

solutions is due to the irreversible reduction of Cu^{+2} .

Apparently, the rate of formation of CuOH^+ is affected by the presence of an adsorbed film. Experimental results with various Tritons of different molecular weights⁷ (Fig. 8) show that the effectiveness in decreasing the rate of formation of CuOH^+ decreases with increasing molecular weight. The half-wave potential of the second wave is shifted to slightly more negative values with decreasing molecular weight. In view of the fact that the solubility of Tritons in water increases with increasing molecular weight, it is considered that the adsorbed layer of Tritons of higher molecular weight is less compact and is more hydrated. Apparently the compactness of the adsorbed layer greatly affects the rate of formation of CuOH^+ and the rate of electron transfer through the adsorbed

layer, as well as the rate of penetration of Cu^{+2} ions (compare the height of the first waves in presence of Triton X-100 and X-305, Figs. 3, 4 and 8).

The small kinetic current in the presence of dodecylamine cations in the sodium perchlorate solution (Fig. 9) is also attributed to the slow formation of CuOH^+ . Apparently, the film of dodecylamine perchlorate is of a more compact nature than that of Tritons, and the kinetic current in the presence of the former is much smaller than that in the presence of Tritons.

Acknowledgment.—Preliminary experiments related to the present study have been carried out at the University of Minnesota in collaboration with Prof. T. Fujinaga of Kyoto University and Dr. I. M. Issa of the University of Cairo.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Equilibrium Polymerization of ϵ -Caprolactam

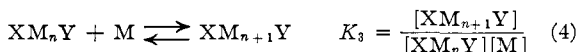
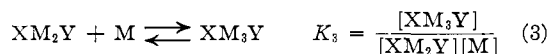
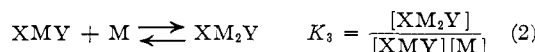
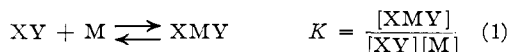
BY A. V. TOBOLSKY AND A. EISENBERG

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A theory applicable to the equilibrium polymerization of ϵ -caprolactam in presence of water is presented and compared with experimental results. The agreement is excellent for low water concentrations. A single formula is developed correlating the initiator concentration (between 0.1 and 1.0 moles/kg.) with the number average degree of polymerization for the temperature range investigated, and the ΔH^0 values for the initiation and propagation steps are given.

I. Introduction

It was pointed out previously^{1,2} that certain types of equilibrium polymerization could be described by the sets of equations



Where XY (subsequently to be written as X) is the initiator (which can be both ionic or non-ionic), M is the monomer and K and K_3 the equilibrium constants for initiation and propagation, respectively. These equations were shown to yield the following results in terms of experimentally determinable quantities¹

$$\bar{P}_n = \frac{1}{1 - K_3[\text{M}]} \quad (5)$$

$$[\text{M}_0] = [\text{M}](1 + K[\text{X}]\bar{P}_n^2) \quad (6)$$

$$[\text{X}_0] = [\text{X}](1 + K[\text{M}]\bar{P}_n) \quad (7)$$

$$\bar{P}_n = \frac{[\text{M}_0] - [\text{M}]}{[\text{X}_0] - [\text{X}]} \quad (8)$$

Where P_n (subsequently to be written as P) is the number average degree of polymerization, $[\text{M}]$ is the equilibrium concentration of monomer and $[\text{X}_0]$ and $[\text{M}_0]$ the initial concentration of initiator and monomer, respectively.

(1) A. V. Tobolsky, *J. Poly. Sci.*, **25**, 220 (1957).

(2) A. V. Tobolsky, *ibid.*, **31**, 122 (1958).

It has been known for a long time that conversion of ϵ -caprolactam (CL) into products of the Nylon 6 polyamide type leads to a state of equilibrium with definite amounts of the initial components. This equilibrium system has been widely investigated in the past, and data describing it are available in the literature. Here an attempt is made to represent the data obtained by two sources^{3,4} over a sufficiently wide range of variables (temperature and initiator concentration) in terms of the theory outlined above in equations 1 through 8.

II. Treatment of Data

The experimental data available in the literature are of the type: a known mole ratio m of H_2O to CL is charged in a vessel; the vessel is brought to a definite temperature and polymerization is carried out to equilibrium. When equilibrium is reached, the value of P and $[\text{M}]$ are determined.

We shall use the concentration units of moles/kilogram; we use this rather than moles/liter because there is a density change when CL converts to polymer.

It is necessary to be able to compute $[\text{M}_0]$ and $[\text{X}]$ from the initial mole ratio m . This is accomplished as indicated

$$[\text{X}_0] = \frac{1000m}{18m + 113} \quad (9a)$$

$$[\text{M}_0] = [\text{M}_{00}] - \frac{[\text{M}_{00}]}{[\text{X}_{00}]}[\text{X}_0] = 8.85 - 0.1594[\text{X}_0] \quad (9b)$$

(3) F. Wiloth, *Z. Physik. Chem., N. F.*, **4**, 66 (1955).

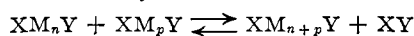
(4) P. F. Van Velden, G. M. Van Der Want, D. Heikens, Ch. A. Kruissink, P. H. Hermans, A. J. Staveman, *Recueil*, **74**, 1376 (1956).

where the molecular weight of H_2O is 18 and that of CL is 113, $[M_0]$ is equal to the moles per kilogram of pure caprolactam (= 8.85) and $[X_0]$ is equal to the moles per kilogram of pure water (= 55.5). The relation (9b) is an obvious consequence of our choice of concentration units.

From a set of values P , $[M]$, $[X_0]$ and $[M_0]$ the constants K and K_3 can be computed by

- (A) K_3 is calculated from equation 5
 (B) $[X]$ is calculated from equation 8
 (C) K is calculated from equation 7 and 8
- $$K = \frac{[X_0] - [X]}{[X][M]P} = \frac{[M_0] - [M]}{[X][M]P^2} \quad (7a)$$

The self-consistency of the data thus obtained may be checked by use of equation 6. It should be pointed out that in the theory as outlined above, the presence of cyclic oligomers is not taken into consideration. They are present in the equilibrium mixture to an extent of at most 5%,⁴ and since the size of the rings varies just as does the length of the open chains, they are assumed not to change the value of P which is normally obtained for the straight chains only. Also reactions of the type



if present, are assumed not to change the number average molecular weight of the polymer at equilibrium since equilibrium properties should not depend on the detailed method by which equilibrium is reached.

Only one point (one value for P , $[X_0]$, $[M_0]$ and $[M]$) is necessary in principle to calculate the equilibrium constants; however, in all three cases investigated, several such points were taken to determine the constancy of K and K_3 .

Once K and K_3 are known for one specific set of data, the curve of P vs. $[X_0]$ (which is perhaps of maximum interest) corresponding to these constants may be calculated as follows: (A) a convenient value for P is assumed and the corresponding value of $[M]$ is calculated from equation 5; (B) the value of $[X_0]$ is then calculated by the simultaneous solution of equations 7b, 8 and 9b

$$[X] = \frac{[X_0]}{1 + K[M]P} \quad (7b)$$

$$P = \frac{[M_0] - [M]}{[X_0] - [X]} = \frac{[M_0] - [M]}{[X_0] - \frac{[X_0]}{1 + K[M]P}} \quad (8b)$$

Inserting equation 9b into 8b, we obtain

$$[X_0] = \frac{8.85 - [M]}{\frac{K[M]P^2}{1 + K[M]P} + 0.1594} \quad (10)$$

Naturally, a value of $[X_0]$ could be assumed and the corresponding value of P calculated but, as can easily be seen, this would involve much more complicated calculations than are encountered in the above method. (It would be necessary to solve simultaneously equations 10 and 5, making $[X_0]$ the independent and P the dependent variable.)

III. Application of the Theory to Experimental Results

Three sets of data ranging from $[X_0] = 0.0883$ mole/kg. up to 44.4 moles/kg. and from $t = 220$

to 253.5° were investigated. These three sets as obtained from the literature are shown in Tables I–III, together with the values recalculated to fit our choice of units.

TABLE I³
 $t = 220^\circ$

$[X_0]$, moles/ mole C.L.	$[X_0]$, moles ^a / kg.	\bar{P}_n	Conversion	$[M]$, moles ^a / kg.	$[M_0]$, moles ^b / kg.
0.01	0.0883	330	0.9450	0.486	8.84
.02	.1762	222	.9450	.485	8.82
.04	.352	152	.9450	.484	8.79
.06	.525	122	.9447	.484	8.77
.08	.700	104	.9442	.488	8.74
.10	.872	92.0	.9440	.489	8.71
.20	1.716	62.4	.9417	.500	8.58
.80	6.28	27.4	.9302	.550	7.85
4.0	21.6	7.92	.8726	.689	5.41
10	34.1	4.21	.7700	.785	3.42
25	44.4	2.38	.5750	.756	1.77

TABLE II⁴
 $t = 221.5^\circ$

$[X_0]$, moles/ mole	$[X_0]$, moles ^a / kg.	\bar{P}_n	Free CL (% of total CL)	$[M]$, moles ^a / kg.	$[M_0]$, moles ^b / kg.
0.060	0.526	120	6.10	0.535	8.77
.118	1.025	80	6.20	.538	8.69
.192	1.650	60	6.41	.550	8.59
.405	3.36	40	7.09	.588	8.31
.635	5.11	30	7.70	.618	8.04
1.11	8.34	20	9.35	.689	7.52
2.00	13.42	13	12.0	.806	6.71

TABLE III⁴
 $t = 253.5^\circ$

$[X_0]$, moles/ mole	$[X_0]$, moles ^a / kg.	\bar{P}_n	Free CL (% of total CL)	$[M]$, moles ^a / kg.	$[M_0]$, moles ^b / kg.
0.060	0.526	100	7.90	0.693	8.77
.082	0.716	80	7.95	.695	8.74
.132	1.142	60	8.12	.703	8.67
.282	2.39	40	8.83	.746	8.47
.450	3.71	30	9.52	.785	8.26
.875	6.80	20	11.33	.881	7.77
2.000	13.41	11.5	16.1	1.081	6.71

^a Calculated from previous column. ^b Calculated from $[X_0]$ by: $[M_0] = 8.85 - 0.1594 [X_0]$.

The values given in Table I are more precise than those in Tables II and III since they were taken from the actual experimental data (smoothed), whereas those in Tables II and III were read off a rather small graph. For that reason, and also since the values in Table I cover a much larger range of $[X_0]$, more extensive work was done on these than on the others. (As can be seen, the findings from all sets of data are quite similar.) The data were treated as outlined in section II and the results are shown below.

1. **Determination of Equilibrium Constants.**—Figure 1 shows the variation of both K and K_3 with $[X_0]$ (on a log scale).

The best value of the equilibrium constants were determined by extrapolation to very low values of $[X_0]$. Results are shown in Table IV.

The variation in the values of K and K_3 with increasing water content (decreasing P) is believed to be due in part to the simplifying assumptions of the theory, in particular to our assumption that

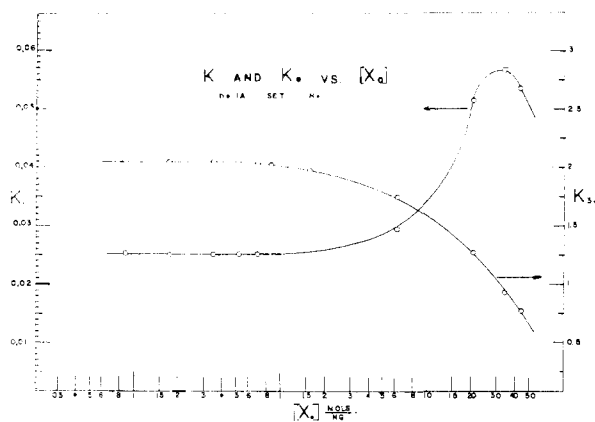


Fig. 1.

(the equilibrium constant) K_3 is identical for the very low chains, that is, that

$$K_3 = \frac{[XMY]}{[XY][M]} = \frac{[XM_2Y]}{[XMY][M]} = \frac{[XM_3Y]}{[XM_2Y][M]} = \dots = \frac{[XM_nY]}{[XM_{n-1}Y][M]}$$

which may be only approximately true. Also a change in the activities of the individual species with concentration may be responsible for this variation. It must be reiterated that the concentration range is from $[X_0] = 0.0883$ to 44.4 moles/kg.

TABLE IV

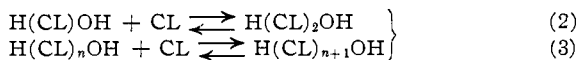
Data set no.	1	2	3
K	0.00251	0.00258	0.00296
K_3	2.05	1.858	1.446
t , °C.	220	221.5	253.5

2. Determination of ΔH^0 Values.—The availability of equilibrium constants for the initiation and propagation reactions involved in the polymerization of CL at several temperatures suggests the possibility of calculating the ΔH^0 of these reactions. This was done using data sets #2 and #3 only, as these had been obtained from the same source. The results obtained are



$$\Delta H^0 = +2240 \text{ cal./mole}$$

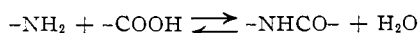
$$\Delta S^0 = -7.4 \text{ e.u.}$$



$$\Delta H_3^0 = -4030 \text{ cal./mole}$$

$$\Delta S_3^0 = -6.9 \text{ e.u.}$$

The ΔH for the reaction



was reported⁴ to lie between -1400 and -6000 cal./mole. Meggy⁵ found $\Delta H = -3560$ for the propagation reaction as described by us using data from B.I.O.S. Report 1472. A calorimetric study of the polymerization⁶ sets the total heat of reaction $Q = 28.5$ -29.0 cal./g. (equal to -3100 to -3160 cal./mole), and Fukumoto⁷ found the heat of condensation between linear polymers to be -6.8 kcal./mole.

(5) A. B. Meggy, *J. Chem. Soc.*, 796 (1953).

(6) S. M. Skuratov, A. A. Strepikheev and E. N. Kanarskaya, *Kolloid. Zhur.*, **14**, 185 (1952); *C. A.*, **46**, 8506d (1952).

(7) O. Fukumoto, *J. Poly. Sci.*, **22**, 263 (1956).

IV. Discussion of Theoretical Results

As can be seen from Fig. 1, for low initiator concentrations (up to $[X_0] = 1$ mole/kg.) both K_3 and K are very constant, and it may be expected that for that region the theoretical predictions should correspond very closely with the experimental results. This was indeed found to be the case, especially for the relationship of P vs. $[X_0]$, which can be seen in Figs. 2, 3 and 4 for the three sets of data in the low region of $[X_0]$ (up to 2 moles/kg.).

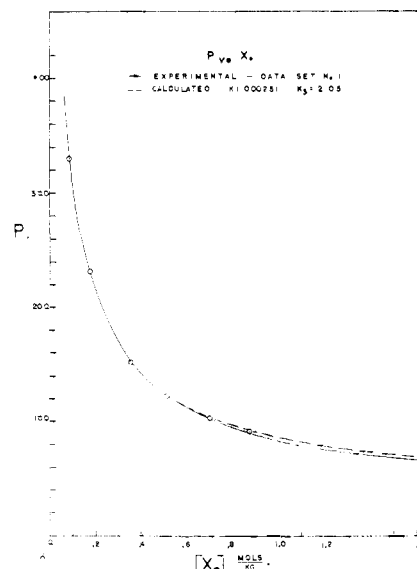


Fig. 2.

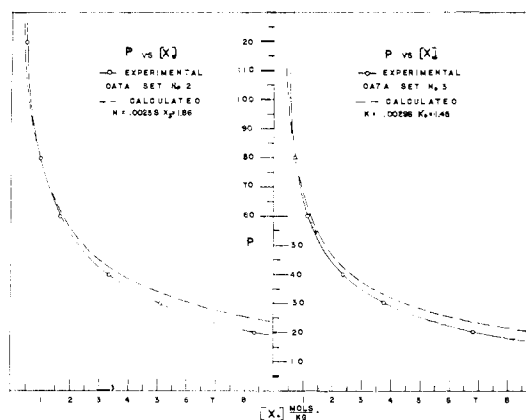


Fig. 3.

Fig. 4.

The theoretically predicted curve for the sensible range of P vs. $[X_0]$ is shown in Fig. 5, together with the data (set No. 1) from which the equilibrium constants were determined. It is interesting to note that for the range $0.06 < [X_0] < 1.0$ a plot of P vs. $[X_0]$ on a log scale yields a straight line corresponding to the equation $P = 87.9 [X_0]^{-0.546}$. In general, the agreement of the theoretical and experimental P 's may be considered excellent up to $[X_0] = 1$ (maximum deviation = 1%). At $[X_0] = 2$, the deviation becomes 3/60, at $[X_0] = 5$ it is 5/30 and at $[X_0] = 10$ it is 7/20.

The curve of $[M]$ vs. $[X_0]$ (shown in Fig. 6 for Set No. 1 only) follows for low $[X_0]$ (up to 0.4 mole/kg.) the theoretically predicted course, while rising

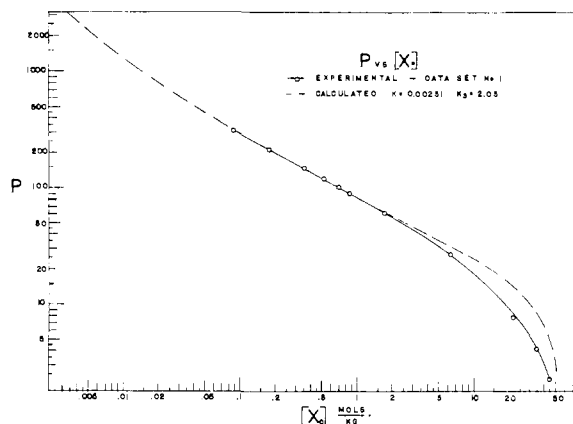


Fig. 5.

for higher values. This rise is also observed from the very beginning for the 2nd and 3rd sets of data, while theory predicts a continuous, although very slow drop in $[M]$ as $[X_0]$ increases (Fig. 6). At very high values of $[X_0]$ the experimental values for $[M]$ again show a slight drop.

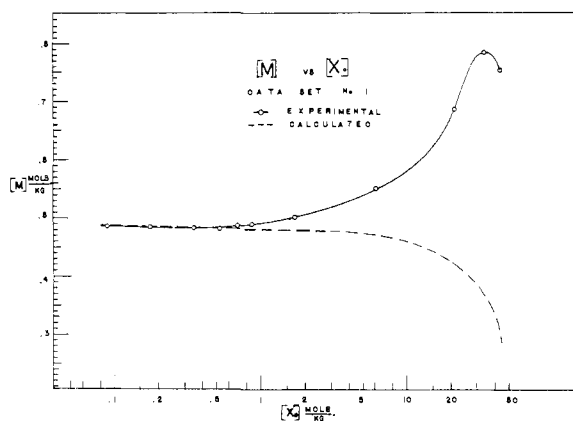


Fig. 6.

The availability of equilibrium constants for three different temperatures suggests the possibility of finding by interpolation of those values (on a $\log K$ vs. $1/T$ graph) the values for the constants at in-

t , °C.	220	230	240	250	260
K	0.00254	0.00266	0.00279	0.00291	0.00304
K_3	1.97	1.79	1.63	1.49	1.36
$[M_{X_0} \rightarrow 0]$	0.508	0.559	0.614	0.671	0.735

termediate temperatures. These values are shown in Table V, together with $[M_{X_0} \rightarrow 0]$, which is the theoretical equilibrium monomer concentration as $[X_0]$ approaches 0.

Graphs of P vs. $[X_0]$ calculated from the above data are shown in Fig. 7. On a log-log scale, linearity is observed for $0.1 < [X_0] < 2.0$ in the tem-

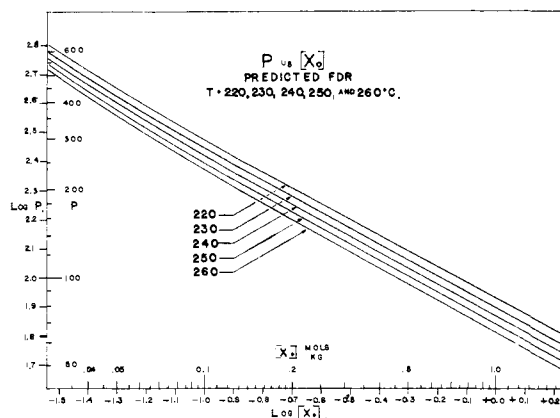


Fig. 7.

perature range investigated, suggesting a single formula which would define the P for any $[X_0]$ in this linear range. The constants A and B corresponding to the equation $\log P = A + B \log [X_0]$ were determined for each temperature, and since an apparently linear relationship exists between these constants and the temperature ($A = 2.456 - 0.00241t$; $B = -0.4365 - 0.000465t$, where t is the temperature in °C.), the required formula is

$$\log P = (2.456 - 0.00241t) - (0.4365 + 0.000465t) \log [X_0] \quad (11)$$

This formula should be also of practical interest since the range of linearity corresponds to the commercially employed range of P values.

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[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, DEPAUW UNIVERSITY]

The Potential of the Tellurium-Tellurium Dioxide Electrode as a Function of pH

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RECEIVED OCTOBER 13, 1958

The electromotive force of the electrochemical cell, $\text{Te}(s)/\text{TeO}_2(s)$ buffer solution//saturated calomel electrode, is determined as a function of pH, at a temperature of 25°. The variation can be represented by the relationship $E = 0.349 - 0.0469\text{pH}$ for the pH range 2.2 to 8.0. In addition the tellurium electrode is shown to be a suitable indicator electrode in acid-base titrimetry.

The reversible oxidation potential E of a metal electrode in contact with a solution that is saturated with a sparingly-soluble oxide of the metal is expressed by the equation

$$E = E^{\circ'} + \frac{2.303RT}{F} \text{pH} \quad (1)$$

provided that the only source of metal ions in solution is through ionization of the oxide. $E^{\circ'}$ is a constant characteristic of the electrode reaction and the other terms have their usual significance.¹ The

(1) See, for example, G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Elsevier Publishing Company, New York, N. Y., 1951, p. 293.