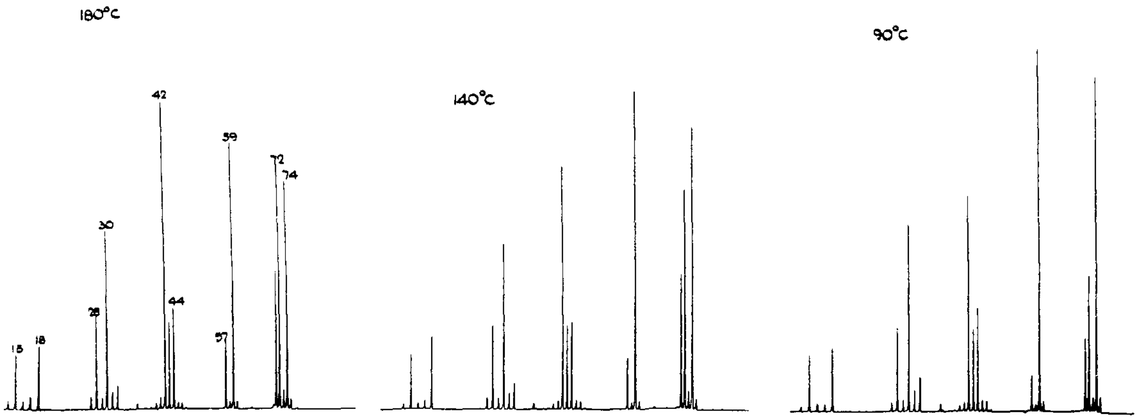

Fig. 1.

The spectrum given by Dibeler, *et al.*, would appear, in the region of the parent ion, to fall somewhere between Figs. 1b and 1c, but the high intensity of some fragment ions (*e.g.*, mass 42) would seem to suggest decomposition. The complete spectrum which we have obtained is given in Table I. There is no difficulty in assigning the ionization processes above mass 57, but below this mass number the empirical formulas of the ions produced by 70 v. electrons have now been identified directly where previously Dibeler, *et al.*, made suggestions about the ion formulas based on appearance potential measurements. Their positive identifications were limited, however, to the ions of masses 15, 42 and 44. The actual ion formulas found often differ from those suggested by Dibeler, *et al.* In some cases the peaks are actually multiplets (*e.g.*, mass 29 is a triplet and mass 43 is a doublet) and it is, therefore, not possible to explain them by a single process. In other cases (mass 32, CH_6N^+; mass 31, CH_5N^+; mass 30, CH_4N^+; mass 28,CH_2N^+) although one ion species predominates, this ion is found to differ from the composition suggested on energetic considerations alone. In the cases of masses 27, 29, 39, 40, 41, 45 and 58 it has now been possible to assign formulas which were not previously possible.

It should be noted that the abundances quoted in Table I are those which obtain for 70 e.v. electrons and it does not necessarily follow that the major species at each mass number will have the lowest ionization potential. A metastable peak 0.7% of the base peak intensity was noted on the low resolution spectrum at mass 47 which corresponds to the transition p → p-15.

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[Contribution from the Frick Chemical Laboratory, Princeton University]

A General Treatment of Equilibrium Polymerization

By A. V. Tobolsky and A. Eisenberg

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A general theory of equilibrium polymerization is presented. Three chemical categories are discussed: equilibrium polymerization in the presence of an initiator, *e.g.*, caprolactam, and two categories that do not involve an initiator, represented by sulfur and by vinyl monomers, respectively. Two mathematical approximations are considered. In certain cases the chemical facts and the experimental results allow a treatment based on a single equilibrium constant. In very many cases, however, a two constant treatment is necessary, *e.g*, caprolactam initiated by water and the polymerization of sulfur. It is suggested that a two constant treatment is also necessary for describing the equilibrium polymerization of vinyl monomers.

A General Treatment of Equilibrium Polymerization.—Three general cases of equilibrium polymerization may be distinguished: we shall classify these cases as Case I, Case II and Case III. We shall designate monomer as M, polymerization initiator (where present) as XY, concentrations (generally in moles per kilogram) will be designated as M, XY, etc.

Case I

$$XY + M \underset{}{\overset{K_a}{\rightleftarrows}} XMY$$

$$XMY + M \overset{K_b}{\rightleftarrows} XM_2Y$$

$$XM_{n-1}Y + M \overset{K_n}{\rightleftarrows} XM_nY$$

Case II

$$M \overset{K_a}{\rightleftarrows} M^*$$

$$M^* + M \overset{K_b}{\rightleftarrows} M^*_2$$

$$M^*_{n-1} + M \overset{K_n}{\rightleftarrows} M^*_n$$

(The asterisk represents an activated state such as a diradical or a zwitterion)

Case III

$$M + M \overset{K_a}{\rightleftarrows} M_2$$

$$M_2 + M \overset{K_b}{\rightleftarrows} M_3$$

$$M_n + M \overset{K_n}{\rightleftarrows} M_n$$

Case I is identified by the fact that an initiator is definitely involved in the polymerization equilibrium. Cases II and III do not involve initiator. We distinguish Case II as comprising those equilibria which involve an activated polymeric species as a final product.

Examples of Case I are the polymerization of ϵ-caprolactam initiated by water, by an amine or by an organic acid. Some cases of cationic and anionic polymerization of vinyl monomers might also fall in this category. Examples of Case II are the thermal polymerization of sulfur and possibly the polymerization of $(PNCl_2)_3$. Examples of Case III are certain types of equilibrium vinyl polymerization and the polymerization of rings (such as ϵ-caprolactam and sulfur) to larger rings. Some of these examples will be treated in detail in the applications.

From the experimental point of view three measurable quantities are of the utmost importance in specifying the equilibrium: (1) the equilibrium concentration of monomer M; (2) the equilibrium number average degree of polymerization P; (3) where initiator is present, the equilibrium concentration of initator XY.

In order to obtain useful relations between M, P, XY and the equilibrium constants K_a, K_b, K_c, . . . K_n . . . we introduce two physically reasonable approximations

$$K_a = K \qquad \text{(a)}$$

$$K_b = K_c = K_d = \ldots = K_n = \ldots = K_3$$

$$K_a = K_b = K_c = \ldots = K_n = \ldots = K_3 \qquad \text{(b)}$$

Whether a given equilibrium falls under approximation (a) or (b) sometimes can be determined from chemical intuition. For example, the polymerization of ϵ-caprolactam by water, which falls under Case I because an initiator is involved, must be treated by approximation (a) because two distinct reactions are involved, the ring opening by water, and the subsequent additions of caprolactam involving ring opening by the long chain amino acids. The polymerization of ϵ-caprolactam by an amine or by an organic acid probably falls under approximation (b) since ring opening during initiation and growth probably is accomplished by the same functional groups. It is thus classified as Case I-b. The polymerization of sulfur very definitely falls under approximation (a), since two entirely different types of equilibrium are involved, namely, the initiation reaction ($S_8 \rightleftarrows S^*_8$) and the propagation reaction ($S^*_x + S_8 \rightleftarrows S^*_{x+8}$). (The notation S*, etc., represents a linear diradical.) Sulfur equilibrium is therefore classified as Case II-a. The polymerization of ϵ-caprolactam to larger rings, clearly Case III, probably falls under approximation (b), since essentially only one reaction is involved in all the equilibrium steps. It is therefore classified as Case III-b. Vinyl polymerization in the absence of initiator has been tentatively classified as Case III-a, and will be discussed later.

The experimental problem is to place monomer (or monomer plus initiator) of known concentration M_0 (and XY_0 where present) in a sealed system. The system is kept at constant temperature until equilibrium is attained. At this point the system is quenched, and the sample analyzed for the equilibrium monomer concentration M, the degree of polymerization P, and, where applicable, the equilibrium initiator concentration XY.

The mathematical problem that must be solved is to relate P and M to K, K_3 and M_0, where M_0 is the initial concentration of monomer. In Case I we have to relate P, M, XY to K, K_3, M_0 and X_0 (short for XY_0) where X_0 is the initial concentration of initiator.

Since Cases I and II have been treated previously,[1-4] the detailed mathematical steps in the treatment of Case III-a only are given

$$\mathrm{M} + \mathrm{M} \overset{K}{\rightleftarrows} \mathrm{M}_2;\ K = \frac{M_2}{MM};\ M_2 = KM^2 \qquad (1)$$

$$\mathrm{M}_2 + \mathrm{M} \overset{K_3}{\rightleftarrows} \mathrm{M}_3;$$

$$K_3 = \frac{M_3}{M_2M};\ M_3 = K_3M_2M = KK_3M^3 \qquad (2)$$

$$\mathrm{M}_3 + \mathrm{M} \overset{K_3}{\rightleftarrows} \mathrm{M}_4;$$

$$K_3 = \frac{M_4}{M_3M};\ M_4 = K_3M_3M = KK_3^2M^4 \qquad (3)$$

$$\mathrm{M}_n + \mathrm{M} \overset{K_3}{\rightleftarrows} \mathrm{M}_{n+1};\ M_{n+1} = KK_3^{n-2}M \text{ for } n > 2 \qquad (4)$$

let N = total equilibrium concentration of polymer molecules

$$\begin{aligned} N &= \sum_{n=2}^{\infty} KK_3^{n-2}M^n \\ &= KM^2 + KK_3M^3 + KK_3^2M^4 + \ldots\ldots \\ &= KM^2[1 + K_3M + K_3^2M^2 + K_3^3M^3 + \ldots\ldots] \end{aligned}$$

$$N = \frac{KM^2}{1 - K_3M} \qquad (5)$$

let W = total equilibrium concn. of monomer segments incorporated in polymer, *i.e.*, $W = \sum_{n=2}^{\infty} nM_n$

$$\begin{aligned} W &= \sum_{n=2}^{\infty} nKK_3^{n-2}M^n \\ &= KM^2[1 + 2K_3M + 3K_3^2M^2 + \ldots\ldots] \end{aligned}$$

$$W = \frac{KM^2}{(1 - K_3M)^2} \qquad (6)$$

it is obvious that $P = W/N$ (here P is the no. av. degree of polymerization)

$$P = \frac{W}{N} = \frac{1}{1 - K_3M} \qquad (7)$$

It is easy to see that

$$M_0 = M + W = M + \frac{KM^2}{(1 - K_3M)^2} \qquad (8)$$

where M_0 is the initial monomer concentration.

Combining equations 7 and 8, and setting $(P - 1)/P = 1$ (valid for $P >> 1$), we get

$$P = \left(\frac{M_0K_3^2}{K} - \frac{K_3}{K}\right)^{1/2} \qquad (9)$$

We note from equation 7 that if $P >> 1$ then $K_3 \simeq 1/M$.

The above results are equally applicable to Case III-b, with the simplification that $K = K_3$, since all constants are identical by assumption b.

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

(2) A. V. Tobolsky, *ibid.*, **31**, 126 (1958).

(3) A. V. Tobolsky and A. Eisenberg, THIS JOURNAL, **81**, 780 (1959).

(4) A. V. Tobolsky and A. Eisenberg, *ibid.*, **81**, 2302 (1959).

TABLE I[a]

Eq.	Case	P	M_0	X_0	P
10	Ia	$1/(1 - K_3M)$	$M(1 + KXP^2)$	$X(1 + KMP)$	$(M_0 - M)/(X_0 - X)$
11	Ib	$1/(1 - K_3M)$	$M(1 + K_3XP^2)$	$X(1 + K_3MP)$	$(M_0 - M)/(X_0 - X)$
12	IIa	$1/(1 - K_3M)$	$M(1 + KP^2)$		$\simeq[(M_0K_3 - 1)/K]^{1/2}$
13	IIIa	$1/(1 - K_3M)$	$M(1 + KMP^2)$		$\simeq[(M_0K_3^2 - K_3)/K]^{1/2}$
14	IIIb	$1/(1 - K_3M)$	$M(1 + K_3MP^2)$		$\simeq(M_0/M)^{1/2}$

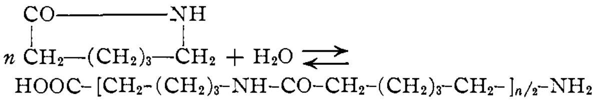
[a] The equation for P given in the last column is not an independent relation but can be derived for the sake of convenience from the preceding equations. In the last three cases the equations for P are valid only for values of $P \gg 1$.

Equation 9 becomes

$$P \simeq (M_0K_3)^{1/2} \simeq (M_0/M)^{1/2} \qquad (9\text{-b})$$

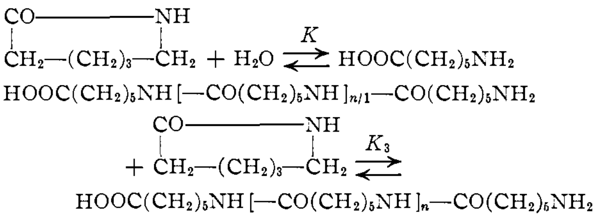
The necessary relations for the other cases have been presented elsewhere.[1-4] The results are summarized in Table I.

Application of Case I.a to the Equilibrium Polymerization of ε-Caprolactam Initiated by Water.—The over-all reaction can be written as



$$n\,\overset{\mathrm{CO}\text{———}\mathrm{NH}}{\mathrm{CH_2{-}(CH_2)_3{-}CH_2}} + \mathrm{H_2O} \rightleftarrows$$
$$\mathrm{HOOC{-}[CH_2{-}(CH_2)_3{-}NH{-}CO{-}CH_2{-}(CH_2)_3{-}CH_2{-}]_{n/2}{-}NH_2}$$

The sequence of equilibria that we use to describe the reaction is



$$\overset{\mathrm{CO}\text{———}\mathrm{NH}}{\mathrm{CH_2{-}(CH_2)_3{-}CH_2}} + \mathrm{H_2O} \overset{K}{\rightleftarrows} \mathrm{HOOC(CH_2)_5NH_2}$$
$$\mathrm{HOOC(CH_2)_5NH[{-}CO(CH_2)_5NH]_{n/1}{-}CO(CH_2)_5NH_2}$$
$$+ \overset{\mathrm{CO}\text{———}\mathrm{NH}}{\mathrm{CH_2{-}(CH_2)_3{-}CH_2}} \overset{K_3}{\rightleftarrows}$$
$$\mathrm{HOOC(CH_2)_5NH[{-}CO(CH_2)_5NH]_{n}{-}CO(CH_2)_5NH_2}$$

$n = 0, 1, 2, 3, 4, \ldots$

At a given temperature, for a given value of M_0 and X_0, P and M were available from data in the literature.[5] Referring to equation 10, Table I, K_3 was immediately obtained from $P = 1/(1 - K_3M)$. X then was obtained from $P = (M_0 - M)/(X_0 - X)$. Finally, K was obtained from $X_0 = X(1 + KMP)$. The consistency of the equilibrium treatment then was checked conveniently by predicting the value of X_0 corresponding to a selected value of P using the values of K and K_3 determined above. Very satisfactory results were obtained.[4]

This procedure was carried out at two temperatures. Application of the van't Hoff equation to the values of K and K_3 gave

$$K = e^{\Delta S^0/R}e^{-\Delta H^0/RT} \qquad (15)$$
$$K_3 = e^{\Delta S_3^0/R}e^{-\Delta H_3^0/RT}$$
$$\Delta S^0 = -6.8 \text{ e.u.} \qquad \Delta S_3^0 = -7.0 \text{ e.u.}$$
$$\Delta H^0 = +2240 \text{ cal./mole} \qquad \Delta H_3^0 = -4030 \text{ cal./mole}$$

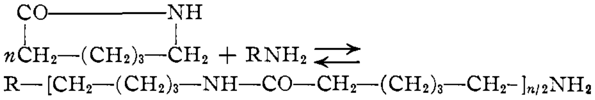
corresponding to the initiation and propagation reactions, respectively. The standard state chosen was 1 mole per kilogram and all concentrations discussed in this paper are based on the units moles/kilogram.

Since $P = 1/(1 - K_3M)$ it may be pointed out that for large values of P

$$M \simeq 1/K_3 \qquad (16)$$

hence in the range of high degrees of polymerization, M is independent of the initiator concentration.

Application of Case I-b to the Equilibrium Polymerization of ε-Caprolactam Initiated by an Alkyl Amine or an Organic Acid.—The over-all reaction can be written as



$$n\overset{\mathrm{CO}\text{———}\mathrm{NH}}{\mathrm{CH_2{-}(CH_2)_3{-}CH_2}} + \mathrm{RNH_2} \rightleftarrows$$
$$\mathrm{R{-}[CH_2{-}(CH_2)_3{-}NH{-}CO{-}CH_2{-}(CH_2)_3{-}CH_2{-}]_{n/2}NH_2}$$

The sequence of equilibria that we use to describe the reaction is

$$\mathrm{RNH_2 + CL} \overset{K_3}{\rightleftarrows} \mathrm{R(CL)NH_2}$$
$$\mathrm{R(CL)_nNH_2 + CL} \overset{K_3}{\rightleftarrows} \mathrm{R(CL)_{n+1}NH_2}$$
$$n = 1, 2, 3, 4 \ldots$$

In the above equations CL represents caprolactam and (CL) represents $-\mathrm{NHCO(CH_2)_5}-$. In this case we take $K = K_3$ as a good approximation since the same functional groups are involved in the equilibria.

No satisfactory equilibrium data exist in the literature for this case. We venture to predict that this equilibrium can be described by using the results of Case I-a above merely by replacing K by K_3.

The first important prediction is obtained from equation 16, namely, $M \simeq 1/K_3$. This shows immediately that the equilibrium concentration of monomer is a function of temperature only and is independent of the nature of the initiator. That is, we can expect the same M whether water or amine is used as the initiator.

The second important consequence is given by the equation below, which can be derived from equation 11 as shown in the Appendix.

$$P \simeq (M_0 - M)/X_0 \simeq (M_0 - 1/K_3)/X_0 \qquad (17)$$

Expressing K_3 as a function of temperature from equation 15, we obtain

$$P \simeq [M_0 - \exp(-4030/RT)\exp(7.0/R)]/X_0 \qquad (18)$$

Equations 16–18 should also apply for other initiators, such as organic acids, dibasic acids or diammines.

Application of Case II-a to the Thermal Polymerization of Sulfur.—The over-all reaction can be written as

$$n\mathrm{S_8} \rightleftarrows \mathrm{S_{8n}}^*$$

the asterisk denoting a diradical. The sequence of steps that we use to describe the final equilibrium is

$$\mathrm{S_8} \overset{K}{\rightleftarrows} \mathrm{S_8}^*$$
$$\mathrm{S_{8n}}^* + \mathrm{S_8} \overset{K_3}{\rightleftarrows} \mathrm{S_{8(n+1)}}^*$$

Approximate data are available in the literature

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(5) F. Wiloth, *Z. physik. Chem.*, *N.F.*, **4**, 66 (1955); P. F. Van Velden, G. M. Van Der Want, D. Heikens, Ch. A. Kruissink, P. H. Hermans and A. J. Staveman, *Rec. trav. chim.*, **74**, 1376 (1956).

giving P and M as a function of temperature.[6] Theoretically, only two experimental values of P and M are needed to describe the sulfur equilibrium in terms of our theory, and both of these points may lie above the so-called "transition temperature" (above which polymer seems to appear suddenly). Referring to equation 12, Table I, at any temperature, K_3 may be calculated immediately from a knowledge of P and M by use of the relationship $P = 1/(1 - K_3M)$. K then may be calculated from $M_0 = M(1 + KP^2)$, recalling that M_0 is a constant equal to 3.90 moles/kilogram over the entire range. If this procedure is repeated for another temperature, plots of ln K *vs.* $1/T$ and ln K_3 *vs.* $1/T$ may be constructed, and ΔH^0, ΔS^0, $\Delta H_3{}^0$ and $\Delta S_3{}^0$ obtained. The results are[3]

$$\Delta S^0 = 23.00 \text{ e.u.} \qquad \Delta H^0 = 32{,}800 \text{ cal./mole}$$
$$\Delta S_3{}^0 = 4.63 \text{ e.u.} \qquad \Delta H_3{}^0 = 3{,}170 \text{ cal./mole}$$

Once K and K_3 are known as a function of temperature, curves of P *vs.* T and M *vs.* T may be constructed. The former is of particular interest, as it very clearly shows the reason for the sudden rise in the viscosity of sulfur upon heating above the "transition temperature." It may be obtained by the simultaneous solution of the equations for P and M_0, yielding

$$M_0 = \frac{P-1}{PK_3} + \frac{K}{K_3}P(P-1)$$

which, for high values of P, can be simplified to

$$P = \left(\frac{M_0K_3 - 1}{K}\right)^{1/2}$$

Application of Case III-a to the Equilibrium Polymerization of Vinyl Monomers.—We consider this equilibrium to take place according to the steps

$$\mathrm{CH_2{=}CHX + CH_2{=}CHX \xrightleftharpoons{K} dimer}$$

$$\mathrm{CH_2{=}CX(CH_2CHX)_{\mathit{n}}{\cdot}CH_2CH_2X + CH_2{=}CHX \xrightleftharpoons{K_3}}$$
$$\mathrm{CH_2{=}CX(CH_2CHX)_{\mathit{n}+1}CH_2CH_2X}$$
$$n = 0, 1, 2, 3, \ldots$$

We should emphasize that the particular manner in which the equilibrium is written need bear no relation whatever to the mechanism. Equilibrium depends only on initial and final states.

From an *a priori* point of view K might well be equal to K_3 and therefore Case III-b might equally be applicable. A decision as to which approximation is correct can be based only on experimental findings.

In treating equilibrium polymerization of vinyl monomers, particularly methyl methacrylate, Dainton and Ivin[7] and Bywater[8] implicitly treat the problem as a one constant case, and derive by other methods the relation which in our notation is (see equation 16)

$$K_3 \simeq 1/M$$

Bywater also carried out measurements of M and hence K_3 at several temperatures.

From Table I, it is clear that this relation is valid for either the one constant Case III-b *or* the two constant Case III-a. Unfortunately, in the work cited only M was determined and so no decision can be made on the basis of the literature data.

If a one constant treatment is indeed applicable, then the degree of polymerization should be related to the equilibrium monomer concentration M as follows (see Table I)

$$P = (M_0/M)^{1/2}$$

For the experimental results of Bywater this would lead to a maximum value of P of 5 at 130°.

We have repeated the experiments of Bywater and do indeed verify fairly closely his results for "equilibrium" monomer concentration, with a reservation discussed later.

However, we have determined P in this system and find a value of 500–650, in definite contradiction to a one constant theory.

Such a result is not at all inconsistent with a two constant theory where

$$P = [(M_0K_3{}^2 - K_3)/K]^{1/2}$$

In fact, from the measured value of P, a value of K can be determined which in fact is *ca.* 3×10^{-5} (*cf.* $K_3 \simeq 3$).

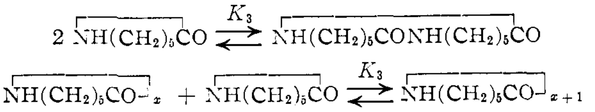
The reservation that we stated above concerning experimental findings is that in our results we find the "equilibrium" monomer concentration obtained in the experimental method of Bywater to depend on the light intensity. The results of Bywater may perhaps be more aptly described as photostationary states rather than equilibrium states. Our results are shown in Table II.

Table II[a]

Sample	Light intensity, arbitrary units	M_0, moles/kg.	Wt. of polymer (0.936 g. charged), g.	M, moles/kg.
a	24	1.27	0.575	0.488
b	21	1.27	.615	.434
c	18	1.27	.684	.341
d	17	1.27	.679	.347
e	13	1.27	.702	.316
f	12	1.27	.694	.327
g	11	1.27	.741	.264

[a] Sample a was held *ca.* 1 inch from a 275 watt Sylvania sun lamp; it was kept at 130° in a bath of G. E. SF 96 silicone oil (transmittance, 0.9 at 300 mμ, 1.0 at 360 mμ); light had to pass through two Pyrex walls. Equilibrium was attained in *ca.* 6–10 hr., and samples were kept at constant temperature and light intensity for *ca.* 16 hr. The solution was quenched in a large excess of methanol and the weight of polymer determined. M was calculated from the difference of monomer input and polymer yield.

Application of Case III-b to the Polymerization of ϵ-Caprolactam to Larger Rings.—The formation of larger ring systems in the course of the polymerization of ϵ-caprolactam is a well-known phenomenon. We consider this equilibrium to be subject to Case III-b, since essentially only one type of reaction is involved in the formation of large rings, which we believe to occur by bond interchange



$$2\,\mathrm{NH(CH_2)_5CO} \xrightleftharpoons{K_3} \mathrm{NH(CH_2)_5CONH(CH_2)_5CO}$$

$$\mathrm{[NH(CH_2)_5CO{-}]_{\mathit{x}}} + \mathrm{NH(CH_2)_5CO} \xrightleftharpoons{K_3} \mathrm{[NH(CH_2)_5CO{-}]_{\mathit{x}+1}}$$

$$x = 2, 3, 4, 5, 6 \ldots$$

Ideally, this equilibrium could be studied with completely dry ϵ-caprolactam at appropriate tempera-

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(6) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952); F. Fairbrother, G. Gee and G. T. Merral, *J. Poly. Sci.*, **16**, 459 (1955).

(7) F. S. Dainton and K. J. Ivin, *Nature*, **162**, 705 (1948).

(8) S. Bywater, *Trans. Faraday Soc.*, **51**, 1267 (1955).

tures, thus eliminating the mechanism of ring-chain equilibrium. Under normal circumstances (*i.e.*, water initiation), two simultaneous equilibria have to be accounted for, *i.e.*, the ring-chain equilibrium and the ring-large ring equilibrium. Since large rings are present only in relatively small concentrations, these may be neglected in studying the ring-chain system, and this actually was done (see Application I-a). Once M is known for this simplified system, it could be regarded as M_0 for the ring–large ring equilibrium.

Appendix 1

Just as in case I-a

$$P = \frac{M_0 - M}{X_0 - X}$$

where X_0 and X are related by the equation

$$X_0 = X(1 + K_3MP)$$

but for high values of P, by equation 16

$$K_3 = \frac{1}{M} \text{ or } K_3M = 1$$

therefore

$$X_0 \simeq X(1 + P) \simeq XP \text{ for } P \gg 1$$

substituting

$$\begin{aligned} P &= (M_0 - M)/(X_0 - X_0/P) \\ &= (M_0 - M)/X_0\,(1 - 1/P), \text{ yielding} \\ P &= (M_0 - M)/X_0 \text{ for } P \gg 1 \end{aligned}$$

PRINCETON, N. J.

[CONTRIBUTION FROM THE PRODUCTS RESEARCH DIVISION, ESSO RESEARCH AND ENGINEERING COMPANY AND THE DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

High Temperature X-Ray Study of Lead Halides and Oxyhalides[1a]

BY H. PAUL JULIEN[1b] AND ROBERT E. OGILVIE

RECEIVED MARCH 19, 1959

Several complexes of lead oxide, lead chloride and lead bromide were studied by X-ray diffraction over the temperature range 20 to 650°. Samples were heated in air in a high temperature furnace attached to a high angle diffractometer. $PbCl_2$ and $PbBr_2$ heated with PbO in air formed stable lead oxyhalides by irreversible reactions. Several new lines were observed in the X-ray diffraction patterns of PbClBr and $2PbO \cdot PbClBr$. Approximate temperatures of formation were determined for PbClBr, $PbO \cdot PbBr_2$, $2PbO \cdot PbBr_2$ and $2PbO \cdot PbClBr$. The "R" form of $PbO \cdot PbBr_2$ was shown to be the only stable variety of the four polymorphic forms reported for this compound. Anisotropic expansion was observed in $PbCl_2$ and PbClBr. Lattice constants were calculated from precise, room temperature X-ray data on three compounds: PbClBr: a = 4.577, b = 7.811, c = 9.172 Å.; $2PbO \cdot PbBr_2$: a = 9.8, b = 12.2, c = 5.83 Å.; $2PbO \cdot PbClBr$: a = 9.7, b = 12.1, c = 5.87 Å. Good agreement with published values was obtained. These results suggest that $2PbO \cdot PbX_2$, like PbO and PbX_2, has a layer structure, with a and b unit cell dimensions almost equal to the sum of the PbO and PbX_2 dimensions, and with the c dimension very nearly equal to that of PbO.

Introduction

Although a vast amount of literature is available on the chemical and physical properties of the lead halides and lead oxides, such information on the lead oxyhalides is less abundant. Moreover, data on the mixed halides (*e.g.*, lead chlorobromide) and on complexes of these mixed halides with the lead oxides are very scanty. This paper presents the results of a high temperature X-ray diffraction study of lead chlorobromide (PbClBr), trilead dioxychlorobromide ($2PbO \cdot PbClBr$), dilead oxydibromide ($PbO \cdot PbBr_2$) and trilead dioxydibromide ($2PbO \cdot PbBr_2$). This study permitted the direct observation of many chemical and physical changes occurring over the temperature range 20–650°.

Calingaert, Lamb and Meyer[1c] studied the lead chloride–lead bromide system by thorough X-ray diffraction analysis. They also investigated the system by thermal analysis, conductivity measurements and aqueous preparations in order to resolve the discrepancies in the earlier literature on the $PbCl_2$–$PbBr_2$ system. They concluded that a compound PbClBr exists which is stable at room temperature. However, no such solid-state compound formation was observed by Harrap and Heymann[2] in their viscosity and equivalent conductance measurements on this $PbCl_2$–$PbBr_2$ system.

A phase study of the lead oxide–lead bromide system by X-ray diffraction was carried out by Lamb and Niebylski,[3] who found published X-ray data only for the compound $PbO \cdot PbBr_2$. Their study showed these data to be in error. A later X-ray study 4 of the $PbBr_2$-rich region of the PbO–$PbBr_2$ system confirmed the existence of a $2PbO \cdot PbBr_2$ but revealed two other compounds rather than the $PbO \cdot PbBr_2$ reported by earlier workers. For the compound $2PbO \cdot PbBr_2$, the two available sets[5,6] of interplanar spacing values reveal several inconsistencies. The only X-ray data in the literature[5] on $2PbO \cdot PbClBr$ are not in good agreement with the two independent sets of data obtained in this work.

Experimental

The lead compounds being studied were heated in a high temperature furnace attached to a standard Norelco high

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[1a] Presented before the Division of Physical Chemistry, 135th national meeting of the American Chemical Society, Boston, Mass., April, 1959.

[1b] Bonded Abrasives Division, The Carborundum Company, Niagara Falls, N. Y.

[1c] G. Calingaert, F. W. Lamb and F. Meyer, THIS JOURNAL, **71**, 3709 (1949).

[2] B. S. Harrap and E. Heymann, *Trans. Faraday Soc.*, **51**, 259 (1955).

[3] F. W. Lamb and L. M. Niebylski, THIS JOURNAL, **75**, 511 (1953).

[4] P. T. Davies, E. V. Garner and B. D. Caddock, *Acta Cryst.*, **7**, 640 (1954).

[5] F. W. Lamb and L. M. Niebylski, *Anal. Chem.*, **23**, 1388 (1951).

[6] "X-Ray Diffraction Patterns of Lead Compounds." The Shell Petroleum Company Limited, Chester, England, 1954.