

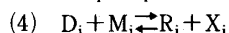
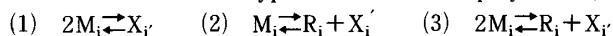
Calculation of Thermodynamic Equilibrium Compositions for Some Multi-component Reaction Systems.

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Abstract

The calculation methods for thermodynamic equilibrium compositions of the reaction system, where the isomerization of reactants as well as of products takes place other than the main reaction, have been demonstrated. The types of reaction employed are,



Corresponding to these types, the equilibrium compositions of some reaction systems have been calculated and shown in the tables.

Introduction

In the petrochemical reactions, the products are often obtained as the mixture of isomers. The calculation of thermodynamic equilibrium compositions for such system has been previously reported in some cases, the examples of which are typical in petrochemistry¹. It may also be possible that even a reactant is isomerized over a catalyst and that the more complex systems must be investigated. In this article, the methods for calculations as well as the examples of thermodynamic equilibrium compositions of such systems are shown to assist the petrochemical research.

Methods for Calculation

Nomenclature

p Total pressure of the reaction system

K_{s_i} ($s = d, m, r$ and $x; i = 1, 2, \dots$) Equilibrium constant

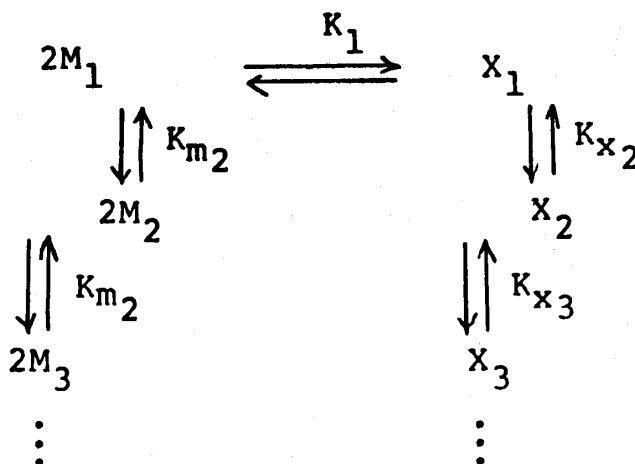
b Ratio of reactant M to D

s_i ($s = d, m, r$ and x) Content of component s at equilibrium

q_e ($q = d_i, m_i, r_i$ and x_i) Concentrations of component q_i at equilibrium

Type 1. Bimolecular reaction shown as scheme 1. Two mol of the reactant, M_1 , react to form one mol of the mixture of isomers, X_i , with decreasing the amounts of substance, where the reactant M_1 is also isomerized.

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The amounts of substance of individual components at equilibrium are as follows ;

$$m_1 = 1 - (m_2 + m_3 + m_4 + \dots) - 2(X_1 + X_2 + X_3 + \dots) \quad (1.1)$$

$$m_i = K_{m_i} m_1 \quad (1.2)$$

$$x_i = K_{x_i} x_1 \quad (1.3)$$

By definition,

$$K_m = 1 + K_{m_1} + K_{m_2} + \dots \quad (1.4)$$

$$K_w = 1 + K_{x_1} + K_{x_2} + \dots \quad (1.5)$$

Then

$$m_1 = (1 - 2x_1 K_w) / K_m \quad (1.6)$$

The equilibrium constant K_1 is

$$K_1 = x_1 K_m^2 (1 - K_w x_1) / (1 - 2K_w x_1)^2 P \quad (1.7)$$

By definition,

$$\sqrt{4K_1 K_w P + K_m^2} = K \quad (1.8)$$

Solving Eq. (1.7)

$$x_1 = (K - K_m) / 2K_w K \quad (1.9)$$

By proper substitution,

$$m_1 = 1/K \quad (1.10)$$

Then, one arrives at following equations, by which the equilibrium compositions can be calculated,

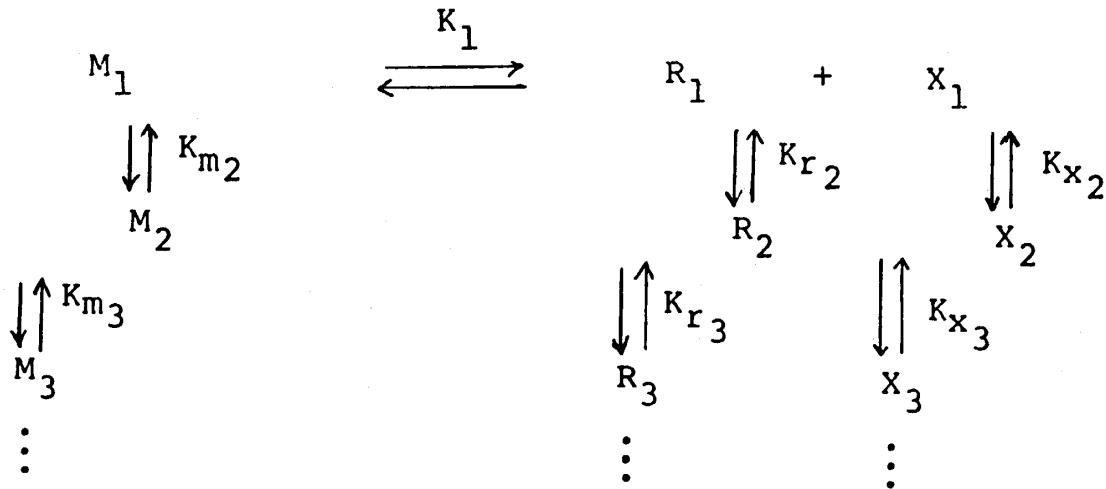
$$m_{1e} = 1/K(1 - K_w x_1) \quad (1.11)$$

$$m_{ie} = K_{m_i} m_{1e} \quad (1.12)$$

$$x_{1e} = (K - K_m) / 2K_w K (1 - K_w x_1) \tag{1.13}$$

$$x_{ie} = K_{x_i} x_1 \tag{1.14}$$

Type 2. Monomolecular reaction shown as scheme 2. One mol of the reactant, M_1 , splits into one mol of the mixture of isomers, R_i , and the other product mixture of isomers, X_i under the reaction pressure, P , with increasing the amounts of substance, where the reactant, M_1 , is also isomerized.



Scheme 2

The amounts of substance of individual components at equilibrium are as follows ;

$$m_1 = 1 - (m_2 + m_3 + \dots) - (x_1 + x_2 + x_3 + \dots) - (r_1 + r_2 + r_3 + \dots) \tag{2.1}$$

$$m_i = K_{m_i} m_1 \tag{2.2}$$

$$r_i = K_{r_i} r_1 \tag{2.3}$$

$$x_i = K_{x_i} x_1 \tag{2.4}$$

By definition,

$$K_m = 1 + K_{m_1} + K_{m_2} + \dots \tag{2.5}$$

$$K_q = 1 + K_{r_1} + K_{r_2} + \dots \tag{2.6}$$

$$K_w = 1 + K_{x_1} + K_{x_2} + \dots \tag{2.7}$$

Then

$$m_1 = (1 - K_w x_1) / K_m \tag{2.8}$$

$$r_1 = K_w x_1 / K_q \tag{2.9}$$

The equilibrium constant K_1 is

$$K_1 = \frac{K_w K_m x_1^2 \cdot P}{K_q (1 + K_w x_1) (1 - K_w x_1)} \quad (2.10)$$

Solving Eq. (2.10)

$$x_1 = \sqrt{K_1 K_q} / \sqrt{K_w K_m P + K_1 K_q K_w^2} \quad (2.11)$$

Then one arrives at following equations,

$$m_{1e} = (1 - K_w x_1) / K_m (1 + K_w x_1) \quad (2.12)$$

$$m_{ie} = K_m m_{1e} \quad (2.13)$$

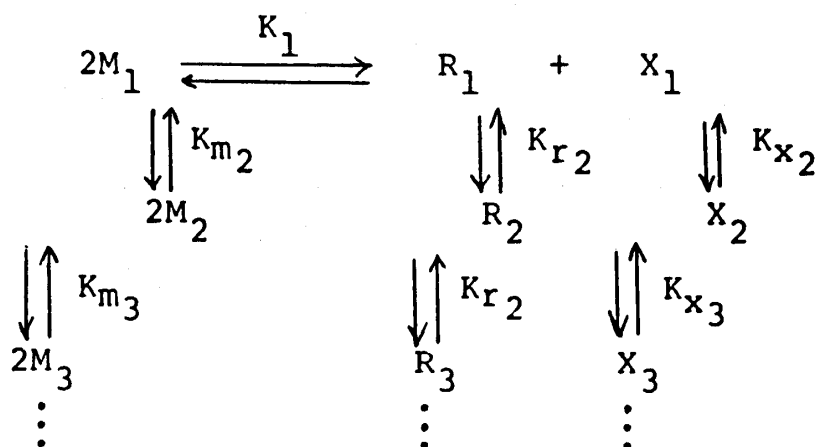
$$r_{1e} = K_w x_1 / K_q (1 + K_w x_1) \quad (2.14)$$

$$r_{ie} = K_r r_{1e} \quad (2.15)$$

$$x_{1e} = x_1 / (1 + K_w x_1) \quad (2.16)$$

$$x_{ie} = K_x x_{1e} \quad (2.17)$$

Type 3. Bimolecular reaction shown as scheme 3. Two mol of reactant, M_1 , react to form one mol of the mixture of isomers, X_i , and the other product mixture of isomers, R_i , where the reactant M_1 is also isomerized.



Scheme 3

The amounts of substance of individual components at equilibrium are as follows ;

$$m_1 = 2 - (m_2 + m_3 + \dots) - 2(x_1 + x_2 + \dots) \quad (3.1)$$

$$m_i = K_w x_i \quad (3.2)$$

$$r_i = K_r r_1 \quad (3.3)$$

$$x_i = K_x x_1 \quad (3.4)$$

By definition,

$$K_m = 1 + K_{m_1}K_{m_2} + \dots \quad (3.5)$$

$$K_q = 1 + K_{r_1} + K_{r_2} + \dots \quad (3.6)$$

$$K_w = 1 + K_{x_1} + K_{x_2} + \dots \quad (3.7)$$

Then

$$m_1 = 2(1 - K_w x_1) / K_m \quad (3.8)$$

$$r_1 = K_w x_1 / K_q \quad (3.9)$$

The equilibrium constant K_1 is,

$$K_1 = K_w K_m^2 x_1^2 / 4K_q(1 - K_w x_1)^2 \quad (3.10)$$

Solving Eq. (3.10)

$$x_1 = 2K / K_w(2K + K_m) \quad (3.11)$$

$$m_1 = 2 / (2K + K_m) \quad (3.12)$$

where

$$K = \sqrt{K_1 K_q K_w} \quad (3.13)$$

Then one arrives at the following equations,

$$m_{1e} = 1 / (2K + K_m) \quad (3.14)$$

$$m_{ie} = K_m m_{1e} \quad (3.15)$$

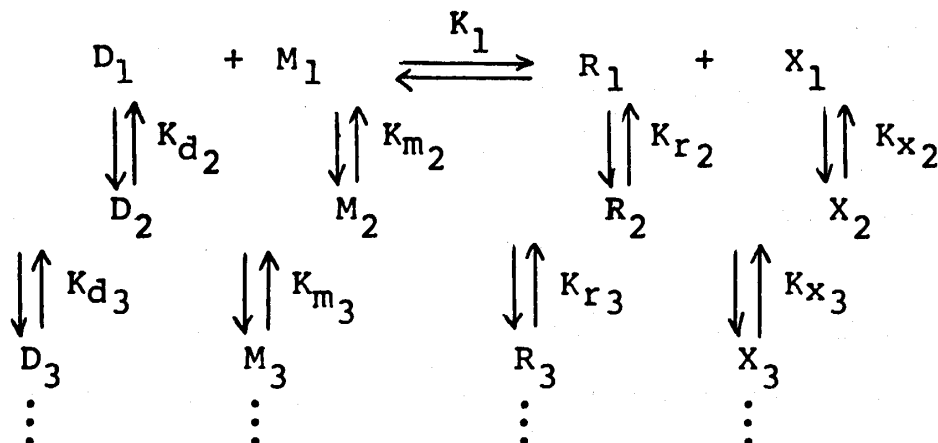
$$r_{1e} = K / K_q(2K + K_m) \quad (3.16)$$

$$r_{ie} = K_r r_{1e} \quad (3.17)$$

$$x_{1e} = K / K_w(2K + K_m) \quad (3.18)$$

$$x_{ie} = K_{x_i} x_{1e} \quad (3.19)$$

Type 4. Bimolecular reaction shown as scheme 4. One mol of reactant, D_1 , reacts with one



Scheme 4

mol of the other reactant, M_1 , to form one mol of the product mixture of isomers, R_i , and one mol of the other product mixture of isomers, X_i , where the reactants D_1 and M_1 are also isomerized.

When the initial ratio of reactants, M_1/D_1 , is b , the amounts of substance of individual components at equilibrium are as follows ;

$$d_i = 1 - (d_2 + d_3 + \dots) - (x_1 + x_2 + \dots) \quad (4.1)$$

$$m_i = b - (m_2 + m_3 + \dots) - (x_1 + x_2 + \dots) \quad (4.2)$$

$$d_i = K_d d_1 \quad (4.3)$$

$$m_i = K_m m_1 \quad (4.4)$$

$$r_i = K_r r_1 \quad (4.5)$$

$$x_i = K_x x_1 \quad (4.6)$$

By definition,

$$K_d = 1 + K_{d_1} + K_{d_2} + \dots \quad (4.7)$$

$$K_m = 1 + K_{m_1} + K_{m_2} + \dots \quad (4.8)$$

$$K_q = 1 + K_{r_1} + K_{r_2} + \dots \quad (4.9)$$

$$K_w = 1 + K_{x_1} + K_{x_2} + \dots \quad (4.10)$$

Then

$$d_1 = (1 - K_w x_1) / K_d \quad (4.11)$$

$$m_1 = (b - K_w x_1) / K_m \quad (4.12)$$

$$r_1 = K_w x_1 / K_q \quad (4.13)$$

The equilibrium constant K_1 is

$$K_1 = \frac{K_w K_d K_m X_1^2}{K_q (1 - K_w x_1) (b - K_w x_1)} \quad (4.14)$$

Solving Eq. (4.14)

$$x_1 = \{K(1+b) - R\} / 2K_w(K - K_d K_m) \quad (4.15)$$

where

$$K = K_1 K_q K_w \quad (4.16)$$

and

$$R = \sqrt{K^2(1-b)^2 + 4KK_d K_m b} \quad (4.17)$$

Then one can calculate the equilibrium compositions by following equations ;

$$d_{1e} = (1 - K_w x_1) / K_d (1 + b) \quad (4.18)$$

$$d_{ie} = K_d d_{1e} \quad (4.19)$$

$$m_{1e} = (b - K_w x_1) / K_m (1 + b) \quad (4.20)$$

$$m_{ie} = K_{m_i} m_{1e} \quad (4.21)$$

$$r_{1e} = K_w x_{1e} / K_q (1 + b) \quad (4.22)$$

$$r_{ie} = K_{r_i} r_{1e} \quad (4.23)$$

$$x_{1e} = x_1 / (1 + b) \quad (4.24)$$

$$x_{ie} = K_{x_i} x_1 \quad (4.25)$$

Applications and Discussion

The thermodynamic data employed for the calculation are appeared in either the report by American Petroleum Institute Research Project 44²⁾, or the book by Stull et al.³⁾ Type 1. The dimerization of C₄ olefins has been employed as an example. Table 1 shows

Table 1. Equilibrium compositions of dimerization of butenes to form 1-octene and cyclooctane under 10 atm.

Temp. /K	concentration /mol%				
	1-	Butene cis-2-	trans-2-	1-octene	cyclooctane
298	0.00	0.01	0.00	0.31	99.68
300	0.00	0.01	0.02	0.35	99.62
400	0.37	1.95	4.20	21.57	71.91
500	5.72	17.82	32.28	36.93	7.25
600	13.67	29.58	48.52	8.01	0.22
700	19.20	31.08	48.19	1.52	0.01
800	24.00	30.29	45.31	0.40	0.00
900	28.29	29.26	42.31	0.14	0.00
1000	32.26	28.02	39.66	0.06	0.00

the equilibrium composition of the system consisting of 1-butene, cis-2-butene, trans-2-butene, 1-octene and cyclooctane under 10 atm. The data appeared in the Ref. 2 were employed for butenes and those in the Ref. 3 were employed for 1-octene and cyclooctane. The composition is much varied depending upon the temperature; the formation of cyclooctane is predominant at the lower temperature, and that of 1-octene shows the maximum at about 500°C.

Type 2. The decomposition of C₁₀ parafins to form C₄ and C₆ parafins has been employed as an example. Table 2 shows the equilibrium system consisting of n-decane, 2-methylnonane, 3-methylnonane, n-butane, 2-methylpropane, n-hexane, 2-methylpentane and 3-methylpentane under 100 atm. The data in the Ref. 2 were used for the calculation. The branched parafins are predominant at the lower temperature.

Table 2. Equilibrium compositions of decomposition of C₁₀ parafins to form C₄ and C₆ parafins under 100 atm.

Temp. /K	Concentration mol%							
	n- Decane	Nonane		n- Butane	2-methyl- propane	n- Hexane	Pentane	
		2-methyl	3-methyl				2-methyl	3-methyl
298	0.00	0.00	0.00	8.98	41.01	3.65	32.24	14.10
300	0.00	0.00	0.00	9.17	40.82	3.74	31.96	14.31
400	0.00	0.00	0.00	17.10	32.90	5.32	28.38	16.30
500	0.00	0.00	0.00	23.12	26.88	9.61	24.32	16.07
600	0.00	0.00	0.00	26.37	23.63	12.20	22.11	15.69
700	0.03	0.04	0.06	29.84	20.09	13.18	20.42	16.34
800	0.11	0.13	0.19	31.83	17.96	14.47	19.92	15.39
900	0.30	0.32	0.47	33.03	16.42	15.78	18.75	14.93
1000	0.65	0.66	0.97	33.72	15.15	16.20	18.02	14.64

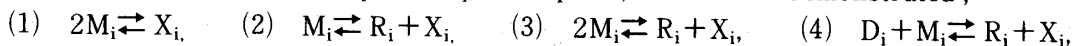
Type 3. The disproportionation of pentenes to form butenes and hexenes has been employed as an example. Table 3 shows the equilibrium system consisting of 1-pentene, cis-2-pentene, trans-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 1-butene, cis-2-butene, trans-2-butene, 2-methylpropene, 1-hexene, cis-2-hexene and trans-2-hexene, cis-3-hexene, trans-3-hexene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl-2-pentene, 3-methyl-cis-2-pentene, 3-methyl-trans-2-pentene, 4-methyl-cis-2-pentene, 4-methyl-trans-2-pentene, 2-ethyl-1-butene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene and 2,3-dimethyl-2-butene. The data in the Ref 2 were used for the calculation; trans-2-olefins are predominant at the high temperature.

The disproportionation of xylenes to form benzene and trimethylbenzenes over aluminium bromide supported on carbon has previously been investigated⁴). This reaction can be shown as $2X_i \rightleftharpoons Q + Y_i$, where X_i and Y_i represent the mixtures of isomers. This type of reaction may also be included in the type 3. The equilibrium compositions, however, have been calculated in the different way, since this system is simpler than type 3.

Type 4. The rather complexed reaction of parafins ($C_4 + C_7 \rightarrow C_5 + C_6$) has been employed as an example. Table 4 shows the equilibrium system consisting of n-butane, 2-methylpropane, n-heptane, 2-methylhexane, 3-methylhexane, n-pentane, 2-methylbutane, 2,2-dimethylpropane, n-hexane, 2-methylpentane, and 3-methylpentane, where the reactant ratio, C_7/C_4 is two at the initial state of the reaction. The data in the Ref. 3 were employed for the calculation. The branched parafins are predominant at the lower temperature.

Conclusion

The calculation methods for thermodynamic equilibrium composition of the following types of reaction system, where the isomerization of reactant isomers, D_i and M_i , as well as that of product isomers, R_i and X_i , take place, have been demonstrated;



The equilibrium compositions calculated for each type are shown in the tables.

Table 3. Equilibrium composition of disproportionation of pentenes to form butenes and hexenes.

Temp. /K	Concentration /mol%														
	C ₅ -olefins						C ₄ -olefins								
	1-	cis-2-	trans-2-	2-Methyl-	3-Methyl-	2-Methyl-	1-	cis-2-	trans-2-	2-Methyl-	1-	cis-2-	trans-2-	cis-3-	trans-3-
Pentene			1-butene		2-butene		Butene		propene		Hexene				
298	0.017	0.356	0.715	5.904	0.109	48.538	0.083	0.810	2.595	18.696	0.003	0.062	0.150	0.027	0.025
300	0.019	0.368	0.747	5.992	0.112	47.952	0.088	0.844	2.685	18.788	0.003	0.064	0.156	0.028	0.016
400	0.113	1.185	1.530	8.839	0.339	35.531	0.423	2.196	4.732	18.881	0.025	0.274	0.453	0.118	0.125
500	0.340	2.103	2.349	10.426	0.704	27.659	1.084	3.382	6.124	17.618	0.088	0.584	0.802	0.249	0.441
600	0.680	2.912	3.000	11.345	1.101	21.713	1.976	4.275	7.013	16.360	0.194	0.933	1.110	0.388	0.973
700	1.100	3.548	3.475	11.730	1.477	17.643	2.990	4.839	7.504	15.183	0.331	1.165	1.345	0.509	1.655
800	1.585	4.004	3.921	11.915	1.843	14.598	4.098	5.172	7.786	14.061	0.504	1.397	1.488	0.613	2.521
900	2.052	4.304	4.151	11.846	2.148	12.350	5.198	5.376	7.776	13.224	0.666	1.629	1.629	0.681	3.330
1000	2.540	4.514	4.396	11.715	2.397	10.606	6.294	5.467	7.736	12.418	0.838	1.704	1.792	0.741	4.190

C ₆ -olefins												
2-Methyl-	3-Methyl-	4-Methyl-	2-Methyl-	3-Methyl-	3-Methyl-	4-Methyl-	4-Methyl-	2-Ethyl-	2,3-Dimethyl	3,3-Dimethyl	2,3-Dimethyl	
			2-	cis-2-	trans-2-	cis-2-	trans-2-	1-	-1-	-1-	-2-	
1-pentene			pentene				butene					
1.066	0.008	0.007	7.160	2.431	3.658	0.220	0.648	0.184	1.184	0.033	5.316	
1.094	0.008	0.007	7.215	2.466	3.707	0.225	0.658	0.188	1.147	0.034	5.326	
2.050	0.047	0.032	7.544	3.372	5.069	0.470	0.937	0.478	1.322	0.060	3.767	
2.926	0.175	0.086	6.863	3.604	5.418	0.740	1.218	0.782	1.551	0.071	2.660	
3.571	0.439	0.160	6.141	3.590	5.397	0.942	1.385	1.060	1.674	0.089	1.993	
4.248	0.813	0.223	5.431	3.430	5.156	1.073	1.465	1.269	1.708	0.088	1.554	
4.335	1.397	0.290	4.856	3.247	4.880	1.173	1.536	1.454	1.748	0.100	1.254	
4.457	2.154	0.532	4.295	3.003	4.514	1.223	1.513	1.559	1.729	0.105	1.011	
4.433	3.117	0.416	3.856	2.794	4.200	1.222	1.491	1.653	1.683	0.102	0.873	

 Table 4. Equilibrium composition of reaction $C_4 + C_7 \rightarrow C_5 + C_6^a$.

Temp. /K	Concentration /mol%											
	n-	2-Methyl-	n-	2-Methyl-	3-Methyl-	n-	2-Methyl-	2,2-Dimethyl	n-	2-Methyl-	3-Methyl	
	Butane	propane	Heptane	hexane	hexane	Pentane	butane	-propane	Hexane	pentane	pentane	
298	0.97	4.40	3.26	22.59	12.85	0.92	12.39	14.65	2.81	19.21	5.95	
300	0.99	4.44	3.32	22.54	12.91	0.95	12.53	14.42	2.84	19.09	5.97	
400	2.57	4.95	6.00	19.97	14.88	2.87	16.76	6.19	4.56	15.12	6.13	
500	3.90	4.55	8.29	17.88	15.61	4.72	16.93	3.24	5.89	12.93	6.06	
600	4.86	4.08	10.88	16.34	15.85	6.21	16.14	2.04	6.85	11.62	5.92	
700	5.54	3.70	11.49	15.19	15.90	7.36	15.27	1.45	7.60	10.73	5.76	
800	6.05	3.40	12.64	14.31	15.84	8.26	14.49	1.13	8.15	10.10	5.63	
900	6.42	3.17	13.56	13.62	15.74	8.98	13.84	0.93	8.29	9.65	5.50	
1000	6.71	2.98	14.29	13.06	15.67	9.53	13.31	0.80	8.92	9.32	5.40	

 a) $C_7/C_4 = 2$ at initial state.

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