution being substantially enriched in meta-xylene in comparison with the original solution, and separating said liquid layers from each other.

4. A process for the concentration of individual xylene isomers from a solution consisting essentially of meta-xylene, at least one additional isomeric xylene and at least one C_{10} aromatic hydrocarbon selected from the class consisting of diethylbenzenes, ethylxylenes and mixtures of diethylbenzenes and ethylxylenes in liquid hydrogen fluoride and BF_3 , said solution containing at least 1 mol of BF_3 per mol of dissolved aromatic hydrocarbons, which process comprises withdrawing BF_3 from said solution in an amount sufficient at least to reduce the concentration of BF_3 in said solution to a value between about 0.5 and about 0.9 mol per mol of aromatic hydrocarbons originally present in said solution and to convert said solution into two immiscible liquid layers, one liquid layer consisting essentially of xylenes of substantially reduced meta-xylene content and the other liquid layer consisting essentially of a second solution of xylenes and at least one C_{10} aromatic hydrocarbon selected from the class consisting of diethylbenzenes, ethylxylenes and mixtures of diethylbenzenes and ethylxylenes in liquid hydrogen fluoride and BF_3 , said second solution being substantially enriched in meta-xylene in comparison with the original solution, separating said liquid layers from each other, removing substantially all the hydrogen fluoride and BF_3 from said second solution, and fractionally distilling hydrocarbons thus derived from said second solution to separate, respectively, a C_8 aromatic hydrocarbon fraction enriched in meta-xylene and a C_{10} aromatic hydrocarbon fraction.

5. A process for the concentration of individual xylene isomers from a solution of meta-xylene and at least one additional isomeric xylene in liquid HF and BF_3 , said solution containing at least 1 mol of BF_3 per mol of contained xylenes, which process comprises withdrawing BF_3 from said solution in a withdrawal zone in an amount sufficient to reduce the concentration of BF_3 in said solution to a value between about 0.5 and about 0.9 mol per mol of aromatic hydrocarbons originally present in said solution and to convert said solution into two immiscible liquid layers, one liquid layer consisting essentially of xylenes of substantially reduced meta-xylene content, and the other liquid layer consisting essentially of a second solution of xylenes in liquid hydrogen fluoride and BF_3 , said second solution being substantially enriched in meta-xylene in comparison with the original solution, removing substantially all the hydrogen fluoride and BF_3 from said second solution to produce a meta-xylene concentrate and

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recycling at least a portion of said meta-xylene concentrate to said withdrawal zone.

6. The process of claim 1 which includes the additional step of distilling the hydrogen fluoride and BF_3 contained in said second solution, thereby recovering xylenes from said second solution.

7. The process of claim 1 wherein the withdrawal of BF_3 is effected in the presence of a low boiling saturated hydrocarbon diluent.

8. A process for the concentration of individual xylene isomers from a solution of meta-xylene and at least one additional isomeric xylene in liquid hydrogen fluoride and BF_3 , said solution containing at least one mol of BF_3 per mol of contained xylenes, which process comprises vaporizing BF_3 from said solution at a temperature between about 100°F. and about 160°F. and a pressure between about 0 and about 75 p. s. i. g., continuing the BF_3 vaporization process until the BF_3 concentration in said solution is reduced to a value between about 0.5 and about 0.9 mol per mol of aromatic hydrocarbons originally present in said solution, thereby to

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convert said solution into two immiscible liquid layers, one liquid layer consisting essentially of xylenes of substantially reduced meta-xylene content and the other liquid layer consisting essentially of a second solution of xylenes in liquid hydrogen fluoride and BF_3 , said second solution being substantially enriched in meta-xylene in comparison with the original solution, separating said liquid layers from each other and recovering xylenes from said second solution.

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