[Contribution from the Istituto di Chimica Industriale Politechnico of Milano]

The Distribution of Products in a Series of Consecutive Competitive Reactions

By G. Natta and E. Mantica

Received October 8, 1951

For series of successive competitive irreversible reactions of the type (1) general expressions have been derived giving the number of moles N_{ABN_i} of the various products as functions of the number of moles of the substance A reacted and of the constants k_2, k_3,. . .k_1,. . .,K_n (called distribution constants) expressed by the ratio of the velocity constants from reactions from 2 to n to that of the first reaction. If the intermediate products AB_r are recycled in the amounts ν_{AB_r} the general expressions above obtained are properly modified. The equations derived have been verified with available experimental data for some series of reactions such as the formation of alkanolamines and halogenation of methane (up to a maximum of $n = 4$). The results obtained are sufficiently satisfactory for the process without recirculation, while further verifications are being made for the process with recycling. Expressions above permit to determine the distribution of products as a function of the number of moles of the initial compound A reacted, without considering the reaction rate. By knowing a reaction rate constant (*e.g.*, that of the first reaction $A + B = AB$) it would be possible to calculate the number of moles which are formed at a given time for all the series of the reactions considered (ref. 7).

The kinetic study of a series of consecutive, competitive and irreversible reactions of the type

$$\begin{array}{lll} A & + B = AB & \\ AB & + B = AB_2 & \\ \cdots\cdots\cdots\cdots & & \quad (1) \\ AB_{i-1} & + B = AB_i & \\ \cdots\cdots\cdots\cdots & & \\ AB_{n-1} & + B = AB_n & \end{array}$$

is of both theoretical and practical interest as a number of industrial chemical processes can be represented by a series of equations of this type. Examples are the halogenations of saturated and unsaturated hydrocarbons, the reactions of alkylene oxides with water, alcohols, ammonia and amines, the alkylations of aromatic hydrocarbons and the esterifications of glycols with polyacids. Also some processes of formation of organic macromolecules follow series of reactions which can be referred to type (1); in particular if $A = B$, we have the reactions of polymerization, for example, those of the vinyl monomers.

The polymerization reactions however are not suitable for the study of the distribution of products as the high chain growth velocity rapidly leads to such complex molecules as to prevent the identification and measurement of the single polymers. On the other hand, the other reactions mentioned above allow more information to be obtained as the difficulties encountered in the isolation of the products, although still considerable, may often be overcome. There are, however, few experimental and theoretical papers on the variation of the composition of a mixture of products as function of the ratio between the initial amounts of the reactants. Still fewer are the papers on the possibility of recycling one or more intermediate products in order to modify, in the desired direction, the final distribution of the products, eliminating those of lesser interest and obtaining a higher yield of those desired.

Previous Works.—Ostwald[1] was the first to make a kinetic study of series of consecutive reactions and the first to attempt to overcome the difficulties involved in integrating the differential rate equations by expressing the concentrations of the various molecular species not as a function of time, but as a function of the reaction products. Later Rakowski[2] solved, in a satisfactory manner, the problem for series of monomolecular consecutive reactions or reactions which may be referred to this type. For a long time, the existence of even one bimolecular stage in the series frustrated the attempts to solve the differential rate equations and, even as recently as 1941, Hirniak[3] was able to declare the non-existence of satisfactory integration formulas of general validity. However, with the assumption of restrictive hypotheses it has been possible to solve the differential equations relating to series of two bimolecular reactions. For example, assuming the second reaction to be very rapid with respect to the first and by means of graphical integration, Natta and Pastonesi[4] in 1937 studied the synthesis of methanol from carbon monoxide and hydrogen as a series of two consecutive, irreversible, bimolecular reactions.

Notation

In 1943 Fuoss[5] was the first to treat four consecutive, concurrent, irreversible reactions and in 1945 Natta on his own[6] and with Simonetta[7] developed very general expressions valid for any number n of reactions. Other works published in recent years on this subject are those of Potter and MacDonald,[8] Potter and McLaughlin,[9] Pshezhetskii and Rubinstein,[10] Ferrero, Berbé and Flamme,[11] Berbé[12] and McMullin.[13] Finally we mention the work of Eldrige and Piret[14] on a system of continuous flow stirred-tank reactors, giving formulas for consecutive reactions, and a recent paper by Natta and Mantica[15] whose results will now be summarized.

---

(1) W. Ostwald, "Lehrbuch der allgemeine Chemie," W. Engelmann, Leipzig, 1902, 2 Aufl., Bd.2, 2 Teil, page 277.

(2) A. Rakowski, *Z. physik. Chem.*, **57**, 321 (1907).

(3) J. Hirniak, *Acta Physicochim.* (*U.R.S.S.*), **14**, 613 (1941); *C. A.*, **37**, 2643⁴ (1943).

(4) G. Natta and G. Pastonesi, *Chimica e Industria* (*Milan*), **19**, 313 (1937).

(5) R. M. Fuoss, This Journal, **65**, 2406 (1943).

(6) G. Natta, *Rend. ist. Lombardo Sci.*, **78**, No. 1, 307 (1945).

(7) G. Natta and M. Simonetta, *ibid.*, **78**, No. 1, 336 (1945).

(8) C. Potter and W. C. MacDonald, *Can. J. Research*, **25B**, 415 (1947); *C. A.*, **42**, 21b (1948).

(9) C. Potter and R. R. McLaughlin, *ibid.*, **25B**, 405 (1947); *C. A.*, **42**, 441i (1948).

(10) S. Ya. Pshezhetskii and R. N. Rubinstein, *J. Phys. Chem. U.S.S.R.*, **21**, 659 (1947); *C. A.*, **42**, 2162f (1948).

(11) P. Ferrero, F. Berbé and L-R. Flamme, *Bull. soc. chim. Belges*, **56**, 349 (1947).

(12) F. Berbé, *Chimie et industrie*, **63**, No. 3 bis, 492 (1950).

(13) R. B. MacMullin, *Chem. Eng. Progress*, **44**, 183 (1948).

(14) J. W. Eldridge and E. L. Piret, *ibid.*, **46**, 290 (1950).

(15) G. Natta and E. Mantica, *Gazz. chim. ital.*, **81**, 164 (1951).

A,B, reactants
AB, AB_2,. . .AB_i,. . .,AB_n, reaction products
AB_r, recycled intermediate reaction product
N_{A_0}, number of moles of reactant A initially present
N_A, number of moles of reactant A present
N_B, number of moles of reactant B present
N_{AB_i}, number of moles of product AB_i present
ν_{AB_r}, number of moles of product AB_r recycled to feed
x_i, number of moles of product AB_i formed
K_i, velocity constant of *i*th reaction
$k_i = K_i/K_1$, distribution constant of *i*th reaction
$(\alpha_i)_n$, *i*th coefficient in the expression of x_n in processes without recirculation of intermediate products
$(\beta_i)_n$, *i*th coefficient in the expression of x_n in processes with recycling of intermediate products

Derivation of Equations

The distribution of the products in a series of consecutive concurrent irreversible reactions carried out in a batch process: Except when all the reactions are irreversible and of the second order, the expression for the reaction rate is

$$dx_n/dt = K_n(x_{n-1} - x_n)N_B \qquad (2)$$

From the ratio of two equations of type (2) there results

$$\frac{dx_n}{dx_m} = \frac{K_n}{K_m} \times \frac{x_{n-1} - x_n}{x_{m-1} - x_m} \qquad (3)$$

The case having the greatest practical interest is that in which $m = 1$ and the following expression is obtained

$$\frac{dx_n}{dx_1} = k_n \frac{x_{n-1} - x_n}{N_{A_0} - x_1} \qquad (4)$$

where N_{A_0} has been substituted for x_0 and $k_n = K_n/K_1$.

Equation 4 is a linear expression which is easily integrated giving the following value for x_n

$$x_n = N_{A_0}\left[1 + (\alpha_1)_n\left(\frac{N_{A_0} - x_1}{N_{A_0}}\right) + (\alpha_2)_n\left(\frac{N_{A_0} - x_1}{N_{A_0}}\right)^{k_2} + \cdots\cdots + (\alpha_n)_n\left(\frac{N_{A_0} - x_1{}^{k_2}}{N_{A_0}}\right)^{k_n}\right] \qquad (5)$$

where

$$(\alpha_i)_n = \frac{k_2k_3\cdot\cdots\cdot k_n}{k_i(k_i - 1)(k_i - k_2)\cdots(k_i - k_n)}(-1)^n \qquad (6)$$

and the term $k_i - k_i$ at the denominator is to be cancelled.

If the quantities N_{A_0}, x_1, x_2, $\cdots$, x_{n-1}, x_n are known, the distribution of products may be calculated with the equations

$$\begin{aligned} N_A &= N_{A_0} \rightarrow x_1 \\ N_{AB} &= x_1 - x_2 \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ N_{AB_i} &= x_i - x_{i+1} \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ N_{AB_n} &= x_n \end{aligned} \qquad (7)$$

The distribution of products in a series of consecutive concurrent irreversible reactions carried out in continuous processes: In continuous processes (continuous stirred tank reactor) with ideal mixing the equations developed above can be simplified further. In fact in this case the equation (3) given above leads to the following value for x_n if we consider the case in which $m = 1$ and bear in mind that all the integration constants are zero

$$x_n = \frac{k_2k_3\cdots\cdot k_n x^n{}_1}{[(N_{A_0} - x_1) + k_2x_1][(N_{A_0} - x_1) + k_3x_1]\cdots[(N_{A_0} - x_1) + k_nx_1]} \qquad (8)$$

The numbers of moles N_{AB_i} present at the end of reaction are still given by equations (7).

The distribution of products in a series of consecutive concurrent irreversible reactions carried out in batch processes with recirculation of intermediate products: If the reactor is fed with intermediate products recycled (generically represented by AB_r) in addition to reactants A and B the equation (3) is modified as

$$\frac{dx_n}{dx_m} = k_n \frac{x_{n-1} + \nu AB_{n-1} - x_n}{x_{m-1} + \nu AB_{m-1} - x_m} \qquad (9)$$

If $m = 1$, substituting again N_{A_0} for x_0 and suppressing $\nu_{AB_{m-1}}$ there follows

$$\frac{dx_n}{dx_1} = k_n \frac{x_{n-1} + \nu AB_{n-1} - x_n}{N_{A_0} - x_1} \qquad (10)$$

which is another easily integrated linear equation. The expression of x_n resulting from integration of (10) is

$$x_n = N_{A_0}\left[1 + (\alpha_1)_n\left(\frac{N_{A_0} - x_1}{N_{A_0}}\right) + (\alpha_2)_n\left(\frac{N_{A_0} - x_1}{N_{A_0}}\right)^{k_2} + \cdots\cdots\cdots + (\alpha_n)_n\left(\frac{N_{A_0} - x_1}{N_{A_0}}\right)^{k_n}\right] + \sum_1^{n-1} r\,\nu AB_r\left[1 + (\beta_{r+1})_n\left(\frac{N_{A_0} - x_1}{N_{A_0}}\right)^{k_{r+1}} + \cdots \cdots + (\beta_n)_n\left(\frac{N_{A_0} - x_1}{N_{A_0}}\right)^{k_n}\right] \qquad (11)$$

where the α coefficients are expressed as in (6), while the coefficients β are given by

$$(\beta_i)_n = \frac{k_{r+1}\,k_{r+2}\cdots k_n}{k_i(k_i - k_{r+1})(k_i - k_{r+2})\cdots(k_i - k_n)}(-1)^{n-r} \qquad (12)$$

and the term $k_i - k_i$ is suppressed in the denominator.

Knowing the values of N_{A_0}, x_1, x_2, $\ldots$, x_n, and of ν_{AB_r} the distribution of products is given by the equations

$$\begin{aligned} N_A &= N_{A_0} - x_1 \\ N_{AB} &= x_1 + \nu_{AB} - x_2 \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ N_{AB_i} &= x_1 + \nu_{AB_i} - x_{i+1} \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ N_{AB_n} &= x_n \end{aligned} \qquad (13)$$

The distribution of products in a series of consecutive irreversible reactions carried out in continuous processes with recirculation of intermediate products: For continuous processes results a modification of the conditions of integration of the equations (9) and (10). In particular from equation (10) the following expression is derived for x_n, bearing in mind that the integration constants are all zero

$$x_n = \frac{k_2\,k_3\cdot\cdots\cdot k_nx_1{}^n}{[(N_{A_0} - x_1) + k_2x_1][(N_{A_0} - x_1) + k_3x_1]\cdot\cdots\cdot[(N_{A_0} - x_1) + k_nx_1]} + \sum_1^{n-1}{}_r \frac{k_{r+1}k_{r+2}\cdots k_nx_1{}^{n-r}\,\nu AB_r}{[(N_{A_0} - x_1) + k_{r+1}x_1][(N_{A_0} - x_1) + k_{r+2}x_1]\cdots(N_{A_0} - x_1) + k_n]} \qquad (14)$$

The distribution of the products is still given by equations (13).

Verification of the Foregoing Equations

The distribution of products in a series of consecutive concurrent irreversible reactions carried out in batch processes: (*a*) *The*

Chlorination of Methane.—The thermal chlorination of methane with gaseous chlorine can be represented by the series of reactions

$$\begin{aligned} &CH_4 + Cl_2 = CH_3Cl + HCl + 23850 \text{ cal.}\\ &CH_3Cl + Cl_2 = CH_2Cl_2 + HCl + 23575 \text{ cal.}\\ &CH_2Cl_2 + Cl_2 = CHCl_3 + HCl + 23860 \text{ cal.}\\ &CHCl_3 + Cl_2 = CCl_4 + HCl + 24280 \text{ cal.}\end{aligned}$$

In addition to these we may consider the explosive reaction between methane and chlorine

$$CH_4 + 2Cl_2 = C + 4HCl + 69648 \text{ cal.}$$

and the reactions of pyrolysis of the intermediate products. However, in normal working conditions with a low Cl_2/CH_4 ratio, the importance of secondary processes can be limited. To verify the applicability of equations (5) and (7) developed above, we have used the data given by Hirschkind[16] which are in good agreement with preceding data by McBee, Hass, Neher and Strickland[17] and by Wilson and Howland.[18]

In Table I we have collected the values of the distribution constants k_2, k_3 and k_4 obtained by introducing into equations (5) the experimental values x_1, x_2, x_3 and x_4 and solving the expressions thus obtained for k_n. Using the values $k_2 = 2.3$, $k_3 = 1.4$ and $k_4 = 0.45$, the numbers of moles of the various products have been calculated with the results shown in Fig. 1 and in Tables A, B and C.[19] The calculated values are compared with the experimental values as shown in the same tables.

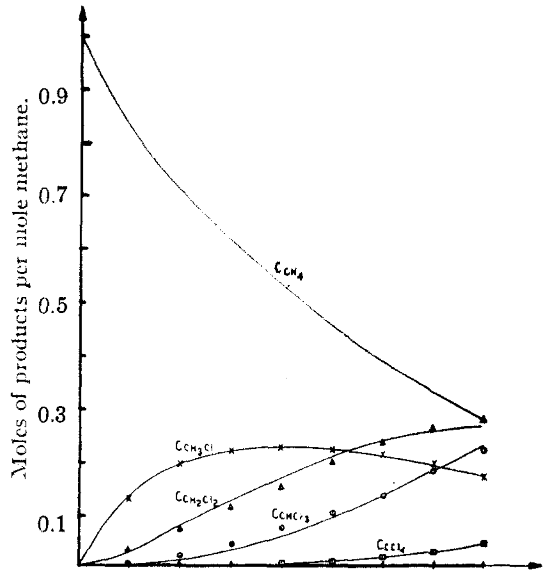


Fig. 1.—Distribution of products in thermal chlorination of methane: ———, calcd. curves; X O ▲ ▣, exptl. values.

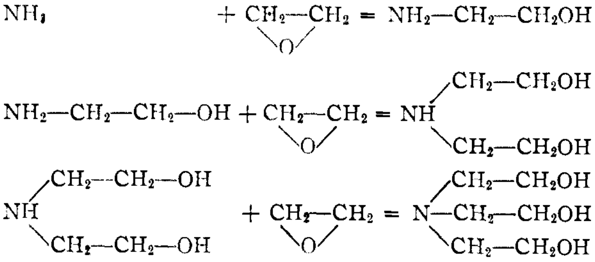
(β) *The Synthesis of Ethanolamines.*—Ethylene oxide reacts with a water solution of ammonia

TABLE I

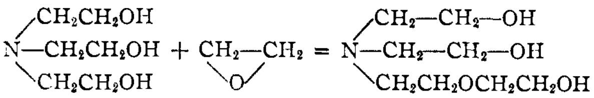
DISTRIBUTION CONSTANTS k_2, k_3 AND k_4 FOR THERMAL CHLORINATION OF METHANE AS FUNCTIONS OF RATIO Cl_2 REACTED/CH_4

Cl_2 reacted/ CH_4	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
k_2	2.95	2.75	2.28	2.30	2.30	2.23	2.23	2.33
k_3	2.0	2.05	2.05	1.90	1.60	1.45	1.35	1.40
k_4	..	..	..	0.42	0.42	0.45	0.44	0.46

giving simultaneously the three ethanolamines according to the series of reactions



A fourth reaction



is also possible but its rate is much slower than that of the foregoing so that this fourth step, and any eventual successive steps, can be neglected without appreciable error.

The data used for our verification are those of Ferrero, Berbé and Flamme,[11] which are in good agreement with those of Potter and McLaughlin.[9] In Table II are given the values of the distribution constants k_2 and k_3 obtained by introducing the above mentioned experimental values into equation (5). With $k_2 = 4.5$ and $k_3 = 3.1$ and the values given in Tables D and E and in Fig. 2 we have

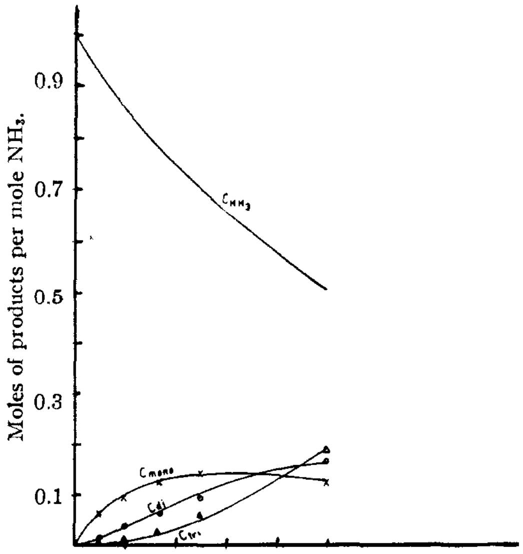


Fig. 2.—Distribution of products in ethanolamines synthesis. Batch process at 15°; ———, calcd. curves; X ⊙ ▲, exptl. values.

---

[16] W. Hirschkind, *Ind. Eng. Chem.*, **41**, 2749 (1949).

[17] E. T. McBee, H. B. Hass, C. M. Neher and H. Strickland, *ibid.*, **34**, 296 (1942).

[18] M. J. G. Wilson and A. H. Howland, *Fuel*, **28**, 127 (1949).

[19] For tables indicated by letter, order Document 3575 from American Documentation Institute, 1719 N. Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.50 for photocopies (6 × 8 inches) readable without optical aid.

calculated the distribution of the products and compared the results with the experimental values.

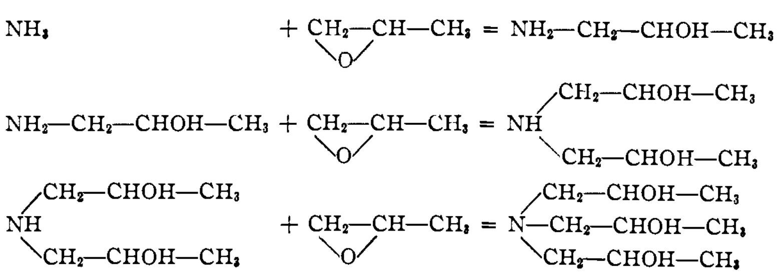
TABLE II

DISTRIBUTION CONSTANTS k_2 AND k_3 AS FUNCTIONS OF RATIO ETHYLENE OXIDE/NH_3 IN ETHANOLAMINES SYNTHESIS

Batch process at 15°

C_2H_4O/NH_3	0.1	0.2	0.333	0.5	1
k_2	5.05	5.45	4.8	4.4	4.55
k_3	4.60	4.40	4.10	4.10	3.05

(γ) *The Synthesis of Isopropanolamines.*—Propylene oxide also reacts with water solutions of ammonia giving simultaneously the three isopropanolamines according to the series of reactions



$$NH_3 + \underset{\diagdown O \diagup}{CH_2—CH}—CH_3 = NH_2—CH_2—CHOH—CH_3$$

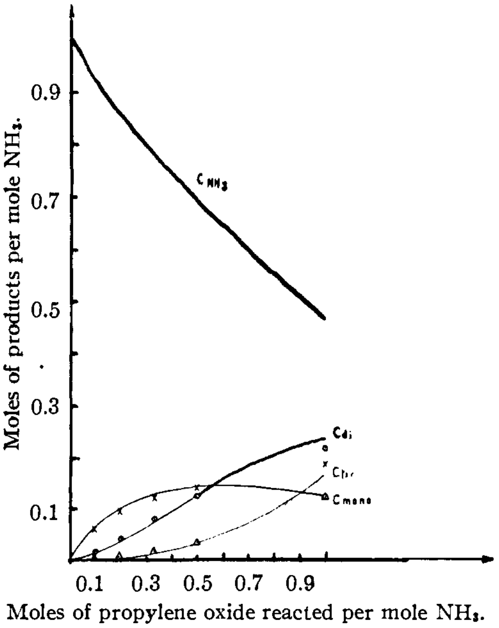
$$NH_2—CH_2—CHOH—CH_3 + \underset{\diagdown O \diagup}{CH_2—CH}—CH_3 = NH\begin{cases}CH_2—CHOH—CH_3\\CH_2—CHOH—CH_3\end{cases}$$

$$NH\begin{cases}CH_2—CHOH—CH_3\\CH_2—CHOH—CH_3\end{cases} + \underset{\diagdown O \diagup}{CH_2—CH}—CH_3 = N\begin{cases}CH_2—CHOH—CH_3\\CH_2—CHOH—CH_3\\CH_2—CHOH—CH_3\end{cases}$$

The successive addition of propylene oxide to triisopropanolamines giving ethers of this product is of minor interest owing to its very different reaction rate.

The data used for our verification were taken from the kinetic study by Berbé[12] on the synthesis of the isopropanolamines.

In Table III are given the values of the distribution constants calculated according to the usual method, while in Tables F and G and in Fig. 3 they are compared with the experimental values. The calculated values were obtained with k_2 = 4.4 and k_3 = 1.7.



Moles of propylene oxide reacted per mole NH_3.

Fig. 3.—Distribution of products in isopropanolamines synthesis. Batch process at 15°: ———, calcd. curves; X ⊙ △, exptl. values.

TABLE III

DISTRIBUTION CONSTANTS k_2 AND k_3 AS FUNCTIONS OF RATIO PROPYLENE OXIDE/NH_3 IN ISOPROPANOLAMINES SYNTHESIS

Batch process at 15°

Propylene oxide/NH_3	0.066	0.1	0.2	0.333	0.5	1
k_2	5.85	5.85	5.45	5	4.4	2.85
k_3	4.15	3	2.5	2.15	1.70	1.60

The distribution of products in a series of consecutive concurrent irreversible reactions carried out in continuous processes: The applicability of equations (8) has been verified with the experimental data contained in the above mentioned paper by Ferrero, Berbé and Flamme.[11] In Table IV are given the values calculated for the distribution constants k_2 and k_3 and these are compared with the values calculated above for the batch process (given in brackets). Assuming k_2 = 4.7 and k_3 = 4.8 the distribution of the various products have been calculated with equations (8) and (7). The results are given in Tables H and I and in Fig. 4 and are compared with the experimental data.

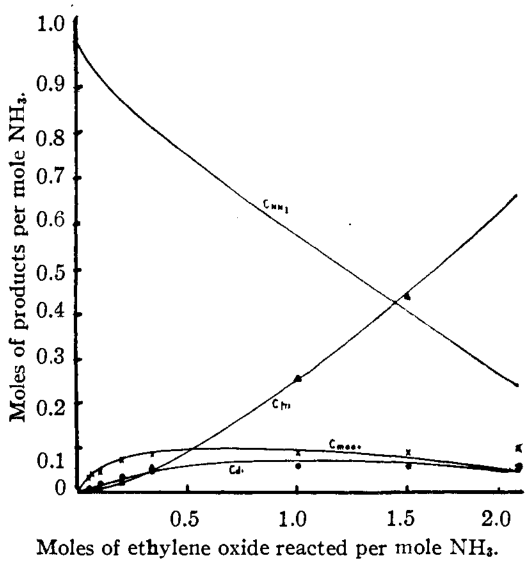
The distribution of products in a series of consecutive concurrent irreversible reactions carried out in batch processes with recirculation of intermediate products. (α) *The Synthesis of Ethanolamines with Recirculation of Monoethanolamine.*—

TABLE IV

DISTRIBUTION CONSTANTS k_2 AND k_3 AS FUNCTIONS OF RATIO ETHYLENE OXIDE/NH_3 IN ETHANOLAMINES SYNTHESIS

Continuous process at 15°. The values in brackets are the constants k_2, k_3 for the batch process.

Ethylene oxide/NH_3	0.05	0.066	0.1	0.2	0.333	1	1.5	2
k_2	4.56	5.23	6.09 (5.05)	5.45 (5.45)	5.07 (4.8)	5.12 (4.55)	3.81	2.08
k_3	3.80	5.95	4.98 (4.60)	4.15 (4.40)	4.87 (4.10)	6.23 (3.05)	5.08	3.15



Moles of ethylene oxide reacted per mole NH_3.

Fig. 4.—Distribution of products in ethanolamines synthesis. Continuous process at 15°: ———, calcd. curves; X ⊙ ▲, exptl. values.

The experimental data for the verification have been taken once more from the paper by Ferrero, Berbé and Flamme.[11] The two cases of recycling monoethanolamine and diethanolamine have been considered separately.

Table V gives the values of the distribution constants k_2 and k_3 calculated in the usual manner while the values of the same constants obtained in processes without recirculation are indicated in brackets.

TABLE V

DISTRIBUTION CONSTANTS k_2 AND k_3 AS FUNCTIONS OF RATIO ETHYLENE OXIDE/NH_3 IN ETHANOLAMINES SYNTHESIS

Batch process at 15° with recycling of 0.164 mole of monoethanolamine per mole NH_3 fed to process. The values in brackets apply to the batch process without recycle

Ethylene oxide/NH_3	0.1	0.2	0.333
k_2	5.45	5.52	4.80
	(5.05)	(5.45)	(4.80)
k_3	4.80	4.22	4.38
	(4.60)	(4.40)	(4.10)

(β) *The Synthesis of Ethanolamines with Recirculation of Diethanolamine.*—Table VI applies to the calculation of distribution constants k_2 and k_3 supposing the recycled product to be diethanolamine. Here again these values are compared with those of the constants k_2 and k_3 for batch processes without recycling, which are given in brackets.

TABLE VI

DISTRIBUTION CONSTANTS k_2 AND k_3 AS FUNCTIONS OF RATIO ETHYLENE OXIDE/NH_3 IN ETHANOLAMINES SYNTHESIS

Batch process at 15° with recycling of the indicated amounts of diethanolamine per mole NH_3 fed to process. The values in brackets apply to the batch process without recycle

Ethylene oxide/NH_3	0.1	0.2	0.333
Diethanolamine recycled, moles per mole NH_3	0.045	0.070	0.0833
k_2	n.d.	3.7	5.65
		(5.45)	(4.80)
k_3	n.d.	4.5	5.25
		(4.40)	(4.10)

The distribution of products in a series of consecutive concurrent irreversible reactions carried out in continuous processes with recirculation of intermediate products: Equations (13) and (14) have also been verified with the experimental data of Ferrero, Berbé and Flamme,[11] and the results given in Table VII apply to the recycling of monoethanolamine while those given in Table VIII apply to the recycling of diethanolamine. In both cases the values obtained for k_2 and k_3 in continuous processes without recycling are given in brackets.

TABLE VII

DISTRIBUTION CONSTANTS k_2 AND k_3 AS FUNCTIONS OF RATIO ETHYLENE OXIDE/NH_3 IN ETHANOLAMINES SYNTHESIS

Continuous processes at 15° with recycling of 0.131 mole of monoethanolamine per mole NH_3 fed to process

Ethylene oxide/NH_3	0.1	0.2	0.333
k_2	5.97	5.67	6.88
	(6.09)	(5.45)	(5.07)
k_3	4.45	4.17	5.90
	(4.98)	(4.15)	(4.87)

TABLE VIII

DISTRIBUTION CONSTANTS k_2 AND k_3 AS FUNCTIONS OF RATIO ETHYLENE OXIDE/NH_3 IN ETHANOLAMINES SYNTHESIS

Continuous process at 15° with recycling of the indicated amounts of diethanolamine per mole NH_3 fed to process

Ethylene oxide/NH_3	0.066	0.1	0.2	0.333
Recycling diethanolamine moles per mole NH_3	0.0287	0.033	0.046	0.060
k_2	n.d.	4.05	5.17	5.16
		(6.09)	(5.45)	(5.07)
k_3	9.08	11.72	8.62	8.05
		(4.98)	(4.15)	(4.87)

Comment.—It can be seen from the above verifications of the calculated distributions of products in a series of consecutive concurrent reactions that, in some instances, there is fair agreement with experimental data (thermal chlorination of methane, synthesis of ethanolamines by batch process), while in other instances there may be considerable discrepancy. These deviations seem to be greater in the case of reactions in the liquid phase and may partly be due to the fact that the molar concentrations have been considered instead of the activities of the species present. In the case in question the two quantities certainly differ appreciably. Another cause of deviation is the eventual inaccuracy of the experimental data which affects, to a greater or lesser extent, all the calculated values.

The fact remains, however, that deviations to a smaller extent and in a preferential direction are noticed also in the thermal chlorination of methane in the gas phase.

In general, there will be noticed a decrement, within certain limits, with the increase of the reacted amounts of the values of the single distribution constants in a manner that must be attributed to some common cause. We believe that a possible explanation may be found admitting that molecules may exist in an activated state at the instant in which they are formed. As these possess a greater reactivity they should increase the reaction rate of every molecular species. In consequence higher values should be reached when the ratio between the activated molecules which are being formed and the pre-existing molecules is maximum. Only a greater abundance of experimental data can resolve the present uncertainties and for this purpose researches have been undertaken on some series of reactions of Type (I).

MILANO, ITALY