

lactone (13) (200 mg, 0.9 mmol) in THF (2 ml) at -78°C under nitrogen was added lithium diisopropylamide (1.0M, 1.0 ml, 1.0 mmol) in THF. The reaction mixture was stirred at -78°C for 10 min and allowed to warm to -45°C over 0.5 h. A mixture of dry HMPA (192 mg, 1.1 mmol) and methyl iodide (890 mg, 6.3 mmol) in THF (1 ml) was added dropwise to the enolate solution at -45°C and the resulting solution was warmed to -20°C for 0.5 h, and quenched with saturated NH_4Cl , dried (MgSO_4), and evaporated to dryness. The residue was subjected to silica gel column chromatography with hexane-ethyl acetate (3:2) as an eluant to yield the methylated lactone (224 mg) in 92 % yield: NMR (CDCl_3) δ 0.89 (br t, $J=5$ Hz, 3H, CH_3), 1.27 (br s, 19H, CH_2 , CH_3), 1.45–2.10 (m, 4H, CH_2), 2.25–2.65 (m, 1H, $\text{CHC}=\text{O}$), 4.00–4.40 (m, 1H, OCH); IR (NaCl) 1735 ($\text{C}=\text{O}$) cm^{-1} .

2-Methyl-2-hydroxymethyl-5-nonylpentanolide, isomalyn-goli de (3). To a solution of the lactone (14) (200 mg, 0.8 mmol) in THF (3 ml) at -78°C under nitrogen was added lithium diisopropylamide (1.0M, 0.9 ml, 0.9 mmol) in THF. The reaction mixture was stirred at -78°C for 0.5 h, warmed to -20°C , and treated with formaldehyde generated from paraformaldehyde (0.5 g) at 180°C . After all the paraformaldehyde was consumed, stirring was continued for an additional 0.5 h. The reaction mixture was quenched with oxalic acid and extracted with ethyl ether. The ether extracts were washed with brine, dried, and condensed under reduced pressure. The residue was subjected to silica gel column chromatography with hexane-ethyl acetate (2:1) as an eluant to give isomalyn-golide (135 mg, 59 %) along with the starting material (54 mg, 27 %): NMR (CDCl_3) δ 0.89 (br t, $J=5$ Hz, 3H, CH_3), 1.27 (br s, 19H, CH_2 , CH_3), 1.45–2.20 (m, 4H, CH_2), 2.95 (br s, 1H, OH), 3.59 (br s, 2H, OCH_2), 4.15–4.60 (m, 1H, $\text{CHC}=\text{O}$); IR (NaCl) 3450 (OH), 1720 ($\text{C}=\text{O}$) cm^{-1} .

Anal. Calcd for $\text{C}_{16}\text{H}_{30}\text{O}_3$: C, 71.07; H, 11.18. Found: C, 71.42; H, 11.43.

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Determination of Rate Constants in Competitive Consecutive (Series) Second-Order Reaction

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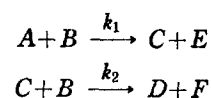
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The kinetics of the reactions of the type $A + B \xrightarrow{k_1} C + E$ and $B + C \xrightarrow{k_2} D + F$ has been analyzed and a method of obtaining approximate values of k_1 and k_2 for the cases where $k_2 \gg k_1$ is proposed.

Introduction

Several detailed numerical procedures have been given for the experimental determination of the individual rate constants k_1 and k_2 in the kinetic systems consisting of two comcompetitive consecutive (series) irreversible second-order

reactions.



Frost and Schwemer¹ developed a method for extracting

the values of k_1 and k_2 solely from a knowledge of the concentrations of A or B as a function of time, which applies to the case of equivalent initial concentrations (e. g., $B_0 = 2A_0$). McMillan² developed a method of obtaining the ratio $K = k_2/k_1$ from a knowledge of the concentration pair of two components at a single time. They are useful mainly for the cases where K is rather small.

In the present work, an approximation method of obtaining k_1 and k_2 that applies for the cases of large values of K is proposed.

Kinetic Expressions

The pertinent rate equations are

$$\frac{dA}{dt} = -k_1AB \quad (1)$$

$$\frac{dB}{dt} = -k_1AB - k_2BC = -k_1B(A + KC) \quad (2)$$

$$\frac{dC}{dt} = k_1AB - k_2BC \quad (3)$$

where A, B and C represent the molar concentrations of the corresponding chemical species. From the material balance conditions

$$A_0 = A + D + C \quad (4)$$

$$2A + C - B = 2A_0 - B_0 \equiv 2a \quad (5)$$

and the known solution³ in the form of implicit function of time

$$\frac{C}{A_0} = \frac{1}{K-1} z(1 - z^{K-1}) \quad (6)$$

where $z \equiv A/A_0$, the concentrations of B and D can be expressed in terms of z as

$$\frac{D}{A_0} = 1 - \frac{K}{K-1} z + \frac{1}{K-1} z^K \quad (7)$$

and

$$\frac{B}{A_0} = \frac{1}{K-1} z[(2K-1) - z^{K-1}] - 2a/A_0 \quad (8)$$

In particular, for the case where $K=1$, the corresponding equations are given by

$$\frac{C}{A_0} = -z \ln z \quad (6')$$

$$\frac{D}{A_0} = 1 - z + z \ln z \quad (7')$$

$$\frac{B}{A_0} = 2z - z \ln z - 2a/A_0 \quad (8')$$

The term $(A + KC)$ appearing in Eq. (2) can also be expressed in terms of z as

$$\begin{aligned} A + KC &= \frac{2K-1}{K-1} A - \frac{KA_0}{K-1} z^K \\ &= 2A + C - A_0 z^K = B + 2a - A_0 z^K \\ &= 2A_0 - (B_0 - B) - A_0 z^K = (B + 2a) - A_0 z^K \end{aligned} \quad (9)$$

It is worth noting that the maximum value of C occurs at

$$z_{\max} = \left(\frac{1}{K}\right)^{\frac{1}{K-1}}; C_{\max} = A_0 z_{\max}^K \quad (10)$$

and the maximum value of C is equal to $A_0 \left(\frac{1}{K}\right)^{\frac{K}{K-1}}$.

Thus, the larger the value of K , the closer the value of z_{\max} to unity; namely, if K is large, the maximum of C occurs at the initial stage of the reaction and the value of KC is always comparable to A for $z \approx z_{\max} (KC_{\max} = A_0 \left(\frac{1}{K}\right)^{\frac{1}{K-1}} = A_0 z_{\max})$, although the value of C_{\max} itself is small (see Table 1 and Figure 1).

Kinetic Equations for B

Eq. (2) can be rewritten, by using Eq. (9), as

$$\begin{aligned} -\frac{dB}{dt} &= k_1 \left[1 + \frac{K}{K-1} (1 - z^{K-1}) \right] AB \\ &= k_1 A_0 B \left[\frac{2K-1}{K-1} z - \frac{K}{K-1} z^K \right] \\ &= k_1 B [(B + 2a) - A_0 z^K] \end{aligned} \quad (11)$$

which holds if $K \neq 1$. On the other hand, combination of Eq. (5) and (6) gives the relationship

$$\begin{aligned} z &= \frac{K-1}{2K-1} \cdot \frac{B+2a}{A_0} + \frac{1}{2K-1} z^K \\ \left(z &= \frac{1}{2-\ln z} \cdot \frac{B+2a}{A_0} \text{ for } K=1 \right) \end{aligned} \quad (12)$$

which allows estimation of the magnitude of z for a given experimental condition by successive approximation. For a sufficiently small value of $A_0 z^K$ in comparison to $B + 2a$, Eq. (11) can be written approximately (exact when $K = \infty$) by

$$-\frac{dB}{dt} \approx k_1 B (B + 2a) = k_1 [2A_0 - (B_0 - B)] B \quad (13)$$

whereas for the cases where $K=1/2$

$$-\frac{dB}{dt} = 1/2 k_1 B (B + 2a) \quad (13')$$

and

$$z^{1/2} = \frac{B+2a}{2A_0}$$

hold exactly. The error in the approximation Eq. (13) is determined by the relative magnitude of $A_0 z^K$ in comparison to $B + 2a$, which is, in turn, related to z by Eq. (12). If the ratio B_0/A_0 is not too small, Eq. (13) should lead to a sufficiently accurate result as long as K is fairly large. The solutions of the above-given rate equations are

$$\ln \frac{B}{B+2a} - \ln \frac{B_0}{B_0+2a} \approx -2ak_1t \quad (K \neq 1, K \neq 1/2) \quad (14)$$

and

$$\ln \frac{B}{B+2a} - \ln \frac{B_0}{B_0+2a} = -ak_1t \quad (K=1/2), \quad (14')$$

respectively. In particular, for equivalent mixtures ($2A_0 = B_0$), the solutions are in the forms

$$\frac{1}{B} - \frac{1}{B_0} \approx k_1t \quad (K \neq 1, K \neq 1/2) \quad (15)$$

and

$$\frac{1}{B} - \frac{1}{B_0} = 1/2 k_1t \quad (K=1/2), \quad (15')$$

respectively. Eq. (15') has been reported in the literature.¹

Eq. (14) can be used for estimation of the value of k_1 from kinetic experiments without too strenuous restriction

on the mixing ratio of the reactants. The $\ln [B/(B+2a)]$ vs. t plot will approach a straight line as the contribution of the term $A_0 z^K$ diminishes. From the slope of the straight line portion, the value of k_1 can be obtained, and the result should be more accurate than that obtained by the previously reported method¹ which relies on overlapping of the experimental Powell plot on the families of calculated ones.

As K tends to zero ($k_2=0$), Eq. (14) can not be used, since the rate equation will not contain $C(A_0-A-B_0-B)$. The solution for such cases is given by the well-known equation

$$\ln \frac{B_0[A_0-(B_0-B)]}{A_0[B_0-(B_0-B)]} = (A_0-B_0)k_1t \quad (16)$$

which can be rewritten in a similar form as Eq. (14):

$$\ln \frac{2B}{2a-B_0+2B} - \ln \frac{B_0}{2a+B_0} = (a-B_0/2)k_1t \quad (16')$$

or

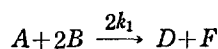
$$\begin{aligned} \ln \frac{B}{B+A_0-B_0} - \ln \frac{B_0}{B_0+2a} &= \ln \frac{B}{B+A_0-B_0} - \ln \frac{B_0}{2A_0} \\ &= (A_0-B_0)k_1t, \end{aligned}$$

which indicates that the treatment of the system as a simple second-order reaction would give approximately twice the value of k_1 ; it is obvious since consumption of B will be a half for $k_2=0$.

On the other hand, for the other extreme case where $k_1 \ll k_2$ (or $k_2=\infty$) hence $2(A_0-A)=B_0-B$ and $C \rightarrow 0$ (but KC is finite) hold, the rate equation is given by

$$\ln \frac{B}{B+2a} - \ln \frac{2B_0}{B_0+2a} = -2ak_1t \quad (14'')$$

which differs from Eq. (14) only by an additional term $\ln 2$ in the left-hand side. Thus, Eq. (14) is essentially the rate equation for



which would represent the system at stationary state $\frac{dC}{dt}=0$

or $C=0$. Benson's Figure 1 and Table I³ indicate that the steady state condition cannot be reached when a large excess of A is used in the reactions with large value of K ; however, in such cases, the magnitude of C becomes negligibly small after a certain length of initial period in view of Eq. (10).

Furthermore, it should be noted that, when A is used in large excess, $B+2a \doteq 2A_0$ in Eq. (13) and $A_0-B_0+B \doteq A_0$ in Eq. (16); thus, the time dependence of B is dominated by the term $\ln B$ (pseudo-first order in B) so that both Eq. (14) and (16') will give straight lines with the slopes in about 1:2 ratio. Therefore, apparent fit of Eq. (16) in the experiment where a large excess of A is used should not be taken as evidence of $K \ll 1$. An example is illustrated in Figure 1.

When the term $A_0 z^K$ is not negligible as in the case where $K < 1$ or $A_0 \gg B_0$, the rate equation

$$\begin{aligned} -\frac{dB}{dt} &= k_1K \left[(B+2a) - \frac{2K-1}{K} A \right] B \\ &= k_1K \left[2(A_0-A) - (B_0-B) + \frac{A}{K} \right] B \end{aligned} \quad (11')$$

which is obtained by substituting Eq. (12) into Eq. (11) gives

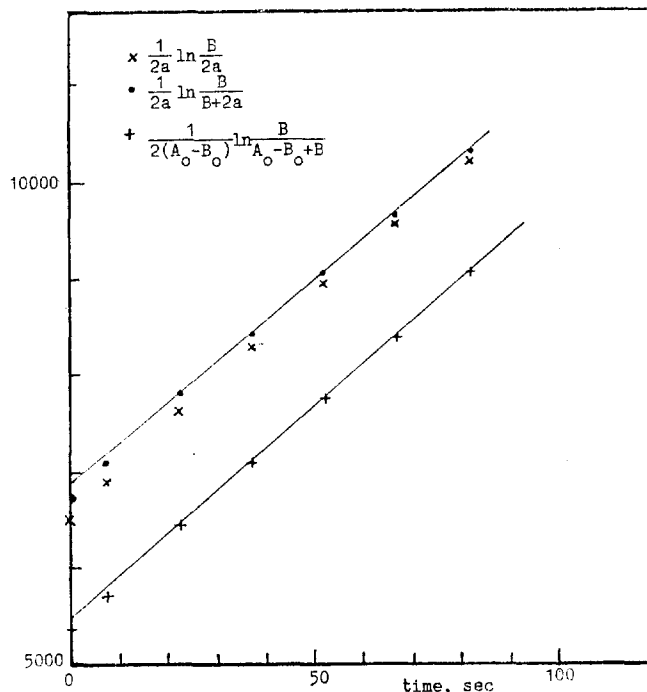


Figure 1. Plots of the kinetic data for $N_2H_4-Br_2$ reaction at $20^\circ C$; $[N_2H_4]_0=20.1 \times 10^{-5} M$, $[Br_2]_0=3.37 \times 10^{-5} M$.

TABLE I: The Value of z for Which the Concentration of C is Maximum

K	$z_{max} = \frac{KC_{max}}{A_0}$	$z_{max}^K = \frac{C_{max}}{A_0}$	K	$z_{max} = \frac{KC_{max}}{A_0}$	$z_{max}^K = \frac{C_{max}}{A_0}$
0.01	0.0095	0.955	2	0.50	0.25
0.1	0.0774	0.774	5	0.699	0.134
0.5	0.25	0.50	10	0.774	0.077
1.0	1/e	0.367	20	0.854	0.043
			40	0.923	0.018
			100	0.955	0.010
			200	0.974	0.005
			500	0.988	0.002

better information. Since the large excess of the reactant A presumes

$$C=2(A_0-A)-(B_0-B) \ll A_0 \doteq A$$

Eq. (11') leads to a pseudo-firstorder rate equation

$$-\frac{dB}{dt} \doteq k_1A_0B$$

provided $C=2(A_0-A)-(B_0-B) \ll \frac{A}{K}$ holds. Thus, if the kinetics deviates from first order in B and simple second-order kinetics treatment gives gradually varying rate constant in an experiment with a large excess of A , one can presume that A/K is not much larger than C . In Figure 1 of McMillan's work², z is plotted against C/A_0 for various values of K from which the condition for negligible contribution of C can be found. As a matter of fact, from Eq. (6), it can be shown that the maximum value of C satisfies

$$\frac{KC_{max}}{A_0} = \left(\frac{1}{K}\right)^{\frac{1}{K-1}} = z_{max} \quad (10')$$

so that KC can be neglected throughout the course of reaction

in comparison to A only for $K < 0.1$ if $A_0 \gg B_0$, as shown in Table 1. Thus, if the term KC can be neglected, the rate equation is represented by

$$-\frac{dB}{dt} \doteq k_1 AB$$

which corresponds to $k_2=0$, whence Eq. (16) should give a constant rate constant. Otherwise, it is better to carry out experiment under the condition of $2A_0 \approx B_0$ so that the magnitude of z decreases rapidly and hence Eq. (14) or (15) can be used, which are valid when $A_0 z^K \ll B+2a$ and $a > 0$ hold.

Finally, rearrangement of Eq. (14) gives

$$B = \frac{B_0}{1 + \frac{B_0}{2a}(1 - e^{-2ak_1 t})} \cdot e^{-2ak_1 t} \quad (17)$$

which predicts the exponential decrease of B for the final stage where $ak_1 t \ll 1$.

For the cases where K is not sufficiently large to make the term $A_0 z^K$ negligible, Frost and Schwemer's method¹ may be the only resort.

Kinetic Equations for A

From the material balance equation (5), B can be expressed in terms of z as

$$B = A_0 \left[2z + \frac{1}{K-1} z (1 - z^{K-1}) \right] - 2a \quad (5')$$

which gives the rate equation for A

$$\begin{aligned} -\frac{dA}{dt} &= k_1 AB = k_1 A_0^2 z \left[\frac{2K-1}{K-1} z - \frac{1}{K-1} z^K - \frac{2a}{A_0} \right] \\ &= -A_0 \frac{dz}{dt} \end{aligned} \quad (18)$$

or

$$\begin{aligned} \ln \frac{A}{A - \frac{K-1}{2K-1} \cdot 2a} - \ln \left[1 - \frac{K-1}{2K-1} \cdot 2a \right] \\ \doteq -k_1 A_0 \frac{2K-1}{K-1} t \end{aligned} \quad (19)$$

if $z^K \ll (2K-1)z$ and $a \neq 0$ hold.

In particular, if $2K-1 \doteq 2(K-1)$, Eq. (19) can be approximated by

$$\ln \frac{A}{A-a} - \ln \frac{B_0}{2A_0} \doteq -2k_1 A_0 t \quad (19')$$

Furthermore, if $a=0$ and $z^K \ll (2K-1)z$, Eq. (18) is integrated to

$$\frac{1}{A} - \frac{1}{A_0} \doteq k_1 \cdot \frac{2K-1}{K-1} t$$

or

$$\frac{A_0}{A} \doteq 1 + k_1 A_0 \frac{2K-1}{K-1} t \quad (19'')$$

The rate equation (19) is valid as long as K is large and $z^K \ll (2K-1)z$ holds. If k_1 is determined from Eq. (14), Eqs. (19') and (19) provide an estimation procedure for K .

Estimation of the Value of K

Svirbely⁴ has suggested that the value of K can be obtained from a measured pair (C, A) of experimental concentrations with the aid of Eq. (6). For fast reactions, the concentration pair after completion of reaction are easier to determine. Since, at the end of the reaction $B=0$, Eq. (12) can be written for $K \neq 1$ as

$$z = \frac{K-1}{2K-1} \cdot \frac{2a}{A_0} + \frac{1}{2K-1} z^K \quad (12')$$

if A is used in excess. If z^K can be neglected in comparison to $(K-1)\frac{2a}{A_0}$, one can approximate Eq. (6) and (7) by

$$\begin{aligned} \frac{C}{A_0} &= \frac{1}{2K-1} \cdot \frac{1}{A_0} [2a - 2A_0 z^K] \\ &\doteq \frac{1}{K-1} \frac{A}{A_0} \left(= \frac{2a}{(2K-1)A_0} \text{ for } B=0 \right) \end{aligned} \quad (6'')$$

and

$$\begin{aligned} \frac{D}{A_0} &= \frac{1}{2K-1} \cdot \frac{1}{A_0} [KB_0 - A_0 + \frac{2K-1}{K-1} z^K] \\ &\doteq 1 - \frac{K}{2K-1} \cdot \frac{2a}{A_0} \quad (\text{for } B=0) \end{aligned} \quad (7')$$

Eq. (6'') indicates that neglect of the z^K term implies the approximation

$$C \doteq \frac{1}{K-1} A \doteq \frac{1}{2K-1} \cdot (B+2a). \quad (6''')$$

Thus, after the reaction is complete, the concentrations of the products satisfy the following relationships:

$$\frac{C}{B_0} \doteq \frac{1}{2K-1} \cdot \frac{2a}{B_0} \quad (20)$$

and

$$\frac{D}{B_0} \doteq \frac{1}{2K-1} \left(K - \frac{A_0}{B_0} \right) \quad (21)$$

$$\begin{aligned} \frac{D}{C} &= \frac{(K-1) - Kz - z^K}{z - z^K} \doteq (2K-1) \frac{A_0}{2a} \\ -K &= \frac{KB_0 - A_0}{2a} = \frac{B_0}{2} \frac{K-1}{\frac{A_0}{B_0}} \end{aligned} \quad (22)$$

provided $z^{K-1} \ll 1$ can be assumed, from which the value of K can be estimated. The proper choice of the value $\frac{2a}{A_0}$ should enable to satisfy the necessary condition for the above-given approximation (see Table 2). If A can be determined accurately at the end of reaction, trial and error method to fit the Eq. (12') will give an estimate of the value of K , but the procedure may be rather cumbersome.

TABLE 2: Product ratio D/C for Various Situations

B_0/A_0	K						
	5	10	20	50	100	200	1000
1.5	13.0	28.0	58.0	148	312	—	—
0.5	4.33	2.67	6.0	16.0	32.7	49.3	66.0
0.2	—	0.55 ₅	1.66	5.00	10.6	16.1	21.7
0.1	—	—	0.52 ₅	2.10	4.71	7.37	10.0
0.01	—	—	—	—	—	0.503	45

Application of the Theory to Experimental Results

The kinetic data⁵ for hydrazine-bromine reaction in 7.2M H₂SO₄ are plotted in Figure 1. Simple second-order treatment by Eq. (16) gives gradually decreasing value of k_1 starting from 97 M⁻¹sec⁻¹ at 7.5 sec to 88 at 82.5 sec. However both Eqs. (14) and (16') give fairly good straight lines that are dominated by $\ln B$. The straight line portion of the competitive consecutive second-order plot of Eq. (14) gives 42 M⁻¹sec⁻¹, whereas the plot of Eq. (16') gives 86 M⁻¹sec⁻¹. The fact that the deviation of initial stage is rather small and diminishes rather rapidly can be attributed to a large value of K so that the magnitude of the term A_0z^K becomes negligible at an early stage of the reaction. Since the point corresponding to $z=0.98$ lies on the straight line, the value of K is inferred to be greater than 10.² Unfortunately, a small

portion of B (mainly N₂H₂ in the present example) is consumed by some side reaction so that estimation of the value of K from stoichiometry may not give results of desirable accuracy, in the present example.

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Temperature Dependence of Self-Diffusion of THO in Copolymer Hydrogel Membrane as a Function of Gel Compositions

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The self-diffusion experiment of THO was performed across a series of copolymer hydrogel membranes at different temperatures. Copolymer hydrogel membranes were prepared by copolymerizing 2-hydroxyethyl methacrylate (HEMA) and 2-aminoethyl methacrylate (AEMA) in the presence of the solvent and the crosslinker, ethylene glycol dimethacrylate (EGDMA). By changing the crosslinker content and the ratio of HEMA and AEMA monomer, two series of copolymer hydrogel membranes were synthesized. The tagging material was THO and efflux of THO was counted on a Liquid Scintillation Counter. The experimental data show that the permeability decreases as the amount of EGDMA and the mole fraction of HEMA increase, and the permeability is proportional to the temperature. The partition coefficient shows a parallel trend with permeability. Using the relationship between viscosity and diffusivity, the viscosity of water within the membrane was obtained. According to the result, the viscosity of water within the membrane has the same value with those of supercooling water. And we obtained the activation energy of THO for transport in the membrane by using Arrhenius plotting.

Introduction

The properties of poly(2-hydroxyethyl methacrylate) (HEMA) hydrogel membrane were investigated by many authors. It is the reason that poly(HEMA) have attracted considerable attentions for medical applications because of their low chemical reactivity, high strength, and high permeability, and have been introduced as important biocompatible materials.¹⁻⁶ The experiments for the transport phenomena have been performed by many authors and given many informations about it. Spacek *et al.*⁷ showed that the diffusion coefficient strongly depends on the structure of the hydrogel membrane investigated. Chen⁸ found that water swelling was changed by the crosslinker content in the dehydrated poly (HEMA) hydrogels. Recently, Kim *et al.*⁹ measured the permeability of THO through fully swollen poly (HEMA) hydrogel membrane with varying the cross-

linker content. They found that diffusion coefficients decrease as the crosslinker contents increase. Refojo *et al.*³ measured the swelling contents in hydrogels at the temperature is varied. They found that the minimum in the amount of water in hydrogel is found in the neighborhood of 60°C and the amount of water in the hydrogel increases up to the freezing and boiling temperature, and the minimum found in the curve in the HEMA hydrogel is independent of the temperature at which the polymerization was carried out. Wisniewski¹⁰ measured the temperature effects of permeation of THO across poly (HEMA) membrane. According to the temperature dependence of diffusion coefficient, they performed the Arrhenius plots and found the activation energy of THO for transport through poly (HEMA) membrane.

In this paper, we measured the permeability and partition coefficient of THO in the copolymer hydrogel membranes with varying the ratio of HEMA and AEMA monomer and