953. *The Equilibrium in the System: Water–6-Hexanolactam (ε-Caprolactam).*

By A. B. Meggy.

Equations are calculated for the activity coefficients of water and polymer in the system water–6-hexanolactam. The equations are expressed in terms of the apparent equilibrium constants and the mol. fractions of water and lactam, and can be evaluated from published data. From the values obtained a composition–temperature diagram for the system can be constructed, showing lines of equal degree of polymerization, of equal partial pressure of water, and of equal lactam content, from 200° to 300°.

In a previous paper [1] the polymerization of 6-hexanolactam (ε-caprolactam) to a linear polyamide was discussed. Recent publications [2–13] provide experimental material for a fresh analysis of the problem.

In the presence of water or of alkali metals or their hydroxides, 6-hexanolactam (I)

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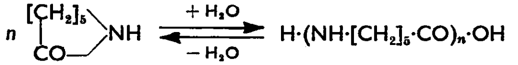
[1] Meggy, *J.*, 1953, 796.
[2] Wiloth, *Makromol. Chem.*, 1954, **14**, 156.
[3] *Idem, ibid.*, 1954, **15**, 98.
[4] *Idem, ibid.*, p. 104.
[5] *Idem, Z. phys. Chem.*, 1955, **5**, 66.
[6] *Idem, Koll. Z.*, 1955, **143**, 129.
[7] *Idem, ibid.*, p. 138.
[8] Hermans, *J. Appl. Chem.*, 1955, **5**, 493.
[9] Van Velden, van der Want, Heikens, Kruissink, Hermans, and Staveman, *Rec. Trav. chim.*, 1955, **74**, 1376.
[10] Yumato, *Bull. Chem. Soc. Japan*, 1955, **28**, 94, 101.
[11] Skuratov, Stipikheev, and Kanarskaya, *Faserforsch. u. Textiltechnik*, 1953, **4**, 390.
[12] Ludwig and Froeber, *ibid.*, 1954, **5**, 277.
[13] Matthes, *Makromol. Chem.*, 1951, **5**, 198; *Chem. Technik*, 1952, 129.

polymerizes to a linear polyamide (II) of 6-aminohexanoic acid. The molten polymer can be spun into fibres (called nylon-6). In the technical process water is the effective catalyst.[8]

(I) 

(II)

The degree of polymerization of the polymer is determined by the equilibrium :

$$x\text{-mer} + y\text{-mer} = (x + y)\text{-mer} + H_2O$$
$$K_1 = (H_2O)([x + y]\text{-mer})/(x\text{-mer})(y\text{-mer}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The polymerization does not go to completion; 5—10% of the lactam remains in the equilibrium mixture. The lactam may be regarded as being in equilibrium with 6-aminohexanoic acid and water :

$$K_2 = (\text{lactam})(H_2O)/(\text{6-aminohexanoic acid}) \quad . \quad . \quad . \quad (2)$$

Lactam is also in equilibrium with polymer :

$$\text{lactam} + x\text{-mer} = (x + 1)\text{-mer}$$
$$K_3 = ([x + 1]\text{-mer})/(x\text{-mer})(\text{lactam}) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In order to develop these equations it is necessary to make two assumptions: (*a*) In eqn. (1), the value of K_1 at any temperature is the same for all values of x and y, including x or $y = 1$. This is the principle of " equal reactivity of all groups " postulated by Flory.[14] If this principle applies, the mol. fraction of the x-mer in a polymer having a number average degree of polymerization n, is $(1 - 1/n)^{x-1}/n^2$. This expression has been tested experimentally, with satisfactory agreement, for poly-6-aminohexanoic acid [2] and for poly(hexamethyleneadipamide).[15] (*b*) In the presence of a diluent, if a_2 is the activity of the whole polymer, and m_x is the mol. fraction of the x-mer in the polymer, then the activity of the x-mer is a_2m_x. This is equivalent to assuming that the interaction between a diluent molecule and the polymer is independent of the length of the polymer chain. This might be expected to be valid for ranges where the length of the polymer chain was considerably greater than the " segment " of the chain which was equivalent to a diluent molecule under the Flory–Huggins lattice theory.[16] It will be shown later that there is evidence that the size of the polymer " segment " in the system polyaminohexanoic acid–water is less than one repeating unit of the polymer, so that the above assumption may be expected to hold down to quite low degrees of polymerization.

On the basis of these two assumptions it is possible to develop eqn. (1)—(3). Let the activity of water in the system be a_1, that of the polymer be a_2, that of lactam be a_3, and the degree of polymerization be n. The activity of the x-mer is $a_2(1 - 1/n)^{x-1}/n_2$; of the y-mer, $a^2(1 - 1/n)^{y-1}/n^2$; and of the $(x + y)$-mer $a_2(1 - 1/n)^{x+y+1}/n^2$. Substituting in eqn. (1), we have :

$$K_1 = a_1n(n - 1)/a_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The mol. fraction of monomer $(x = 1)$ in the polymer is $1/n^2$. Hence :

$$K_2 = a_1a_3n^2/a_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The ratio $(x + 1)$-mer/x-mer $= (n - 1)/n$. Hence :

$$K_3 = (n - 1)/na_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Eqns. (4), (5), and (6) are not independent; by combining any two, the third is obtained : $K_1 = K_2K_3$.

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[14] Flory, *Chem. Rev.*, 1946, **39**, 174.
[15] Taylor, *J. Amer. Chem. Soc.*, 1947, **69**, 638.
[16] Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, New York, 1953.

For the purposes of the phase rule, the system lactam–water may be regarded as a system of two components, *viz.*, water and the " unit " –NH·[CH$_2$]$_5$·CO–. A system of two components in the presence of a liquid phase and a vapour phase has two degrees of freedom, temperature and composition. If the temperature and composition of the system are defined, all other properties of the system are defined, such as the activities a_1, a_2, a_3, the proportions of unit mols. as polymer and lactam, the degree of polymerization of the polymer, the proportion of free water and of water bound as terminal groups of the polymer, and the partial pressures of water and lactam in the vapour phase.

The composition may be defined conveniently as follows :

$$N_1 = (\text{mols. of water})/(\text{mols. of water} + \text{mols. of unit})$$
$$N_2 = (\text{mols. of unit as polymer})/(\text{mols. of water} + \text{mols. of unit})$$
$$N_3 = (\text{mols. of unit as lactam})/(\text{mols. of water} + \text{mols. of unit})$$

$$N_1 + N_2 + N_3 = 1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

" Mols. of water " includes both free water and water bound as terminal groups of the polymer. In the present treatment the cyclic dimers, trimers, and tetramers are included in the polymer.

Other systems could be used to define the composition. " Free water " could be used instead of total water:[3, 4, 8, 9] for this one requires to know the degree of polymerization of the polymer. Or " moles./litre " of the components, requiring a knowledge of the density.[9] " Moles./kilogramme " has also been employed.[9] None of these offers any advantage. It would certainly be convenient if methods for defining the composition could be found for which $N_1 = a_1$, $N_2 = a_2$, and $N_3 = a_3$; but none of the other possibilities does this, and in view of the complexity of the system it is impossible to derive such a system theoretically. Deviations from ideal behaviour are to be expected on the following grounds : (1) a heat of mixing arising from the interaction of water with –CO·NH– groups; (2) a Debye–Hückel effect, arising from the change in the concentration of –CO$_2^-$ and –NH$_2^+$ groups, and of the dielectric constant, with composition; and (3) an abnormal entropy of mixing, such as is always found in polymer–solvent systems.

From the Gibbs–Duhem equation, we have :

$$N_1\left(\frac{\partial \ln a_1}{\partial N_1}\right)_T + N_2\left(\frac{\partial \ln a_2}{\partial N_1}\right)_T + N_3\left(\frac{\partial \ln a_3}{\partial N_1}\right)_T = 0 \quad . \; . \; . \quad (8)$$

From eqn. (6), by taking logarithms and differentiating with respect to N_1, at constant temperature, and since $(\partial \ln K_3/\partial N_1)_T = 0$, we obtain :

$$\left(\frac{\partial \ln a_3}{\partial N_1}\right)_T = \left(\frac{\partial}{\partial N_1} \cdot \ln \frac{n-1}{n}\right)_T$$

Substituting in eqn. (8) gives :

$$N_1\left(\frac{\partial \ln a_1}{\partial N_1}\right)_T + N_2\left(\frac{\partial \ln a_2}{\partial N_1}\right)_T = -N_3\left(\frac{\partial}{\partial N_1} \cdot \ln \frac{n-1}{n}\right)_T \quad . \; . \quad (9)$$

From eqn. (4), by taking logarithms and differentiating with respect to N_1 at constant temperature, and since $(\partial \ln K_1/\partial N_1)_T = 0$, we derive :

$$\left(\frac{\partial \ln a_1}{\partial N_1}\right)_T - \left(\frac{\partial \ln a_2}{\partial N_1}\right)_T = -\left[\frac{\partial}{\partial N_1} \cdot \ln n(n-1)\right]_T \quad . \; . \; . \quad (10)$$

Hence :

$$(N_1 + N_2)\left(\frac{\partial \ln a_1}{\partial N_1}\right)_T = -N_2\left[\frac{\partial}{\partial N_1} \cdot \ln n(n-1)\right]_T + N_3\left(\frac{\partial}{\partial N_1} \cdot \ln \frac{n}{n-1}\right)_T \quad (11)$$

$$(N_1 + N_2)\left(\frac{\partial \ln a_2}{\partial N_1}\right)_T = N_1\left(\frac{\partial}{\partial N_1} \cdot \ln n(n-1)\right)_T + N_3\left(\frac{\partial}{\partial N_1} \cdot \ln \frac{n}{n-1}\right)_T \quad (12)$$

From these equations it is possible to calculate $(\partial \ln a_1/\partial N_1)_T$ and $(\partial \ln a_2/\partial N_1)_T$ if N_2, N_3, and n are known over the range from $N_1 = 0$ to 1. But the equations are unsuitable for graphical integration, since as $N_1 \longrightarrow 0$, $\ln n(n-1) \longrightarrow +\infty$; and as $N_1 \longrightarrow 1$, $\ln n(n-1) \longrightarrow -\infty$, and $\ln n/(n-1) \longrightarrow +\infty$.

Let an " apparent equilibrium constant," $\bar{K}_1$, be defined by :

$$\bar{K}_1 = (N_1/N_2)\ n(n-1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

Then

$$\left[\frac{\partial}{\partial N_1}\cdot \ln n(n-1)\right]_T = \frac{1}{\bar{K}_1}\cdot\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T + \frac{1}{N_2}\left(\frac{\partial N_2}{\partial N_1}\right)_T - \frac{1}{N_1} \quad . \quad . \quad (13)$$

Similarly,

$$\bar{K}_3 = (n-1)/nN_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

and

$$\left(\frac{\partial}{\partial N_1}\cdot \ln\frac{n}{n-1}\right)_T = -\frac{1}{\bar{K}_3}\cdot\left(\frac{\partial \bar{K}_3}{\partial N_1}\right) - \frac{1}{N_3}\cdot\left(\frac{\partial N_3}{\partial N_1}\right)_T \quad . \quad . \quad . \quad (14)$$

Also, if $a_1 = \gamma_1 N_1$, and $a_2 = \gamma_2 N_2$, then :

$$(\partial \ln a_1/\partial N_1)_T = (\partial \ln \gamma_1/\partial N_1)_T + 1/N_1 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and

$$(\partial \ln a_2/\partial N_1)_T = (\partial \ln \gamma_2/\partial N_1)_T + \frac{1}{N_2}\cdot\left(\frac{\partial N_2}{\partial N_1}\right)_T \quad . \quad . \quad . \quad . \quad (16)$$

Combining eqns. (11) with (13), (14), and (15), and since, from (7), $(\partial N_3/\partial N_1)_T = -(1 + \partial N_2/\partial N_1)_T$, we find :

$$(N_1 + N_2)\left(\frac{\partial \ln \gamma_1}{\partial N_1}\right)_T = -\frac{N_2}{\bar{K}_1}\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T - \frac{N_3}{\bar{K}_3}\cdot\left(\frac{\partial \bar{K}_3}{\partial N_1}\right)_T \quad . \quad . \quad . \quad (17)$$

Combination of eqns. (12) with (13), (14), and (15) gives :

$$(N_1 + N_2)\left(\frac{\partial \ln \gamma_2}{\partial N_1}\right)_T = \frac{N_1}{\bar{K}_1}\cdot\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T - \frac{N_3}{\bar{K}_3}\cdot\left(\frac{\partial \bar{K}_3}{\partial N_1}\right)_T \quad . \quad . \quad . \quad (18)$$

Check : from eqns. (17) and (18) we have :

$$\left(\frac{\partial \ln \gamma_1}{\partial N_1}\right)_T - \left(\frac{\partial \ln \gamma_2}{\partial N_1}\right)_T = -\frac{1}{\bar{K}_1}\cdot\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (19)$$

From eqns. (4) and (4*a*), $K_1/\bar{K}_1 = \gamma_1/\gamma_2$; $\ln \gamma_1 - \ln \gamma_2 = \ln K_1 - \ln \bar{K}_1$

Hence,

$$\left(\frac{\partial \ln \gamma_1}{\partial N_1}\right)_T - \left(\frac{\partial \ln \gamma_2}{\partial N_1}\right)_T = -\frac{1}{\bar{K}_1}\cdot\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Now $\ln \gamma_1$ and $\ln \gamma_2$ can be evaluated by graphical integration from eqns. (17) and (18), if the values of N_2, N_3, $\bar{K}_1$, and $\bar{K}_3$ are known over the whole range from $N_1 = 0$ to 1. The integration constants will depend upon the standard states selected for water and polymer.

The necessary data can be obtained from recent publications.[3,4,8-10,12,13] If W_1 is the number of moles of water per mole of lactam in the initial reaction mixture, and W_3 is the weight fraction of lactam in the mixture (polymer + lactam) at equilibrium, it is found empirically that W_3 varies linearly with W_1. We have :

At 221·5° $\qquad W_3 = 0{\cdot}059 + 0{\cdot}035W_1$ . . . . (20)

At 253·5°, $\qquad W_3 = 0{\cdot}076 + 0{\cdot}042W_1$ . . . . (21)

$$N_1 = W_1/(1 + W_1);\ N_2 = (1 - W_3)/(1 + W_1)\ ;\ N_3 = W_3/(1 + W_1)$$

The activity of a solvent in a polymer–solvent system can usually be evaluated, in the region of high concentration, by regarding the system as a mixture of solvent molecules and " segments " of the polymer which act as independent molecules. The activity of the solvent is then proportional to the mol. fraction as given by (mols. of solvent)/(mols. of solvent + mols. of " segments ").

Eqn. (20) and (21) may be written in the form :

$$W_3 = 0\cdot059(1 + W_1/1\cdot69) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20a)$$

$$W_3 = 0\cdot076(1 + W_1/1\cdot81) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21a)$$

From eqn. (20*a*), the addition of 1·69 mols. of water to the polymer–lactam mixture when $W_1 = 0$ will double W_3, the mols. of lactam. From eqn. (6), the activity of lactam, a_3, is constant, except in so far as $(n - 1)/n$ varies from unity. Therefore, the addition of 1·69 mols. of water has doubled the total number of mols. in the system, and the mixture of polymer and lactam from 1 mol. of lactam, at equilibrium, contains 1·69 (mols. + segments). Of these, 0·059 are lactam, so that 0·94 mole of polymer contains 1·63 " segments," and the " segment weight " is 65, equal to 3·6 water molecules. From eqn. (21*a*) at 253·5°, the segment is 0·53 of a unit and the segment weight 60, equal to 3·35 water molecules. A similar calculation for the system thymol–polyaminohexanoic acid [10] gave a value of 2·3 for the ratio " segment weight "/molecular weight of diluent, constant from 200° to 275°. A polymer chain of 6 units would consist of 10 segments with respect to water; therefore, even at this low degree of polymerization one might expect interaction between polymer chains and water molecules to be independent of chain length, and the same as for higher degrees of polymerization.

TABLE 1.

W_1	E	W_3	W_2	N_1	N_2	N_3	n	$\bar{K}_1$	$\bar{K}_3$
$T = 221\cdot5°$.									
0	0	0·059	0·941	0	0·941	0·059	∞	(750)	16·9
0·05	0·070	0·061	0·939	0·0476	0·894	0·058	119	748	17·1
0·1	0·099	0·063	0·937	0·0909	0·852	0·057	84·1	743	17·3
0·2	0·141	0·066	0·934	0·167	0·778	0·055	58·4	720	17·9
0·4	0·204	0·073	0·927	0·286	0·662	0·052	40	672	18·8
0·6	0·259	0·080	0·920	0·375	0·575	0·050	31·3	619	19·4
0·8	0·310	0·087	0·913	0·444	0·508	0·048	25·9	564	20·0
1·0	0·360	0·094	0·906	0·500	0·453	0·047	22·1	515	20·3
1·2	0·408	0·101	0·899	0·545	0·409	0·046	19·3	473	20·6
1·4	0·453	0·108	0·892	0·583	0·372	0·045	17·3	440	20·9
1·6	0·494	0·115	0·885	0·615	0·341	0·044	15·7	416	21·3
1·8	0·532	0·122	0·878	0·643	0·314	0·0435	14·4	397	21·4
2·0	0·578	0·129	0·871	0·667	0·290	0·043	13·2	368	21·5
$T = 253\cdot5°$.									
0	0	0·076	0·924	0	0·924	0·076	∞	(520)	13·2
0·05	0·083	0·078	0·922	0·0476	0·878	0·074	97·6	511	13·3
0·1	0·120	0·080	0·920	0·0909	0·836	0·073	68	495	13·5
0·2	0·172	0·084	0·916	0·167	0·763	0·070	47	473	13·9
0·4	0·243	0·093	0·907	0·286	0·648	0·066	33	466	14·6
0·6	0·306	0·101	0·899	0·375	0·562	0·063	26	434	15·2
0·8	0·355	0·110	0·890	0·444	0·495	0·061	22	414	15·7
1·0	0·403	0·118	0·882	0·500	0·441	0·059	19·2	396	16·1
1·2	0·442	0·126	0·874	0·545	0·398	0·058	17·3	386	16·4
1·4	0·480	0·135	0·865	0·583	0·361	0·056	15·8	376	16·7
1·6	0·516	0·143	0·857	0·615	0·330	0·055	14·5	365	16·9
1·8	0·546	0·152	0·848	0·643	0·303	0·054	13·6	364	17·1
2·0	0·580	0·160	0·840	0·667	0·280	0·053	12·7	354	17·4

In Table 1 are given experimental values for W_1, the mols. of water per mol. of lactam in the original reaction mixture; W_3, the weight fraction of lactam in the dry reaction product, and E, the milliequivalents of end groups per g. in the dry reaction product. The figures were obtained from the graphical data published by Hermans, and van Velden, and their co-workers.[8, 9] From them the following derived quantities have been calculated; W_2, the weight fraction of polymer in the dry reaction product; n, the number average degree of polymerization; the mol. fractions N_1, N_2, and N_3, as previously defined; and the apparent equilibrium constants $\bar{K}_1$ and $\bar{K}_3$. The experimental values extend only from $N_1 = 0$ to $N_1 = 0{\cdot}667$. Over this range N_2, N_3, and $\bar{K}_3$ are linear functions of N_1 at both 221·5° and 253·5°, and it will be assumed that they can be extrapolated linearly from $N_1 = 0{\cdot}667$ to $N_1 = 1{\cdot}0$. The values for N_2 and N_3 calculated from Matthes's data[13] at 220° are in agreement with this extrapolation.

$\bar{K}_1$ is a linear function of N_1 at 253·5° over the range $N_1 = 0$—$0{\cdot}667$, and it will be assumed that it can be extrapolated linearly to $N_1 = 1{\cdot}0$. At 221·5°, $\bar{K}_1$ is not linear from $N_1 = 0$ to $N_1 = 0{\cdot}45$, but appears to be so from $N_1 = 0{\cdot}45$ to $N_1 = 0{\cdot}667$, and it will be assumed that it can be extrapolated linearly to $N_1 = 1{\cdot}0$. The plot of $\bar{K}_1$ at 221·5° and 253·5° against N_1 is shown in Fig. 1. The plot of $\bar{K}_1$ for 7-aminoheptanoic acid from $N_1 = 0{\cdot}667$ to $N_1 = 1{\cdot}0$ at 220°, from Wiloth's data,[3] is also shown. It will be seen that this is linear, and the slope is almost the same as for $\bar{K}_1$ for 6-aminohexanoic acid, so that the linear extrapolation appears to be justified. The plots of $\bar{K}_1$ at 221·5° and 253·5° cross at $N_1 = 0{\cdot}70$. The slope of the curve for $\bar{K}_1$ at 221·5° from $N_1 = 0$ to $N_1 = 0{\cdot}45$ is determined by assuming that $(\partial\bar{K}_1/\partial N_1)_T = 0$ at $N_1 = 0$, and decreases linearly to -850 at $N_1 = 0{\cdot}45$; from then onwards it remains constant. The plot of $-(\partial\bar{K}_1/\partial N_1)_T$ is also shown on Fig. 1. The abrupt change at $N_1 = 0{\cdot}45$ is unsound mathematically, but the values obtained for $(\partial\bar{K}_1/\partial N_1)_T$ are probably sufficiently accurate. The plot of $\bar{K}_1$ in this region fits the experimental points reasonably.

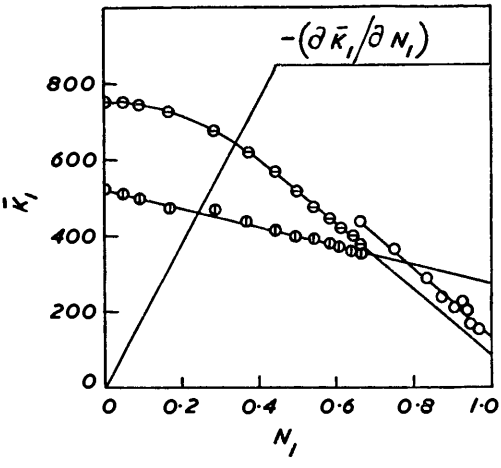

Fig. 1. *$\bar{K}_1$ for 6-aminohexanoic acid at* ⊖ 221·5° *and* ⦶ 253·5°, *and for* ○ *7-aminoheptanoic acid at* 220°.

From the plots of N_2, N_3, $\bar{K}_1$, and $\bar{K}_3$ against N_1, extrapolated where necessary, the values of these quantities at regular increments of N_1 were obtained. These are given in Table 2; from them the corresponding values of $(\partial \ln \gamma_1/\partial N_1)_T$ and $(\partial \ln \gamma_2/\partial N_1)_T$ were calculated. The values of $\ln \gamma_1$ and $\ln \gamma_2$ were obtained by summing the differential by the trapezoidal rule; a more accurate method is probably not justified. The magnitude of the integration constant is determined by the standard states chosen for water and polymer.

For water, the standard state is liquid water at the temperature of the reaction. Then $\ln \gamma_1 = 0$ when $N_1 = 1{\cdot}0$; and when $N_1 = x$, $\ln \gamma_1 = -\int_{N_1=x}^{N_1=1} (\partial \ln \gamma_1/\partial N_1)\mathrm{d}N_1$.

For polymer, the standard state is polymer of infinite chain length ($N_1 = 0$), and in equilibrium with its lactam at the reaction temperature. This convention is both mathematically convenient and experimentally sound. Polymer free from lactam would, under this convention, have a positive free energy, but above its melting point it would quickly revert to the equilibrium mixture of polymer and lactam, for which, by this convention, $\Delta F = 0$.

Since $\ln a_2 = \ln N_2 + \ln \gamma_2 = 0$ when $N_1 = 0$, $\ln \gamma_2 = -\ln N_2$ when $N_1 = 0$; when $N_1 = x$, $\ln \gamma_2 = -\ln N_2(N_1 = 0) + \int_{N_1=0}^{N_1=x} (\partial \ln \gamma_2/\partial N_1) \mathrm{d}N_1$.

Table 2 gives the values for $\log \gamma_1$, $\log \gamma_2$, and γ_1/γ_2 from $N_1 = 0$ to $N_1 = 1{\cdot}0$, at 221·5° and at 253·5°.

The values depend on the correctness of the extrapolation of $\bar{K}_1$ from $N_1 = 0{\cdot}70$ to $N_1 = 1{\cdot}0$; the influence of $\bar{K}_3$ is relatively small. The apparent equilibrium constant for eqn. 5, $\bar{K}_2 = \bar{K}_1/\bar{K}_3$, has a limiting value of 3·75 at 221·5°, and 14 at 253·5°, when $N_1 = 1$. It follows that in a dilute solution of 6-aminohexanoic acid, about 80% will be converted into lactam at 221·5°, and 93% at 253·5°. Technical data [12] show that when the polymer is heated with 64 mols. of water at 220°, 60% is converted into lactam, and the remainder is not all 6-aminohexanoic acid; some dimer and trimer are present. At 260°, with 32 mols. of water, conversion into lactam is 76%. It follows that $\bar{K}_1$ cannot be very small, in the limit; it must be at least 2—3 times $\bar{K}_3$. If $\bar{K}_1$ at 221·5° is extrapolated linearly to 50 at $N_1 = 1$, instead of 90, this will not affect the value of $\log \gamma_2$ from $N_1 = 0$ to $N_1 = 0{\cdot}7$, since the standard state for polymer is at $N_1 = 0$, and the integal is summed from $N_1 = 0$. Beyond $N_1 = 0{\cdot}7$, the deviation is considerable, owing to the increase in $1/\bar{K}_1$ in $\frac{N_2}{\bar{K}_1}\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T$. The value of $\log \gamma_1$ is affected throughout the whole range, since the standard state for

TABLE 2.

N_1	N_2	N_3	$\bar{K}_1$	$\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T$	$\bar{K}_3$	$\left(\frac{\partial \bar{K}_3}{\partial N_1}\right)_T$	$\log \gamma_1$	$\log \gamma_2$	γ_1/γ_2	K_1
					T = 221·5°.					
0	0·94	0·059	750	0	16·7	7·3	−0·205	0·0264	0·587	440
0·05	0·89	0·058	746	− 90	17·0	,,	−0·204	0·0257	0·589	439
0·1	0·84	0·057	740	−180	17·4	,,	−0·201	0·0248	0·594	440
0·2	0·745	0·055	712	−370	18·1	,,	−0·189	0·0208	0·617	439
0·3	0·65	0·052	665	−560	18·9	,,	−0·168	0·0117	0·661	439
0·4	0·55	0·050	600	−750	19·6	,,	−0·141	−0·0063	0·733	440
0·5	0·455	0·047	515	−850	20·35	,,	−0·109	−0·0373	0·847	436
0·6	0·355	0·045	432	,,	21·05	,,	−0·077	−0·0836	1·016	439
0·7	0·26	0·042	347	,,	21·8	,,	−0·047	−0·150	1·267	440
0·8	0·16	0·040	262	,,	22·6	,,	−0·022	−0·248	1·684	441
0·9	0·065	0·037	175	,,	23·3	,,	−0·004	−0·406	2·524	442
0·965	0	0·035	120	,,	23·8	,,	−0·0002	−0·570	3·71	445
1·0	0	0	90	,,	24·0	,,	0	−0·696	4·96	447
									Mean =	440
					T = 253·5°.					
0	0·92	0·076	520	−245	12·7	6·7	−0·1043	0·0343	0·727	378
0·05	0·88	0·075	510	,,	13·05	,,	−0·0952	0·0331	0·744	379
0·1	0·83	0·073	497	,,	13·4	,,	−0·0863	0·0314	0·763	379
0·2	0·73	0·069	473	,,	14·05	,,	−0·0696	0·0262	0·802	379
0·3	0·63	0·066	447	,,	14·6	,,	−0·0541	0·0185	0·846	378
0·4	0·54	0·063	423	,,	15·25	,,	−0·0401	0·0080	0·895	379
0·5	0·44	0·059	398	,,	16·1	,,	−0·0279	−0·0057	0·950	378
0·6	0·345	0·056	374	,,	16·75	,,	−0·0175	−0·0229	1·013	379
0·7	0·25	0·052	350	,,	17·45	,,	−0·0093	−0·0441	1·083	379
0·8	0·15	0·049	325	,,	18·1	,,	−0·0036	−0·0701	1·165	379
0·9	0·055	0·045	300	,,	18·75	,,	−0·0007	−0·1010	1·260	378
0·955	0	0·045	287	,,	19·1	,,	−0·0002	−0·1204	1·319	379
1·0	0	0	275	,,	19·4	,,	0	−0·1373	1·373	378
									Mean =	379

water is $N_1 = 1$, and the integal is summed towards $N_1 = 0$. Calculation shows that $\log \gamma_1$ would be increased by about 0·01 from $N_1 = 0{\cdot}7$ to $N_1 = 0$, corresponding to an error of 28% at $N_1 = 0{\cdot}7$, but only about 5% over the range $N_1 = 0$—$0{\cdot}1$. It seems probable that at 221·5° $\log \gamma_1$ and $\log \gamma_2$ are within 5—10% of the true values from $N_1 = 0$ to $N_1 = 0{\cdot}1$, and that the error is no greater at 253·5°.

The value of the true equilibrium constant K_1 is 440 at 221·5° and 379 at 253·5°. From these values, $\log K_1$ is given by :

$$\log K_1 = 1{\cdot}569 + 531/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$\Delta H = -2{\cdot}42$ kcal./mole, and $\Delta S = 7{\cdot}16$ cal./mole^{-1} degree^{-1}. These values are different from those previously calculated, which were based on data from an alkali-catalysed polymerization.[1] The reaction between a carboxyl and an amino-group (to form an amide) appears to be exothermic in the polyamide melt; the reaction between glycine molecules to form glycine peptides in the solid state is endothermic, as calculated from the heats of combustion.[17] The difference may be due to the heats of fusion. The rather low value for the entropy of the reaction suggests that in the melt the carboxyl and amino-groups exist largely as uncharged groups, and not as zwitterions.

The equilibrium between steam and polyaminohexanoic acid at 293° has been studied by Meacock.[18] In his experiments a polymer in which some of the terminal groups were acetylated was held at 293° for several hours in an atmosphere of steam. At 293° the saturation pressure of steam is 76·9 atm.; the activity of steam at 1 atm., referred to liquid water as standard state, is 0·013. In one series of experiments the polymer contained 0·00836 equiv. of CO_2^- and 0·00373 equiv. of NH_3^+ per mole (113 g.), and hence 0·992 equiv. of $-CO{\cdot}NH-$. Assuming that the activity of the polymer is unity, since the amount of free water in the system will be very small under these conditions, and inserting these values in the expression, $K_1 = (H_2O)(-CO{\cdot}NH-)/(CO_2^-)(NH_3^+)$, gives $K_1 = 414$ at 293°; for a second series of experiments, in which the polymer contained 0·00678 equiv. of CO_2^- and 0·00452 equiv. of NH_3^+, $K_1 = 421$. The agreement between the two series and the constancy of the end-group values during several hours, indicate that these are true equilibrium values. The value for K_1 at 293° calculated from eqn. (24) is 321. The discrepancy is probably due to lactam. In Meacock's experiments, although the total vapour pressure over the melt was 1 atm., an appreciable part of this was due to lactam, so that the partial pressure of steam was less than 1 atm. A partial pressure of lactam of 0·25 atm. would be sufficient to bring Meacock's result into agreement with that calculated from eqn. (24). At 293° the melt would contain about 10% of lactam.[10] Since the boiling point of the lactam is about 275°, and since its activity in the polymer melt will be greater than its weight fraction, a partial pressure of 0·25 atm. is quite possible.

From the data in Table 2, the temperature–composition diagram for the system can be constructed, with lines of equal lactam content, lines of equal partial pressure of water, and lines of equal degree of polymerization.

In order to plot the lines of equal lactam content on the diagram, it is necessary to have the graphs of lactam content (W_3) against water content (W_1) for several temperatures. Two such graphs are available from the experimental data,[9] at 221·5° and 253·5°, and have been employed in calculating the values in Table 2. Others were constructed in the following way. The plot of $\log W_3$ against $1/T$ is a straight line; [1,10] consequently the values of W_3 at different temperatures can be obtained from this plot, by using the values of W_3 at 221·5° and 253·5° when $W_1 = 0$. The graphs of W_3 against W_1 at these temperatures are linear, and intersect at $W_1 = -2{\cdot}43$; $W_3 = -0{\cdot}026$; and it may be assumed that all the graphs of W_3 against W_1 pass through the same point; such a relationship has been shown to hold for the system thymol–polyaminohexanoic acid.[10] From this set of graphs the value of W_1, and hence of N_1, for which W_3 has a given value at a given temperature, may be read off (Fig. 2).

The lines of equal partial pressure of water are obtained in the following way. The

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[17] Wrede, *Z. phys. Chem.*, 1910, **75**, 92.
[18] Meacock, *J. Appl. Chem.*, 1954, **4**, 173.

activity of water in the system is given by $N_1 \gamma_1$; since, in general, log γ_1 will be a linear function of $1/T$ to a first approximation, the function (log N_1 + log γ_1) may be plotted as a linear function of $1/T$, for different values of N_1, by using the corresponding values of γ_1 at 221·5° and 253·5°. If the saturation pressure of water vapour at any temperature is p atm. the activity of water at that temperature when the partial pressure of water vapour is 1 atm. is $1/p$, and log $1/p$ will be a linear function of $1/T$. The values of $1/T$ at which (log N_1 + log γ_1) intercepts log $1/p$ give the values of N_1 and T for which $p_{H_2O} = 1$ atm. The intercepts with log $2/p$, log $0{\cdot}5/p$, etc., give the values for which $p_{H_2O} = 2$ atm., 0·5 atm., etc. These graphs are shown in Fig. 3.

FIG. 2. *Plot of W_3 against W_1 for different temperatures.*

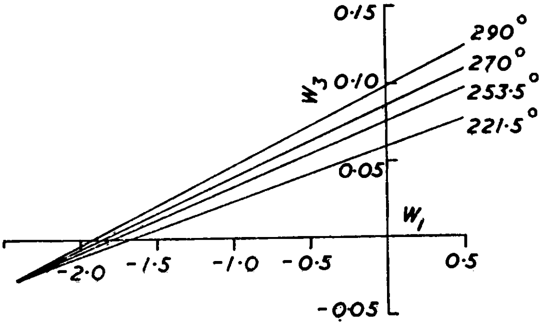
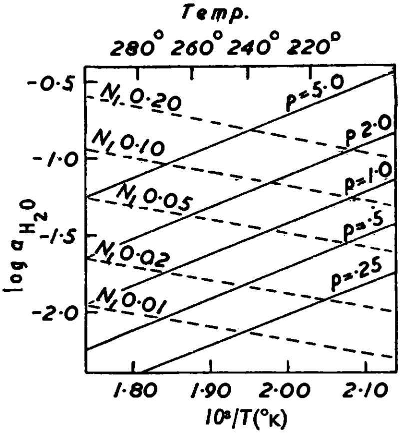


FIG. 3.



——— *Plot of* log $p/p_{sat.}$ *against* $1/T$ *for different values of* p.
– – – – *Plot of* (log N_1 + log γ_1) *against* $1/T$ *for different values of* N_1.

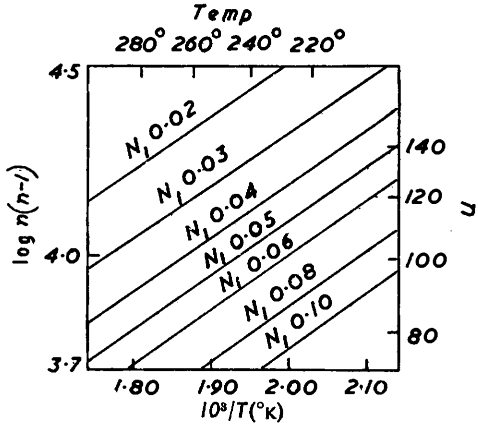
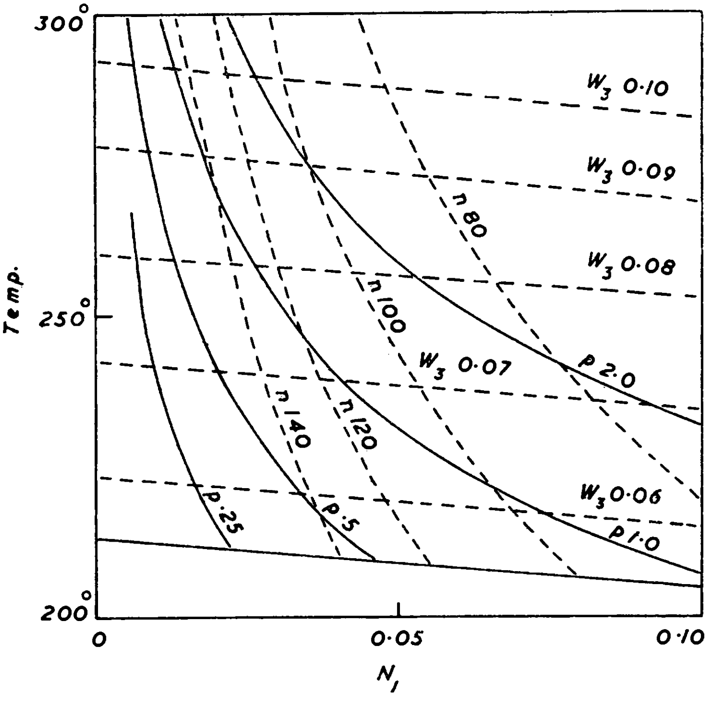


FIG. 4. *Plot of* (log $\bar{K}_1$ – log N_1 + log N_2) *against* $1/T$ *for different values of* N_1.

From eqn. (4*a*) we have: log $\bar{K}_1$ – log N_1 + log N_2 = log $n(n - 1)$; and log $\bar{K}_1$ = log K_1 – log γ_1 + log γ_2; since these are linear functions of $1/T$, log $\bar{K}_1$ may be so regarded. log N_2 is not strictly linear with respect to $1/T$, but varies only slightly with temperature, and no great error would be introduced by assuming it to vary linearly. (log $\bar{K}_1$ – log N_1 + log N_2) was plotted against $1/T$ for different values of N_1, the values of $\bar{K}_1$ and N_2 at 221·5° and 253·5° being used. The values of $1/T$ for which the function is equal to log $n(n - 1)$ when n = 80, 100, 120, etc., give the values of T and N_1 for which n has these values (Fig. 4).

The composition–temperature diagram from 200° to 300°, and from $N_1 = 0$ to $N_1 = 0{\cdot}1$, is shown in Fig. 5; this is the technically important region. Spinnable polymers must lie to the left of the line $p = 1{\cdot}0$; to the right of this line the partial pressure of steam over the melt is greater than 1 atm., and bubbles will be formed at the spinneret. The higher the spinning temperature, the higher the lactam content of the melt, and the higher also the partial pressure of lactam. The minimum degree of polymerization for fibre formation is about 80; all polymers for which p_{H_2O} is less than 1 atm. have degrees of polymerization greater than this; this is in agreement with the technical observation that the polymer melt can be blanketed with steam at atmospheric pressure without causing depolymerization. This is not possible with polyesters. The maximum degree of polymerization which is desirable is probably around 140—160; beyond this, difficulty arises during drawing. Fig. 5 shows that at 270° the polymer having a degree of polymerization of 140 has a partial pressure of water vapour of 1 atm., in addition to a significant partial pressure of lactam. In order to spin at these temperatures it is necessary to have some method of controlling the degree of polymerization other than the activity of water in the system, and this can be done by the addition of acetic or benzoic acid, which acylate some of the terminal amino-groups.

FIG. 5. *Temperature–composition diagram for the system*: *6-hexanolactam–water.*



At 260°, when $N_1 = 0{\cdot}025$, the partial pressure of water is 1 atm. The degree of polymerization is about 130, so that of the total water in the system, about 0·008 mol. is bound on the terminal groups of the polymer, and 0·017 mol. is free water. This is equivalent to 0·27% by weight on the polymer. If the polymer is to be melt-spun after being washed with water to remove the free lactam, it will have to be dried to less than 0·27% of free water if bubble formation at the spinneret at 260° is to be avoided.

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