DISTRIBUTION REACTION PRODUCTS IN BENZENE CHLORINATION

BATCH VS. CONTINUOUS PROCESS PROCEDURES

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CHLORINATION of hydrocarbons is a unit process * in chemical engineering which is of considerable importance. Monochlorobenzene is produced commercially on a large scale as the essential intermediate in the production of phenol, aniline, *DDT*, and a host of other organic intermediates. Dichlorobenzene is manufactured on a large scale, the para-isomer being used as a larvicide and the ortho-compound as a solvent and heat-exchange medium. Chlorination of toluene is a primary unit process in the preparation of benzyl alcohol, benzaldehyde and benzoic acid. Chlorination of ethyl benzene is a primary unit process in the preparation of dichlorostyrene whose polymers and copolymers are of considerable interest. Chlorination of phenol on the one hand and the chlorination of acetic acid on the other, are primary unit processes in the preparation of the important weed-control compound, dichlorophenoxyacetic acid (*2-4-D*). Chlorination of aliphatic hydrocarbons is carried out industrially on a large scale to produce a variety of chlorinated solvents and intermediates.

The present paper is a contribution to the technology of chlorination as a unit process and is concerned with the distribution of successive chlorination products which result in the substitutive chlorination of hydrocarbons. A later paper will deal with addition reactions and the complicated problem of parallel chemical reactions which compete for chlorine during the chlorination process.† The mathematical treatment which follows has been deduced in general terms so that it is of general application within the limitations of the assumptions which are clearly stated in this paper. By way of illustration the method has been applied to the chlorination of benzene up to and including trichlorobenzene.

Distribution of the various substitution products is of considerable importance to the chemical engineer. He is usually interested in producing certain of these products to the exclusion of others, or to produce them in definite proportions, depending upon economic considerations. He usually approaches the problem of plant design by demanding from the research department experimental data showing the distribution of the successive chlorination products as a function of the amounts of chlorine introduced. This will usually be furnished by the research chemist on the basis of experimental chlorination of the hydrocarbon in question as a batchwise process. The data may be of questionable accuracy, and the chemical engineer may wish to extend the experimental curves into a region beyond the range of the data. The whole design of the plant including reaction vessels, fractionating columns and auxiliary equipment, will depend upon just such considerations. The chemical engineer may get the "bee in his bonnet" to design a continuous chlorination plant, and unless he is aware of the penalties involved, proven capacity and performance may be in practice very different from what he designs on the basis of batch-chlorination data.

The purpose here is to show how the whole family of curves, which represent compositions of the various components as functions of the amount of chlorine introduced, depends solely upon the relative reaction rates of the compounds being chlorinated. These relative reaction rates may be obtained by a single experiment preferably carried out at the point which represents the maximum concentration of any particular component, one experiment to a maximum. Moreover, the degree of chlorination at which the maximum will occur can be predicted within very close limits. The theoretical composition curves can then be deduced and extrapolated with confidence into regions where experimental technique would be difficult. There will be a separate family of curves for batch chlorination, another for single-stage continuous chlorination, and another for two-stage continuous chlorination. Each family of curves is determined by the relative reaction rates which, as pointed out, can be determined by a surprisingly limited number of experiments.

In the treatment of the subject, the plan will be first to set up the fundamental equations; second, to state the final equations in usable form; and third, to illustrate their use by applying them to the chlorination of benzene. Mathematical derivations of the final formulas have been omitted. So far as known, these equations have not appeared elsewhere in the literature.‡

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* Defined by R. Norris Shreve.

† Since writing this manuscript the author has learned that an exhaustive investigation of this subject has been made by Dr. John W. Churchill (Mathieson Alkali Works, Inc.), and that a paper is in preparation.

‡ Batch chlorination of benzene has also been mathematically treated by M. F. Jourion, *Annales de Chemie* (*9*), 14, 215-321 (1920), but the results are presented in less usable form. His experimental results agree well with those presented in this paper.

Table 1.—Batch Chlorination of Benzene

Calculated Compositions

$r = 8$ $\quad s = 30$

r	A	B	C	D	Method
0.000	1.000	0	0	0	Equation 20
0.414	.600	.386	.014	0	
0.760	.300	.640	.060	0	
1.057	.100	.743	.157	0	
1.172	.050	.728	.222	0	
1.349	.010	.631	.359	....	
1.595	....	.422	.561	.017	Equation 21 $v = .70$
2.045	....	.038	.879	.083	$v = .96$
2.204	....	.024	.748	.228	$v = .97$
2.768	....	.005	.222	.773	$v = .98$

Observed Compositions

					sp. gr. 30/20
0.740	.316	.627	.057		1.050
0.890	.207	.697	.096		1.089
0.970	.155	.725	.123		1.105
1.140	.063	.735	.203		1.146
1.477	....	.564	.437	.013	1.211
1.715	....	.320	.646	.034	1.250
1.910	....	.140	.820	.044	1.273
1.918	....	.130	.825	.046	1.275
2.090	....	.025	.855	.125	

Assumptions

1. Conditions are such that chlorine enters the benzene ring by substitution of hydrogen only.
2. Reactions are irreversible.
3. Relative rates of reaction are proportional to the relative molal concentrations of the components reacting.
4. Relative rates of reaction are referred to a specific set of reacting conditions, such as temperature, catalyst.
5. Distribution of components is independent of the speed with which chlorine is introduced.
6. Concern is with the distribution of mono-, di-, tri- and higher substitution products without regard to the proportion of isomers in any such product.
7. The course of the reaction is

$$A \rightarrow B \rightarrow C \rightarrow D$$

where

A = benzene
B = monochlorobenzene
C = dichlorobenzene
D = trichlorobenzene

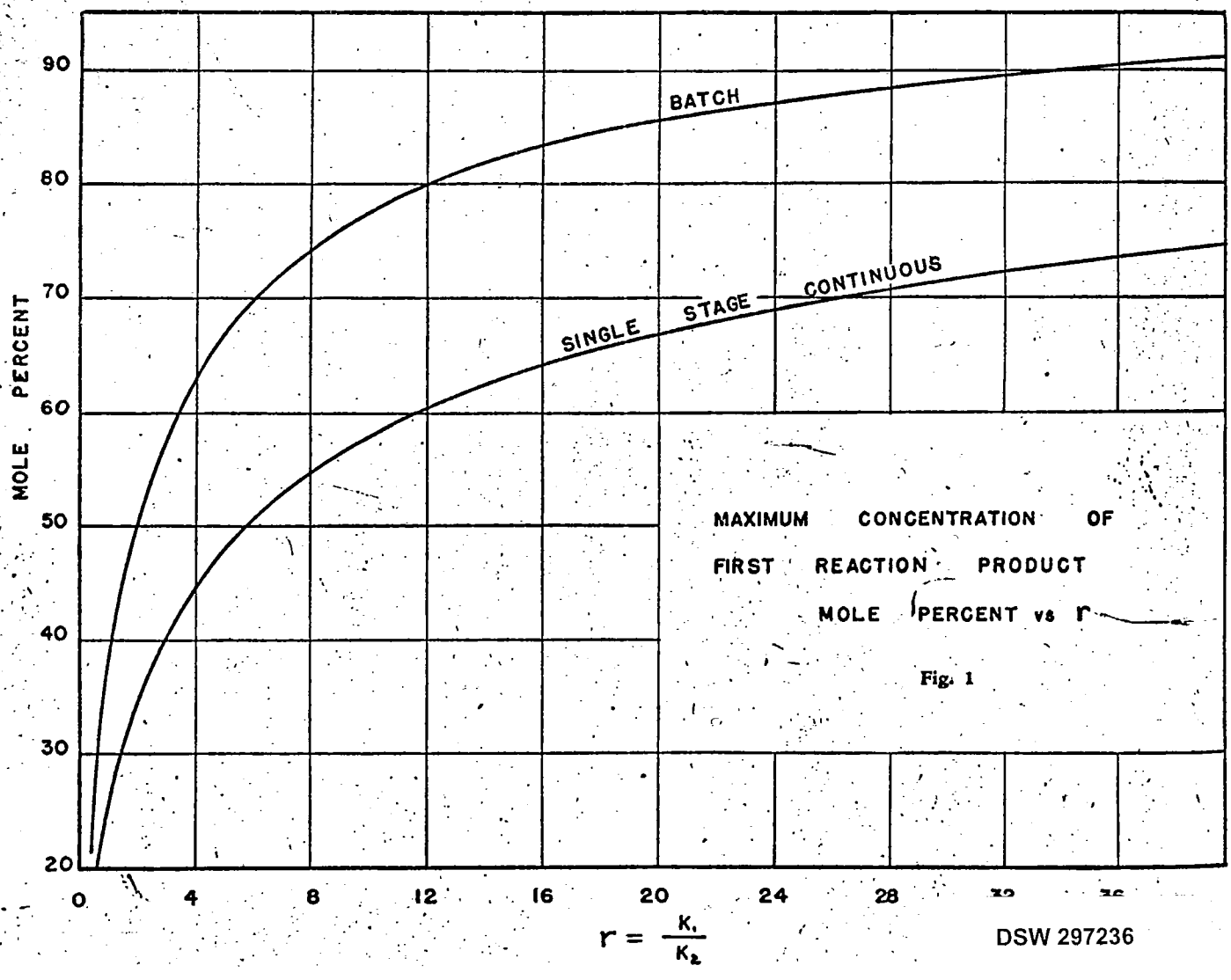

Fig. 1

8. The accompanying mathematical treatment is limited to the chlorination up to, but not beyond trichlorobenzene.

9. In continuous single or multistage reaction systems, the liquid composition within each stage is assumed to be uniform and constant.

Fundamental Equations

A = mole fraction benzene
B = mole fraction monochlorobenzene
C = mole fraction dichlorobenzene
D = mole fraction trichlorobenzene
x = total atoms of chlorine per mole of benzene constituent

$$A + B + C + D = 1 \quad (1)$$

$$B + 2C + 3D = x \quad (2)$$

$$\frac{dA}{dt} = -k_1 A^* \quad (3)$$

$$\frac{dB}{dt} = k_1 A - k_2 B \quad (4)$$

$$\frac{dC}{dt} = k_2 B - k_3 C \quad (5)$$

$$\frac{dD}{dt} = k_3 C \quad (6)$$

Let $k_1/k_2 = r$ and $k_2/k_3 = s$

From Equations (3) and (4) we obtain

$$\frac{dB}{dA} = \frac{B - rA}{rA} \quad (7)$$

From Equations (5) and (6) we obtain

$$\frac{dC}{dD} = \frac{sB - C}{C} \quad (8)$$

There are five unknowns—A, B, C, D, and x, and four Equations (1), (2), (7), and (8), from which it is desired to express A, B, C, and D as functions of x.

Equations (7) and (8) apply, in differential form, to batch chlorinations, in which the components vary with respect to time, and to x. In continuous chlorination, after a steady state is reached,

$$\frac{dB}{dA} = \frac{B}{A} \text{ and } \frac{dC}{dD} = \frac{C}{D}$$

It is clear therefore that batch chlorination will result in a different distribution of products than continuous chlorination, when compared at corresponding values of x. Likewise, continuous chlorination will be effected by the number of stages into which the reaction system is divided.

* In Equations (3)-(6), chlorine concentration has been omitted for the sake of simplicity. It cancels out in Equation (7) and (8).

We will now consider these cases in order.

Batch Chlorination

The linear homogeneous equation

$$\frac{dB}{dA} = \frac{B - rA}{rA} \quad (7)$$

integrates readily to

$$B = \frac{r}{r-1}(A^{1/r} - A) \quad (9)$$

Noting that, for benzene, D is negligible as long as A is appreciable,

$$\begin{aligned} 2A + 2B + 2C &= 2 \\ B + 2C &= x \\ \hline 2A + B &= 2 - x \end{aligned} \quad (10)$$

Combining with Equation (9),

$$x = 2 - \left(\frac{r-2}{r-1}\right)A - \left(\frac{r}{r-1}\right)A^{1/r} \quad (11)$$

$$B = \frac{r}{r-1}\left[\left(\frac{2-B-x}{2}\right)^{1/r} - \left(\frac{2-B-x}{2}\right)\right] \quad (12)$$

Differentiating Equation (12) with respect to x and setting

$$\frac{dB}{dx} = 0,$$

we obtain the maximum value of B_m as follows,

$$B_m = r^{-1/(r-1)} \quad (13)$$

at which maximum, the corresponding value of x is

$$x_m = 2 - B_m\left(1 + \frac{2}{r}\right) = 2 - r^{-1/r-1}\left(1 + \frac{2}{r}\right) \quad (14)$$

Equations (13) and (14) are evaluated in Table 4 and are plotted in Figures 1 and 2. Inspection reveals that for all values of r between 4 and 32, the maximum occurs within the narrow range of $x = 1.05$ to 1.07.

A single experimental analysis for B at this critical value for x is sufficient to determine r by means of Equation (13) or the plot, Figure 1. From this value of r, A, B, and C

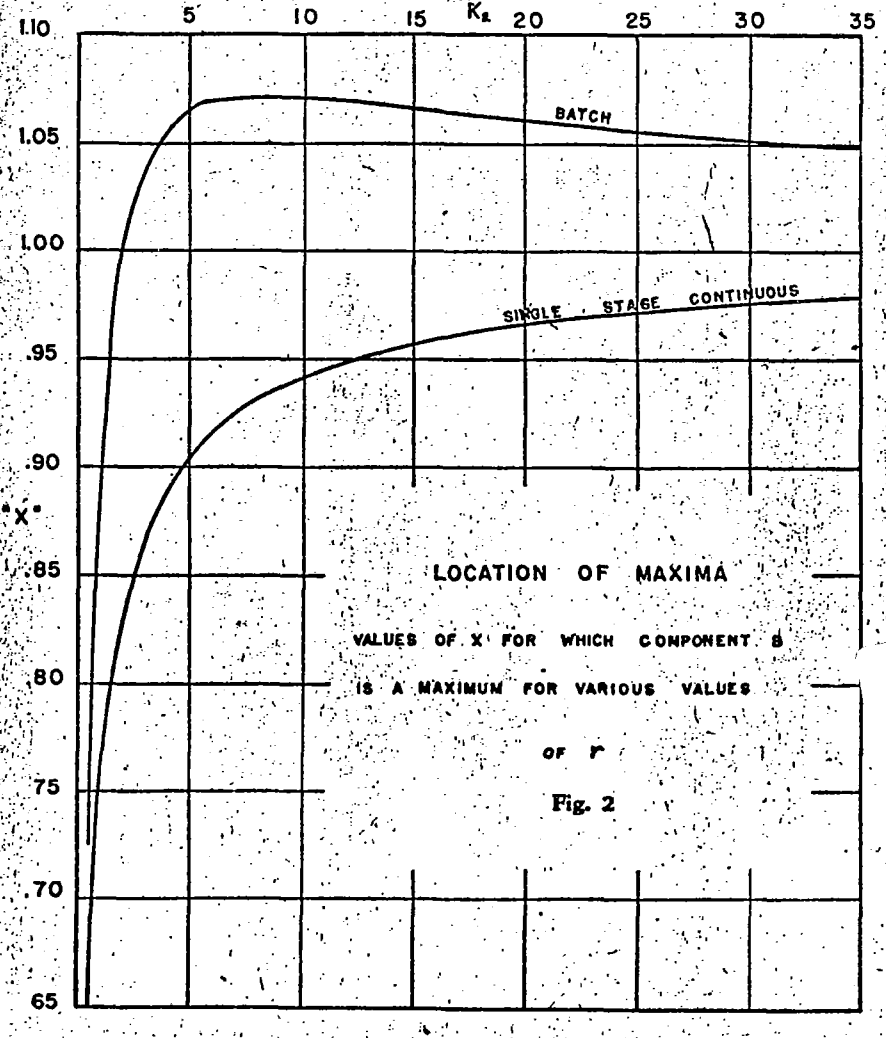

Fig. 2

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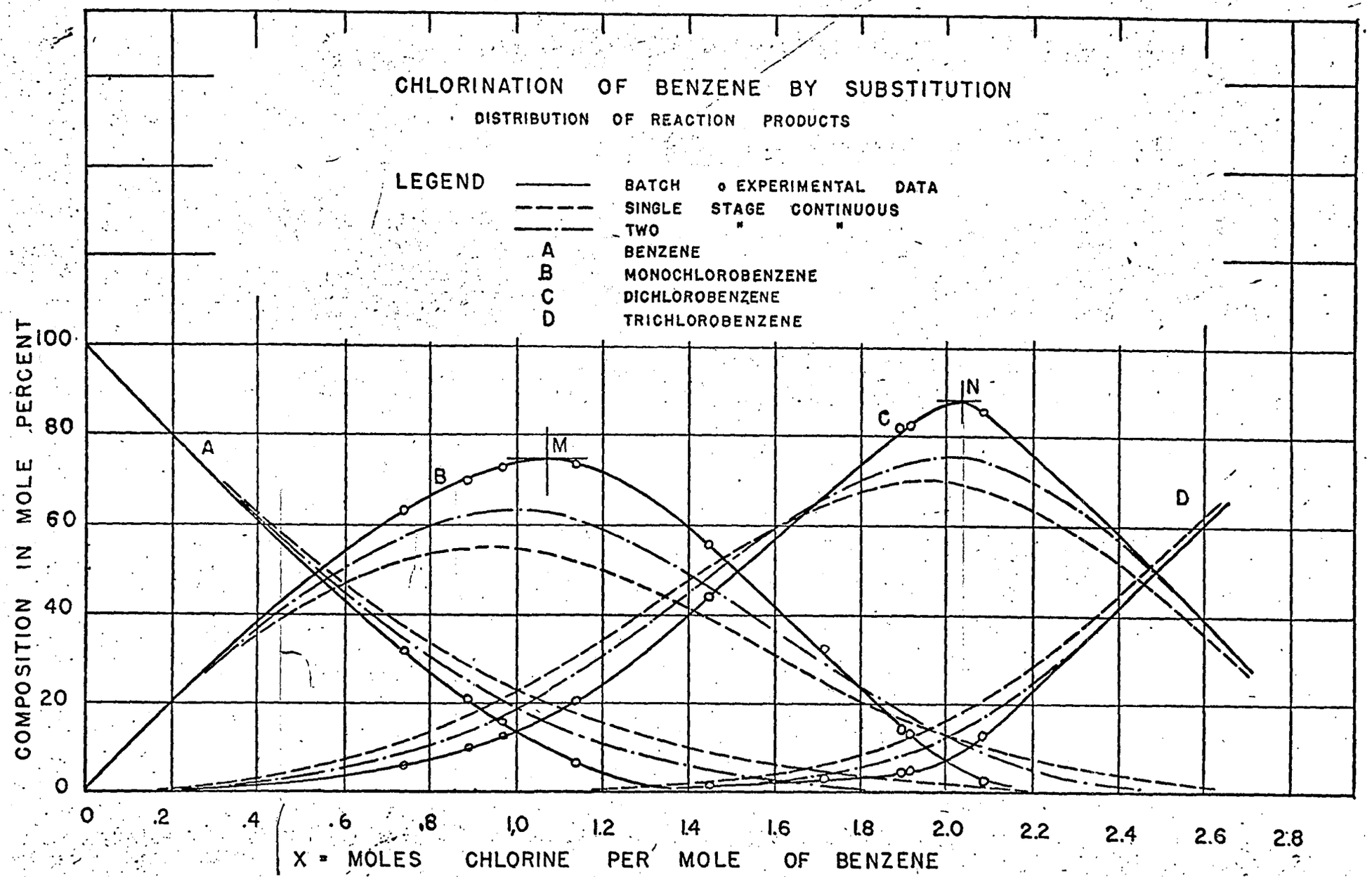

Fig. 3

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be readily calculated for all values of x up to about 1.5, or the place where D becomes appreciable.

Noting that when D becomes appreciable, A becomes insignificant,

$$\begin{aligned} B + C + D &= 1 \\ B + 2C + 3D &= x \\ \hline C + 2D &= x - 1 \end{aligned}$$

$$\begin{aligned} 2B + 2C + 2D &= 2 \\ B + 2C + 3D &= x \\ \hline B \qquad - D &= 2 - x \end{aligned}$$

whence

$$C = -1 - 2D + x \qquad (15)$$

$$B = 2 + D - x \qquad (16)$$

From (15),

$$\frac{dC}{dD} + 2 = \frac{dx}{dD} \qquad (17)$$

Substituting these values in the previous Equation (8)

$$\frac{dC}{dD} = \frac{sB - C}{C}$$

we obtain

$$\frac{dD}{dx} = \frac{x - 2D - 1}{(1-s)x + (s-2)D + (2s-1)} \qquad (18)$$

The above equation can be integrated by letting $v = \dfrac{D-1}{x-3}$

$$x = 3 + K\left[\frac{v + \dfrac{1}{s-2}}{v-1}\right]^{-\frac{s+1}{2(s-1)}} \cdot [1 + (s-3)v - (s-2)v^2]^{-\frac{1}{2}} \qquad (19)$$

In the above equation, K is the integration constant. We note that when $x = 0$, $D = 0$, and $v = \frac{1}{3}$, from which K can be readily calculated. If experimental data are available in the range of $x = 1.5$ to 2.5, it is preferable to determine K by substituting known values of D and x. In Equation (19) s is the relative reaction velocity of mono and di, and may be estimated by noting that where C is a maximum,

$$s = \frac{C_m}{B}$$

s can also be estimated with only slight error from the maximum value itself (*see* Figure 1).

Having thus determined K and s, the value of x at arbitrary values of D is readily calculated, and at these values of x, the values of B and C follow from Equations (15) and (16).*

Experimental Benzene was chlorinated in a 2 l. flask provided with excellent agitation, and a reflux condenser. A temperature of 55° C. was maintained. Anhydrous ferric chloride was used as a catalyst. The amount of chlorine introduced was judged by specific gravity. A series of runs was made, each to a definite specific gravity. The product from each run was settled, then fractionated in a 10-plate laboratory column. Product was divided into cuts so that in each cut not more than two components were present. Composition of each cut was estimated by specific gravity from previously determined density-composition plots for the system in question. In this way an accurate material balance was obtained. High boilers were driven over by the use of a "chaser," i.e., diphenyl. Results are judged accurate to 0.5%.

Table 2.—Single-Stage Continuous Chlorination of Benzene

Calculated Compositions

	$r = 8$			$s = 30$	
x	A	B	C	D	Method
0.301	.713	.274	.0136	.0000	Equation 25-30 incl.
0.485	.556	.404	.0404	.0001	Equation 25-30 incl.
0.720	.3845	.5125	.1025	.0007	Equation 25-30 incl.
1.074	.1990	.5301	.2654	.0045	Equation 25-30 incl.
1.358	.1095	.4375	.4375	.0151	Equation 25-30 incl.
1.615	.0558	.2974	.595	.0425	Equation 25-30 incl.
1.960	.0210	.1400	.700	.1400	Equation 25-30 incl.
2.232	.0085	.0620	.620	.3100	Equation 25-30 incl.
2.635	.0021	.0164	.3275	.6545	Equation 25-30 incl.

Table 3.—Two-Stage Continuous Chlorination of Benzene

Calculated Compositions, Second Stage

	$r = 8$				$s = 30$		
x	A	B	C	D	Method		
0.500	.535	.430	.035	....	Equation 38	$B_1 = .235$	$C_1 = .008$
.750	.337	.577	.086	....	Equation 38	$B_1 = .334$	$C_1 = .020$
1.000	.187	.627	.186	....	Equation 38	$B_1 = .416$	$C_1 = .041$
1.250	.094	.563	.343	....	Equation 38	$B_1 = .479$	$C_1 = .071$
1.522*	.039	.415	.531	.015	Equation 38	$B_1 = .520$	$C_1 = .110$
1.730†	.010	.288	.661	.041	Equation 42	$C_1 = .164$	$D_1 = 0$
2.000	....	.124	.752	.124	Equation 42	$C_1 = .228$	$D_1 = .002$
2.250	....	.039	.672	.289	Equation 42	$C_1 = .296.$	$D_1 = .004$
2.500	....	.007	.486	.507	Equation 42	$C_1 = .370$	$D_1 = .010$

* Originally calculated for $x = 1.5$, assuming no D, then adjusted.
† Originally calculated for $x = 1.75$, assuming no A, then adjusted.

Data are recorded in Table 1 and plotted as large circles in Figure 3. From these data the maximum concentration of monochlorobenzene was judged to be $B_m = 0.745$ at $x = 1.070$, from which $r = 8.0$ by Equation (13) or Figure 1.

The maximum concentration of dichlorobenzene was judged to be $C_m = .885$ at $x = 2.040$, from which $s = 30(\pm 1)$ by Equation (13) or Figure 1.

Theoretical Chlorination Curves: Using the above values of r and s, Equation (9) becomes

$$B = \frac{8}{7}(A^{\frac{1}{8}} - A) \qquad (20)$$

and Equation (19) becomes

$$x = 3 + K\left[\frac{v + .0357}{v - 1}\right]^{-31/58} [1 + 27v - 28v^2]^{-\frac{1}{2}} \qquad (21)$$

When $x = 2.0$, D observed = .065, whence $v = 0.935$. From this, we evaluate $K = -5.642$.

From the above, A, B, C, and D were calculated for values of x ranging from 0 to 2.5, and they are tabulated in Table 1 and plotted in Figure 3. It is noted that the observed experimental points in all cases lie on the theoretical curves, within limits of experimental error. The curves are not exact beyond $x = 2.5$ because of the appearance of tetrachlorobenzene, which has not been taken into account in the derivation of the formulas.

* In the foregoing analysis, Equations (7), (9), and (13) are strictly valid for all values of r. On the other hand, the simplifying assumptions made in deriving Equation (19) are valid only for values of r and s greater than about 4. When higher reaction products appear in appreciable percentages in the early stages of chlorination, r and s obviously have lower values, and a more rigorous mathematical treatment is indicated.

TABLE 4.—LOCATION OF MAXIMUM FOR COMPONENT B

	Batch		Single Stage Continuous	
r	B_m	x_m	B_m	x_m
0.5	.250	.750	.172	.656
1.0	.368	.896	.250	.750
2	.500	1.000	.343	.829
4	.630	1.055	.444	.889
9	.760	1.070	.563	.937
16	.832	1.065	.640	.960
25	.875	1.055	.695	.972
36	.903	1.047	.735	.980

Continuous Chlorination

Single Stage: The fundamental equations are

$$A+B+C+D=1 \quad (1)$$

$$B+2C+3D=x \quad (2)$$

$$\frac{B}{C}=\frac{rA-B}{B} \quad (22)$$

$$\frac{C}{D}=\frac{sB-C}{C} \quad (23)$$

The above set of simultaneous equations are most easily solved in terms of m, the allowable ratio of monochlorobenzene to dichlorobenzene in the reactor product. That is,

$$\text{Let } m=\frac{B}{C} \quad (24)$$

then

$$A=\frac{m(m+1)(sm-1)}{Q} \quad (25)$$

$$B=\frac{rm(sm-1)}{Q} \quad (26)$$

$$C=\frac{r(sm-1)}{Q} \quad (27)$$

$$D=\frac{r}{Q} \quad (28)$$

$$x=\frac{r[(sm-1)(m+2)+3]}{Q} \quad (29)$$

where

$$Q=m(m+1)(sm-1)+rm(sm-1)+r(sm-1)+r \quad (30)$$

Putting in m at values ranging from 20 to .05 compositions are obtained as listed in Table 2, and plotted in Figure 1.

It is readily seen that continuous chlorination results in a greater proportion of higher chlorinated products than batch chlorination, at all values of x. Continuous chlorination is therefore less favorable than batch chlorination at any given value of x, but can be made as favorable by chlorinating to some lower value of x and recycling the underchlorinated material after isolation of the desired material.

The maximum in the monochlorobenzene curve occurs at

$$B_m=\frac{r}{(r^{1/2}+1)^2} \quad (31)$$

at

$$x_m=\frac{r(1+2r^{-1/2})}{(r^{1/2}+1)^2}=1-\frac{1}{(r^{1/2}+1)^2} \quad (32)$$

The above maxima are evaluated in Table 4 and plotted in the lower curve of Figure 1.

No experimental data are offered in confirmation of these curves. However, in commercial operation of continuous liquid-phase chlorination plants making monochlorobenzene, the usual operating point is such that the chlorinator product contains about 40 Wt. % monochlorobenzene, 5 Wt. % dichlorobenzene, balance benzene. Such an operating point lies close to the predicted curve.

($x=.387$, $A=.645$, $B=.325$, $C=.031$)

Two-Stage: The simplifying assumption is now made that an equal amount of chlorine is introduced in each stage of the reaction system, while the liquid flows continuously through the first and second stage in series. It is further assumed that mixing is thorough, and the composition uniform and steady in each vessel. Denoting the stage by subscripts, Equations (22) and (23) become, for the second stage,

$$\frac{B_2-B_1}{C_2-C_1}=\frac{rA_2-B_2}{B_2} \quad (33)$$

$$\frac{C_2-C_1}{D_2-D_1}=\frac{sB_2-C_2}{C_2} \quad (34)$$

$$x_2=2x_1 \quad (35)$$

This set of equations is not so easily solved as those for single-stage chlorination. The biquadratic equations that result are moreover inconvenient to use. We therefore divide the solution into two cases:

Case 1—where D is negligible

Case 2—where A is negligible

Case 1—D negligible, for x up to about 1.5

$$A_2+B_2+C_2=1 \quad (36)$$

$$B_2+2C_2=x_2 \quad (37)$$

Combining Equations (36) and (37) with (33) and solving for B_2:

$$(2-r)B_2^2+(2x_2+2r-4C_1-2C_1r-4B_1)B_2+[rx_2^2-(2r+2C_1r)x+4C_1r]=0 \quad (38)$$

which can be written

$$P\cdot B_2^2+Q\cdot B_2+R=0 \quad (38a)$$

whence

$$B_2=\frac{-Q+\sqrt{Q^2-4PR}}{2P} \quad (39)$$

In solving this equation for a definite value of x_2, one has only to read off the values of B_1 and C_1 at $x_1=\frac{1}{2}x_2$, from the single-stage continuous curves which are plotted in Figure 1.

Case 2—A negligible, for x over 1.75

$$B_2+C_2+D_2=1 \quad (40)$$

$$B_2+2C_2+3D_2=x_2 \quad (41)$$

Combining Equations (40) and (41) with (34) and solving for D_2:

$$(s-2)D_2^2+[(3-s)x_2-(s+2)D_1+(2s-3-C_1)]D_2+[-x^2+(2+C_1+D_1s+D_1)x-(1+C_1+2D_1s+D_1)]=0 \quad (42)$$

which can be written

$$P'\cdot D_2^2+Q'\cdot D_2+R'=0 \quad (42')$$

whence

$$D_2=\frac{-Q'+\sqrt{Q'^2-4P'R'}}{2P'} \quad (43)$$

As before, read off C_1 and D_1 at $x_1=\frac{1}{2}x_2$ from the single-stage continuous curves already plotted in Figure 1.

In the overlapping region between Case 1 and Case 2, where $x=1.5$ to 1.75, the above equations are not strictly correct, but may be adjusted to take account of the small amount of D or A present respectively.

Calculated values of A, B, C, and D are tabulated in Table 3, and are plotted in Figure 3.

It is seen that two-stage chlorination gives a distribution of products intermediate between single-stage chlorination and batch chlorination. The method can be extended if desired, to calculate the distribution for a greater number of stages than two. The greater the number of stages, the closer the approach to batch distribution.