338. *Thermodynamic Properties of a Saturated Polymerising Vapour. Part II.*[1] *Latent Heats and Vapour Pressures for a Polymerising Substance: Reversible, Stepwise Association in the Gas Phase.*

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The saturated vapour of a reversibly polymerising species A, like the vapours of isomerising or associating substances, has anomalous thermal properties. These properties for a polymerising vapour are investigated here for the special case in which the stepwise association constant $K_{i,i+1}$ for the general step in polymerisation

$$A + A_i \rightleftharpoons A_{i+1}; \quad \Delta H_{i,i+1} = -Q_{i,i+1}$$

is independent of i.

Expressions in terms of the individual latent heat of vaporisation of monomer (L_1), the stepwise enthalpy of association ($-Q$), and the stepwise association constant (K), have been derived for the contributions of the mobile equilibria to the temperature coefficient of the latent heat and to the curvature of the vapour-pressure line:

$$\left(\frac{\mathrm{d}L}{\mathrm{d}T}\right)_r = \frac{KP}{1 + KP}\,\frac{Q(Q - L_1)}{\boldsymbol{R}T^2} \qquad \left(\frac{\mathrm{d}\Lambda}{\mathrm{d}T}\right)_r = KP(1 + KP)\,\frac{(Q - L_1)^2}{\boldsymbol{R}T^2}.$$

The forms of these expressions correspond to much more gradual temperature- and pressure-dependence of the anomalies than is the case for a vapour in which an equal degree of polymerisation is reached as the result of a single m-fold association: very sharp maxima in reactive contributions characterise the latter.

The predictions of this model are compared with the observed behaviour of hydrogen fluoride. Although there are other reasons for rejecting it, agreement found is about as good as that for the single hexamerisation. In an Appendix the possibility of simple modifications to the model to allow for variation of the stepwise association constant from one step to another are considered. The case $K_{i,i+1} = K(i + 1)/i$ leads to tractable formulæ and simple results.

THE preceding paper[1] dealt with the thermodynamic properties of the saturated vapour of hydrogen fluoride from the standpoint[2] of a single m-fold association ($m = 6$). At the other extreme of possible behaviour is a gas in which there is an infinite series of polymeric species in mobile equilibrium, a typical elementary reaction and its appropriate equilibrium constant being represented by the equations

$$\mathrm{A} + \mathrm{A}_i \rightleftharpoons \mathrm{A}_{i+1} \qquad i = 1, 2, 3, \cdots$$

$$p_{i+1}/p_i p_1 = K_{i,i+1}$$

where p_i is the partial pressure of i-mer. In its most general form, this represents an infinite number of independent reactions. Particular interest attaches to the simplest case,[3] in which $K_{i,i+1}$ is independent of i, that is in which the equilibrium constant of association is the same for every step. The importance of the model is as a standard against which more complex systems may be compared, and as a contrast to the single

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[1] Part I, Armitage, Gray, and Wright, preceding paper.

[2] Gray, *Proc. Roy. Soc.*, 1961, *A*, **264**, 516.

[3] Kuhn, *Ber.*, 1930, **63**, 1503; Flory, *J. Amer. Chem. Soc.*, 1936, **58**, 1877; Lassettre, *Chem. Rev.*, 1937, **20**, 259.

m-fold association. Some of the properties of such systems have been evaluated by polymer chemists and may be found in standard texts.[4] The model is employed here to derive general expressions for the temperature coefficient of latent heat and for the curvature of the vapour-pressure line for a substance with such a polymerising vapour: this application is novel.

The development adopted begins by setting out the basic equations for chemical equilibrium in a reversibly polymerising vapour and deriving expressions for the equation of state, for the enthalpy of the equilibrium vapour, and for the relationship between real and apparent latent heats of vaporisation. The basis is one formula-weight of monomer. Expressions are here developed in terms of individual latent heats, since these afford an elegant and simple treatment. The variation of the degree of polymerisation along the saturation line, which is needed to derive expressions for $(\mathrm{d}L/\mathrm{d}T)_\mathrm{r}$ and $(\mathrm{d}\Lambda/\mathrm{d}T)_\mathrm{r}$, is evaluated in these terms.

Such a model for a polymerising vapour has been suggested [5] by Ginell * to represent other aspects of the behaviour of gaseous hydrogen fluoride (in which species other than monomer and hexamer are known [6] to occur). Though there are other reasons for rejecting its validity, the simple model gives fair agreement [7,8] with volumetric (P–V–T) data, but not [9] with thermal (C_p–P–T) data. Its predictions are here compared with the observed properties of the saturated vapour of hydrogen fluoride, and, in particular, with experimental values of $\mathrm{d}L/\mathrm{d}T$ and $\mathrm{d}\Lambda/\mathrm{d}T$. No corrections have been made for gas imperfections, for, in view of the sweeping approximations which the application of this theory to hydrogen fluoride already requires, such corrections are superfluous.

More sophisticated forms of this one-parameter model have been suggested, *e.g.*, by Lassettre [3] and by Maclean *et al.*[8] The latter propose, for hydrogen fluoride:

$$K_{1,2} = K'; \quad K_{i,i+1} = (i-1)K/i \qquad \text{where } i = 2, 3, \cdots$$

Forms such as these are considered in an Appendix.

The Basic Equations for Reversible, Stepwise Polymerisation into an Infinite Number of Chains.—A vapour in which monomer units, A, associate in the gaseous phase to an infinite number of polymers can be described in terms of equilibria of the type

$$\mathrm{A} + \mathrm{A}_i \rightleftharpoons \mathrm{A}_{i+1}, \tag{1}$$

where i takes values from 1 to infinity.

If the partial pressure of the ith species is p_i, and K_i (Rossotti's K_q, where $q = i + 1$) is the equilibrium constant for the step shown above, then

$$P_{i+1} = K_{i,i+1}p_ip_1. \tag{2}$$

If $K_{i,i+1}$ is independent of i over a range of temperature, then the enthalpy change associated with the step shown above is also constant, and

$$P_{i+1} = K^ip_1^{i+1}. \tag{3}$$

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* Ginell's paper is marred by numerous errors, both in his own development and in his treatment of Blatz and Tobolsky's work. All the results in it are wrong, and it is unfortunate that they are finding a place in the literature, *e.g.*, in Simons's " Fluorine Chemistry."

[4] See, *e.g.*, Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1953.

[5] Ginell, *J. Colloid Sci.*, 1948, **3**, 1; see also Blatz and Tobolsky, *J. Phys. Chem.*, 1945, **49**, 77.

[6] See, *e.g.*, Smith, *J. Chem. Phys.*, 1958, **28**, 1040; *J. Mol. Spectroscopy*, 1959, **3**, 473.

[7] Spalthoff and Franck, *Z. Elektrochem.*, 1957, **61**, 348.

[8] Maclean, Rossotti, and Rossotti, unpublished work; see also Rossotti and Rossotti, *J. Phys. Chem.*, 1961, **65**, 1376.

[9] Franck and Meyer, *Z. Elektrochem.*, 1959, **63**, 571.

The total pressure $P = \sum_{1}^{\infty} p_i$ can be found by summing † the geometric series

$$P = \sum_{i=0} K^i p_1^{i+1} = p_1/(1 - Kp_1)$$

This result can be rearranged to give p_1 in terms of P as

$$p_1 = P/(1 + KP). \qquad (4)$$

If the density of the vapour is ρ, then a route from experimental data to a value for K is afforded by the evaluation of the quantity $\rho \boldsymbol{R}T/M_1$ (where M_1 is the molecular weight of monomer) which is the pressure P^* that the vapour would exert if it were entirely monomeric

$$P^* = \sum_{1}^{\infty} ip_i = \sum_{1}^{\infty} iK^{i-1}p_1^{\,i} = p_1/(1 - Kp_1)^2.$$

By substituting for p_1 from above we obtain

$$P^* = P(1 + KP). \qquad (5)$$

This result can also be written (for M_1 g. of vapour):

$$PV^g = \boldsymbol{R}T/(1 + KP), \qquad (6)$$

which is a form of the equation of state for such a system. The quotient $P^*/P(= P/p_1 = \rho \boldsymbol{R}T/M_1P)$ is identical with the association factor Z of Jarry and Davis,[10] the f of Briegleb and Strohmeier,[11] and the $\bar{q}$ of Rossotti and Rossotti.[12] The identity in the form, $Z = 1 + KP$, will be useful later.

The relation between real and apparent latent heats of vaporisation. The apparent latent heat of vaporisation is defined by the expression $\Lambda = \boldsymbol{R}T^2 \,\mathrm{d}\ln P/\mathrm{d}T$. Now the exact form of the Clapeyron–Clausius equation can be written:

$$L = TP(V^g - V^l)\,\mathrm{d}\ln P/\mathrm{d}T.$$

So long as $V^l \ll V^g$, then for the model under discussion, which obeys the equation of state $PV^g(1 + KP) = \boldsymbol{R}T$, this expression can be written:

$$(1 + KP)L = \boldsymbol{R}T^2\,(\mathrm{d}\ln P/\mathrm{d}T) = \Lambda. \qquad (7)$$

For systems involving only ideal mixtures of perfect gases, $(1 + KP) = Z$, and the general relation, $LZ = \Lambda$, follows. Since $Z > 1$, the apparent latent heat always exceeds the latent heat of vaporisation per formula weight of monomer.

The enthalpy of the equilibrium vapour and individual latent heats of vaporisation. The natural reference states in the system are the pure gaseous monomer and the gaseous polymers (each at unit pressure), and the equilibrium liquid mixture.

If the K's are all equal over a range of temperature, then the enthalpy of the reaction

$$\mathrm{A} + \mathrm{A}_i \rightleftharpoons \mathrm{A}_{i+1}; \quad \Delta H_{i,i+1} = -Q_{i,i+1}$$

is also independent of i. If this enthalpy change is $-Q$, then H_i^g, the enthalpy of the ith polymer in the gaseous phase, is related to that of the $(i + 1)$th, H_{i+1}^g, as follows:

$$H_{i+1}^g = H_i^g - Q + H_1^g = (i + 1)H_1^g - iQ.$$

Now, if one formula-weight of A is considered (*e.g.*, 20·01 g. in the case of hydrogen fluoride)

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† The summation is only valid if $Kp_1 < 1$, but this condition will be satisfied for any value of KP, since K, P, and p_1 are necessarily positive.

[10] Jarry and Davis, *J. Phys. Chem.*, 1953, **57**, 600.

[11] Briegleb and Strohmeier, *Z. Elektrochem.*, 1953, **57**, 662, 668.

[12] Rossotti and Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, 1961.

when discussing the enthalpy of the gaseous equilibrium mixture, the number of moles of the ith polymer in the mixture is p_i/P^*. Since, in an ideal mixture, there is zero enthalpy of mixing

$$H^g = \sum_1^\infty [ip_iH_1^g - (i-1)p_iQ]/P^*$$

and, the sum being again expressed in terms of K and P, the enthalpy of the equilibrium vapour is given by

$$H^g = H_1^g - QKP/(1+KP).$$

Similar expressions can be derived for the individual latent heats of vaporisation. Since

$$L = H^g - H^l \text{ and } L_1 = H_1^g - H^l$$

therefore $$L = L_1 - QKP/(1+KP) \tag{8}$$

and also, since $$L_i = H_i^g - iH^l$$

therefore $$L_i = iL_1 - (i-1)Q. \tag{9}$$

Whilst it is useful to have explicit expressions for the latent heats of vaporisation of any of the polymers, that for L_1 is particularly serviceable, because its use gives very simple formulæ. It may be noted that $L_1 > L$, since Q, K, and P are always positive.

The Temperature-dependence of the Degree of Polymerisation in the Saturated Vapour.—The degree of polymerisation, $Z = (\sum ip_i)/(\sum p_i)$, depends on both temperature and pressure. Since it has been shown that $Z = 1 + KP$, differentiation with respect to temperature along the saturation line yields

$$\left(\frac{dZ}{dT}\right)_{\text{sat.}} = \left[\frac{d}{dT}(1+KP)\right]_{\text{sat.}} = K\left(\frac{dP}{dT}\right)_{\text{sat.}} + P\frac{dK}{dT},$$

K being a function of temperature only. Application of the definition of Λ and of the van't Hoff isochore ($dK/dT = -QK/\boldsymbol{R}T^2$) leads to

$$(dZ/dT)_{\text{sat.}} = KP(\Lambda - Q)/\boldsymbol{R}T^2. \tag{10a}$$

By means of eqn. (7) and (8) this can also be expressed as

$$(dZ/dT)_{\text{sat.}} = KP(1+KP)(L_1 - Q)/\boldsymbol{R}T^2 \tag{10b}$$

Since K, P, and T are positive, $(dZ/dT)_{\text{sat.}}$ has the same sign as $(\Lambda - Q)$ or $(L_1 - Q)$. When $L_1 > Q$, the degree of polymerisation in the saturated vapour increases with increased temperature. When $L_1 < Q$, it diminishes. The condition for the degree of polymerisation in the saturated vapour to be independent of temperature is, from (7) and (8) as well as (10),

$$L_1 = L_2 = \cdots L_i = \cdots Q = \Lambda$$

i.e., all the individual latent heats are the same and equal to the stepwise enthalpy of dissociation.

The Temperature-dependence of the Latent Heat of Vaporisation.—On the assumption of stepwise polymerisation with equal changes in thermodynamic function for each step, L is equal to $L_1 - QKP/(1+KP)$. This equation can be differentiated with respect to temperature along the saturation line to give an expression for dL/dT:

$$\frac{dL}{dT} = C_{p1}^g - C_p^l - \frac{Q}{(1+KP)^2}\left[\frac{d(KP)}{dT}\right]_{\text{sat.}},$$

where Q is assumed not to vary with temperature or pressure. By use of eqn. (10b) this yields

$$\frac{\mathrm{d}L}{\mathrm{d}T} = C_{p1}{}^{g} - C_{p}{}^{l} + \frac{KP}{1 + KP}\,\frac{Q(Q - L_1)}{\boldsymbol{R}T^2}. \tag{11}$$

This expression for the temperature coefficient of latent heat can be divided into " frozen " and " reactive " contributions.

The " frozen " contributions to $\mathrm{d}L/\mathrm{d}T$. The " frozen " contributions is $(C_{p1}{}^{g} - C_{p}{}^{l})$ which is recognisable as the temperature coefficient of L_1, the latent heat of vaporisation of monomer. It is always negative.

The " reactive " contribution to $\mathrm{d}L/\mathrm{d}T$. The reactive contribution is $Q(Q - L_1)KP/(1 + KP)\boldsymbol{R}T^2$. Since Q, KP, and L_1 are necessarily positive the sign of the reactive contribution is the same as the sign of $(Q - L_1)$. The reactive contribution to $\mathrm{d}L/\mathrm{d}T$ is positive if $Q > L_1$, vanishes when $Q = L_1$, and is otherwise negative. Unlike a single m-fold association, for which there is a factor $(\beta - \beta^2)$ where β is the degree of association, there is no maximum in the function $KP/(1 + KP)$.

The Curvature of the Vapour-pressure line, $\mathrm{d}\Lambda/\mathrm{d}T$.—$\Lambda$ and L have been shown to be related by the expression $\Lambda = L(1 + KP)$. Differentiation of this equation along the saturation vapour pressure line gives $\mathrm{d}\Lambda/\mathrm{d}T$, a measure of the curvature of this line:

$$\mathrm{d}\Lambda/\mathrm{d}T = (\mathrm{d}L/\mathrm{d}T)(1 + KP) + L[\mathrm{d}(KP)/\mathrm{d}T]_{\text{sat.}}$$

Since $\mathrm{d}L/\mathrm{d}T$, $[\mathrm{d}(KP)/\mathrm{d}T]_{\text{sat.}}$, and L are known in terms of KP, L_1, Q, and $C_{p1}{}^{g} - C_{p}{}^{l}$ it is possible to substitute in terms of these parameters. The result obtained is

$$\mathrm{d}\Lambda/\mathrm{d}T = (C_{p1}{}^{g} - C_{p}{}^{l})(1 + KP) + KP(1 + KP)(Q - L_1)^2/\boldsymbol{R}T^2 \tag{12}$$

which can again be separated into a " frozen " and a " reactive " contribution.

The " frozen " contribution. $(\mathrm{d}\Lambda/\mathrm{d}T)_f$ is $(C_{p1}{}^{g} - C_{p}{}^{l})(1 + KP)$, and is always negative. It is identical with the " frozen " contribution appropriate to a single m-fold association.

The "reactive" contribution. The "reactive" contribution, which is due to the mobile equilibrium in the vapour phase, is given by

$$\left(\frac{\mathrm{d}\Lambda}{\mathrm{d}T}\right)_r = KP(1 + KP)\,\frac{(Q - L_1)^2}{\boldsymbol{R}T^2}.$$

It is never negative. It vanishes when $Q = L_1$ (or when $KP = 0$, in which case there is no polymerisation). It has no sharp maximum, although the combination of the three factors, $[KP(1 + KP)]$, $(Q - L_1)$, and T^{-2}, may give rise to a low maximum in the reactive contribution.

Numerical Comparison with Hydrogen Fluoride.—It is of interest to examine whether the model gives a good account of the thermal properties ($\mathrm{d}L/\mathrm{d}T$ and $\mathrm{d}\Lambda/\mathrm{d}T$) of the saturated vapour of hydrogen fluoride: it has been used in the past in attempts to correlate P–V–T data [5,7,8] and C_p–P–T data.[9] All the experimental values and most of the data for calculations have been evaluated in Part I. However, a value must be chosen for Q, the stepwise enthalpy increase on dissociation. For Q, one can either pick the value which best fits these experimental data, or one can derive an " experimental " value from other thermal measurements. Franck and Meyer [9] present a graph ($\log P_m$ against $T_m{}^{-1}$) displaying the locus of experimental values of pressure and temperature at which the heat capacity of hydrogen fluoride vapour is a maximum which implies a value $Q = ca.$ 8000 cal. mole^{-1}. This is the value adopted here. Comparison between calculation and observation is made in the Table.

For $\mathrm{d}L/\mathrm{d}T$, calculation successfully predicts positive values from —45° to 100°; agreement is best at 0° and 59° and worst at 100°.

For $d\Lambda/dT$, calculation fails to predict the correct sign except at —45°, and though the absolute size of the disrepancy is reasonable at —45° and 0°, it is rather large at 50° and 100°.

The discrepancies are, of course, due in part to the inadequacy of the model. However, because $(Q - L_1) \ll Q$, comparison is exceedingly sensitive to the value chosen for Q. A slightly larger value of Q, while remaining consistent with the ($\log P_m$ against T_m^{-1}) graph, could reduce the discrepancies to insignificance.

Calculated and experimental values for dL/dT and $d\Lambda/dT$.

Temperature (°c)	—45	0	50	100
$Z\ (= 1 + KP)$	4·11	3·69	$3{\cdot}01_5$	2·45
$(Q - L_1)$ (cal./20·01 g.)	515	484	590	485
$(dL/dT)_{\text{calc.}}$ (cal. deg.$^{-1}$)	26·9	14·7	9·2	0·8
$(dL/cT)_{\text{exp.}}$ (cal. deg.$^{-1}$)	—	15 *	12·3	9·3
$(d\Lambda/dT)_{\text{calc.}}$ (cal. deg.$^{-1}$)	19·6	—0·9	—7·9	—15·2
$(d\Lambda/dT)_{\text{exp.}}$ (cal. deg.$^{-1}$)	9·8	8·1	6·3	5·0

* Average of two discordant values.

Conclusions.—This model of a reversibly polymerising saturated vapour with a uniform stepwise association constant is most important as a standard of one possible extreme of behaviour. In concept, it is sharply differentiated from a saturated vapour in which there is single m-fold association.

The chief contrast is in the relative abundance of the different polymeric species. This model necessarily implies greatest abundance of the smallest species and continuously diminishing abundance with increasing size, whatever the pressure

$$n_1 > n_2 > n_3 \cdots \quad > n_i > n_{i+1} \cdots$$

For a single m-fold association, however, only n_1 and n_m are not zero and n_m can exceed n_1, if certain criteria are satisfied. The fact that, in the saturated vapour of hydrogen fluoride, H_6F_6 may be more abundant than H_2F_2, H_3F_3, H_4F_4, and H_5F_5 is the quantitative objection to the simple assumptions above as the basis for a model for hydrogen fluoride.

There are also, however, strong resemblances between the two models. Both an m-fold association and an infinite series of polymerisations give rise to anomalies in the thermodynamic properties of the unsaturated vapours. For the polymerisation model here discussed, the sign of the anomalous, reactive contributions is determined by the sign of the discriminant $(\Lambda - Q)$ or $(L_1 - Q)$:

	$Q > L_1$	$Q = L_1$	$Q < L_1$
$(dZ/dT)_{\text{sat}}$	—	0	+
$(dL/dT)_r$	+	0	—
$(d\Lambda/dT)_r$	+	0	+

Since, by relations (8) and (9),

$$(\Lambda - Q) = (L_1 - Q)(1 + KP) \text{ and } (L_1 - Q) = (L_i - L_{i-1})$$

the criteria $\Lambda \gtreqless Q$ can also be expressed as $L_i \gtreqless L_{i-1}$. For the case of a single m-fold association, the equivalent criteria are $\Lambda \gtreqless D_m$ or $L_m \gtreqless L_1$.

Finally, there is the question of modifying the specification of the one-parameter, stepwise-polymerisation model in a simple way, whether to imitate a known real system more closely or to illuminate implicit assumptions in the original model. For instance, to imitate hydrogen fluoride better, it would be necessary to emphasise the lower polymers at the expense of both monomer and higher polymers. Another modification might omit all odd- or all even-numbered polymers. In the Appendix, two simple modifications are examined: a more complex one is considered by Lassettre.[3] The important features are the thermodynamic implications of both the original model and the modifications. The original model implies not only that $\Delta H_{i,i+1}$ is constant ($= -Q$), but also that the stepwise entropy of polymerisation, $\Delta S_{i,i+1}$, is a constant ($= -S$). The former assumption is in accord with expectations based on additivity of bond energies, the latter is not, though the error is less serious for higher than for lower polymers.

APPENDIX

Modifications to the One-parameter Model

The simple form of one-parameter model used above leads, for any assigned value of KP, to a unique distribution of polymeric species. The question arises whether a different distribution can be described by any flexible yet simple modification, and usefully employed as a model for real systems. Two such modifications are indicated below. In each there is only one basic parameter K, but the dependence on i of $K_{i,i+1}$ is now specified.

Type (1): $K_{i,i+1} = K[(i+1)/i]$.—In this modification, successive $K_{i,i+1}$'s increase in size and the abundance of species falls off less rapidly. From the new choice of $K_{i,i+1}$ it follows that:

$$p_{i+1} = (i+1)K^i p_1^{i+1}$$

$$P = p_1/(1 - Kp_1)^2$$

$$P^* = p_1(1 + Kp_1)/(1 - Kp_1)^3$$

and $Z = (1 + Kp_1)/(1 - Kp_1)$ or $Kp_1 = (Z - 1)/(Z + 1)$.

The principal formulæ are similar to those of the simple case:

$$H^g = H_1^g - Q2Kp_1/(1 + Kp_1) = H_1^g - Q(Z - 1)/Z$$

$$\left(\frac{dZ}{dT}\right)_{\text{sat.}} = (Z - 1)(Z + 1)\frac{Q - L_1}{RT^2}$$

$$\frac{dL}{dT} = \frac{dL_1}{dT} + \frac{(Z - 1)(Z + 1)}{2Z^2}\,\frac{(Q - L_1)Q}{RT^2}$$

$$\frac{d\Lambda}{dT} = Z\frac{dL_1}{dT} + \frac{(Z - 1)(Z + 1)}{2}\,\frac{(Q - L_1)^2}{RT^2}.$$

Type (2): $K_{i,i+1} = K[i/(i+1)]$.—In this modification, successive $K_{i,i+1}$'s decrease in size, and the abundance of species falls off more rapidly. From the choice of $K_{i,i+1}$ it follows that

$$p_{i+1} = \frac{1}{i+1}K^i p_1^{i+1} \qquad KP = \sum_1^{\infty}\frac{(Kp_1)^i}{i} = -\ln(1 - Kp_1)$$

i.e., $$Kp_1 = 1 - \exp(-KP) \qquad P^* = \sum_1^{\infty} K^{i-1}p_1^i = p_1/(1 - Kp_1).$$

This formulation does not lead to such simple forms as either the original or the first modification.

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