Mathematical description of the lines of monovariant phase equilibria on the MnO-SiO$_2$ phase equilibrium diagram

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When analyzing a number of phase equilibrium diagrams of various types of systems, the regular relationship was found during the formation of phase crystallization fields in the form of a correlation dependence of the osmotic coefficient of a crystallizing component on the ratio of its activity in the liquid and solid phases. The Bjerrum-Guggenheim osmotic coefficient serves as a measure of the deviation of the energy properties of a real system from the ideal one described by the Schroeder-Le Chatelier equation. Mathematical expressions for the liquidus and solidus lines are obtained in the form of semi-empirical dependences on a single analytical basis, which make it possible to calculate the temperature dependence of the composition. Thus, a theoretically substantiated method for the mathematical description of the lines of monovariant phase equilibria has been developed, based on the regularities of the behavior of components in the melt. Mathematical expressions represent the crystallization fields of the phases of the MnO-SiO$_2$ system for the corresponding components and compounds using the Schroeder-Le Chatelier equation and the correlation dependence of the osmotic coefficient Φ', experimental and calculated data of the Bjerrum-Guggenheim osmotic coefficient (Φ_i) are calculated. The type of variation in the Bjerrum-Guggenheim osmotic coefficient depends on the intermolecular interaction of the components in the melt. If only van der Waals forces of interaction between the components in the melt prevail, then a correlation dependence is observed. When groups from the initial compounds are formed in the melt, or processes of dissociation or, conversely, association occur, the osmotic coefficient is described by a curvilinear dependence. The paper presents mathematical expressions for the fields of crystallization of phases of the MnO-SiO$_2$ system in the form of semi-empirical dependencies. The nature of the change in the Bjerrum-Guggenheim osmotic coefficient of the crystallizing component depending on the ratio of its activity in the liquid and solid phases is shown.

Keywords: manganese, silicium, Bjerrum-Guggenheim coefficient, phases, crystallization, activity, phase equilibrium diagram, mathematical model.

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Introduction

Necessity of theoretical generalization of accumulated and experimental data with establishment of interaction between thermodynamic and physical-chemical properties of multi-component heterogeneous systems, with obtaining relationships in the form of generalized mathematical models, seems to be important for acceleration of putting into practice the achievements of physical chemistry of complicated systems in industrial technology. First of all, it concerns the phase equilibrium diagrams, phase composition and correlation between composition and properties of complicated systems, because they just make the base for the most efficient prediction of the rational compositions and methods for obtaining the new and high-efficient alloys and materials [1, 2]. Thereby solving of this problem is important both from practical and general scientific point of view.

Essential successes in the field of development of the thermodynamic theory of metallurgical melts were achieved during recent years. In particular, complicated quasi-chem-

ical theory of the "encircled atom" and cluster theory of solutions were developed together with the theories of regular and sub-regular solutions. The suggestion that the properties (and structure) of melts are determined mainly by size of particles and forces of inter-particle interaction makes the base of all these theories [3-6].

All above-mentioned directions have the same disadvantage: they require preliminary determination of conditional interaction parameters and often enthalpy of mixing of solutions, what stipulates conduction of special researches.

Development of scientific grounds of creation of high-quality complex alloys and of development of the technology for manufacture of these alloys is connected with creation and putting into practice the new, more efficient and resource-saving methods for investigation of the phase equilibrium diagrams. First of all it concerns the use of phase equilibrium diagrams for extraction of information about thermodynamic properties and structure of phases, which is incorporated in these diagrams.

The problem of solving the reversed Gibbs problem is connected with decoding of phase equilibrium diagrams and obtaining from it the thermodynamic information, namely relative and excessive functions of mixing the components in the melt. Actually the problem consists of two parts: creating these functions in analytical form and then their transformation to thermodynamic functions of heterogeneous phases on the base of the main laws of thermodynamics [1, 7].

The results of the early works [8-10] allowed to solve correctly the direct Gibbs problem, namely to obtain analytical dependence of phase compositions on temperature using Bjerrum-Guggenheim osmotic coefficient (Φ_i) and to determine in details the real location of the lines of phase equilibriums. The value Φ_i in the researched approach for revealing the features of phase equilibriums in various systems corresponds completely to the boundary conditions for practically all types of phase equilibrium diagrams: eutectic, isomorphic, with limited solubility in solid state, with retrograde solidus etc., which can be met in the nature and were predicted by N. S. Kurnakov [11, 12]. Mathematical examinations of the graphs of Φ_i function for the phases crystallized near their melting temperature T_{mel}, which were previously carried out by the authors, displayed that all types of liquidus lines that were met in different phase equilibrium diagrams, can be divided to five groups in general.

The aim of this work concludes in studying the regularities of phase transformations in metals and alloys on the base of the technique of mathematical description of the line of multi-variant phase equilibriums, using Bjerrum-Guggenheim osmotic coefficient.

Methods and materials

When processing the ores on carbonaceous ferromanganese and silicomanganese via usual technologies, possibility of forming low-melting intermediate (and sometimes even primary) slags is inevitable, while these slags are additionally characterized by very low toughness and very high electric conductivity after melting.

Manganese is presented in ore in the form of MnO_2, Mn_2O_3, MnO oxides. Manganese and silicon oxides are bound during slag forming in strong Mn_2SiO_4 and $MnSiO_3$ compounds, what complicates manganese and silicon reduction, lowers the process temperature and leads to accumulation of fluid manganese-rich slags and increases manganese losses with slag.

First of all we mean use of the phase equilibrium diagrams for extraction of included information about thermodynamic properties and structure of phases.

The problem of solving the reversed Gibbs problem is connected with decoding of the phase equilibrium diagrams and obtaining from it the thermodynamic information, namely relative and excessive functions of mixing the components in the melt. Actually the problem consists of two parts: creating these functions in analytical form and then their transformation to thermodynamic functions of heterogeneous phases on the base of the main laws of thermodynamics [1, 7]. The presented $MnO-SiO_2$ phase equilibrium diagram is related to the kind of equilibrium diagrams, i.e. it is built on the base of thermo-chemical calculations.

Research and results

Three crystallization areas are considered by the authors in this system: MnO in the system $MnO-SiO_2$, $2MnO\cdot SiO_2$ (Mn_2SiO_4) in the system $2MnO\cdot SiO_2 - MnO$ and $2MnO\cdot SiO_2$ (Mn_2SiO_4) in the system $2MnO\cdot SiO_2 - SiO_2$. The system $MnO-SiO_2$ itself has one congruently melting compound Mn_2SiO_4 at the melting temperature 1345 °C [13-17].

Let's consider the first MnO crystallization area in the system $MnO-SiO_2$ (**Fig. 1**). This area is rather wide and it begins from the MnO melting temperature (2123 K) to eu-
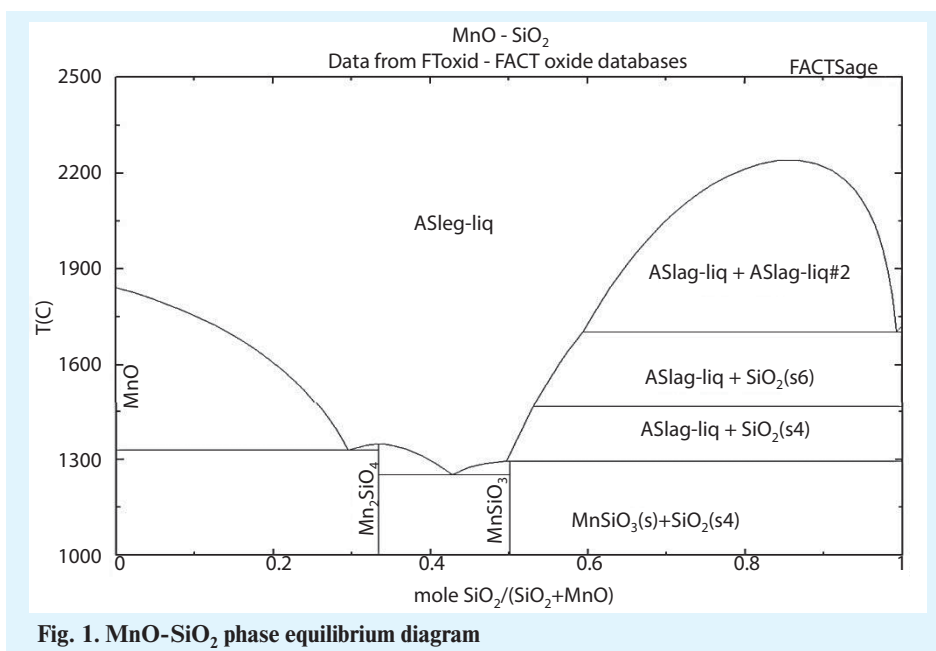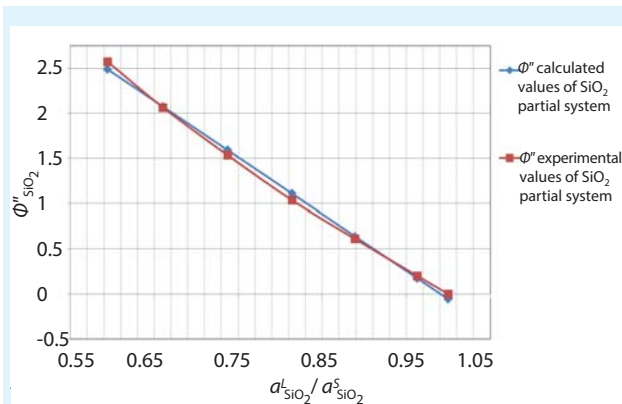

Fig. 1. MnO-SiO$_2$ phase equilibrium diagram

Table 1. Initial data of MnO crystallization areas in the system MnO-SiO$_2$

t, °C	T, K	$X^L_{SiO_2}$	$X^S_{SiO_2}$	$\ln (X^L_{SiO_2}/X^S_{SiO_2})$	$a^L_{SiO_2}/a^S_{SiO_2}$	$\ln a^L_{SiO_2}/a^S_{SiO_2}$	Φ''_{SiO_2}
1850	2123	1	1	0	1	0	0
1800	2073	0.83	1	-0.1863	0.9635	-0.0372	0.1996
1700	1973	0.825	1	-0.1924	0.8894	-0.1172	0.6095
1600	1873	0.82	1	-0.1985	0.8140	-0.2058	1.0373
1500	1773	0.82	1	-0.1985	0.7375	-0.3044	1.5341
1400	1673	0.818	1	-0.2009	0.6605	-0.4148	2.0649
1315	1588	0.817	1	-0.2021	0.5948	-0.5196	2.5707

Fig. 2. Relationship between the Bjerrum-Guggenheim osmotic coefficient Φ''_{op} and activity correlation a^L_{MnO}/a^S_{MnO} for SiO$_2$

Table 2. Comparative analysis of the calculated and experimental data for the MnO crystallization area in the system MnO- SiO$_2$

$X^L_{SiO_2}$	$X^L_{SiO_2}$ (calc.)	Φ''_{SiO_2}	Φ''_{SiO_2} (calc.)
1	1.0000	0	-0.057
0.83	0.8057	0.1996	0.1722
0.825	0.8320	0.6095	0.6375
0.82	0.8309	1.0373	1.1109
0.82	0.8258	1.5341	1.5906
0.818	0.8188	2.0649	2.0745
0.817	0.8115	2.5707	2.4868

Table 3. Initial data in the field of Mn$_2$SiO$_4$ crystallization in the system 2MnO·SiO$_2$ – MnO

t, °C	T, K	X^L_{MnO}	X^S_{MnO}	$\ln X^L_{MnO}/X^S_{MnO}$	$a^L_{2MnO\cdot SiO_2}/a^S_{2MnO\cdot SiO_2}$	$\ln a^L_{2MnO\cdot SiO_2}/a^S_{2MnO\cdot SiO_2}$	$\Phi''_{2MnO\cdot SiO_2}$
1345	1618	0.666	0.666	0	1	0	0
1335	1608	0.6877	0.666	0.032	0.9476	-0.0538	0.2926
1325	1598	0.6889	0.666	0.033	0.8973	-0.1084	0.5578
1315	1588	0.689	0,.666	0.034	0.8491	-0.1636	0.8384

tectics. MnO-SiO$_2$ phase equilibrium diagram was taken from the «FactSage» software complex [14].

The working schedule according to the technique of mathematical description of the lines of mono-variant phase equilibriums in the phase equilibrium diagram is based on the concept of Bjerrum-Guggenheim osmotic coefficient and described in the works [1, 7-10].

Thermodynamic data of SiO$_2$ melting enthalpies H_m = 27222.15 kJ/mol at the melting temperature T_m=2123 K were used for processing of initial temperature and composition data in accordance to the Fig. 1 [18, 19].

The initial data on the temperature and corresponding composition up to the eutectic line 1588 K are presented in the **Table 1**.

Then, using the calculated data of the osmotic coefficient, the graph of Φ''_{op} relationship from a^L_{MnO}/a^S_{MnO} was built (**Fig. 2**).

Presence of only van der Waals forces of interaction between the components in the melt is typical for this area and is displayed as a straight dependence between the Bjerrum-

Guggenheim osmotic coefficient and MnO activity correlation in solid and liquid phases for an ideal state. Calculated value of the functional relationship was found. Mathematical expression of the relationship between Φ''_{op} and a^L_{MnO}/a^S_{MnO} is presented by the following equation (1), with correlation coefficient R_{xy} = -0.998 for linear relationship, and it is practically distinct straight line [18, 19]:

$$\Phi''_{calc} = 6.2205 - 6.2775 \cdot a^L_{MnO}/a^S_{MnO}, \; R_{xy} = -0.9981 \quad (1)$$

Thermodynamic interaction between the components is very weak, structure of both components is constant, i.e. no phase transitions occur and no groups between these components are formed [15].

Using the Schroeder-Le Chatelier equation for an ideal system, as well as the equation which characterizes deviation of properties of the real system from an ideal one, we obtained the calculated values of X^L and X^S components in accordance with the mathematical relationship (2) [8-10]:

$\ln X^{L}_{MnO-SiO_2} =$

$$= \frac{\frac{27222.15}{8.3143}\left(\frac{1}{2123}-\frac{1}{T}\right)+\int\limits_{T}^{Tm}\left[\frac{1}{RT^2}\int\limits_{T}^{Tm}C_p dT\right]dT}{6.2205-6.2775\cdot exp\left[\frac{27222.15}{8.3143}\left(\frac{1}{2123}-\frac{1}{T}\right)+\int\limits_{T}^{Tm}\left[\frac{1}{RT^2}\int\limits_{T}^{Tm}C_p dT\right]dT\right]} \quad (2)$$

Then the obtained results (2) -were compared with the experimental values. Both data are presented in the **Table 2**.

Let's consider now the Mn_2SiO_4 crystallization area in the system $2MnO\cdot SiO_2-MnO$. The same operations as in the first area were conducted. The data from the phase equilibrium diagram (see Fig. 2) were taken for the temperature interval 1618-1588 K and the composition which corresponds for this interval. The initial data are presented in the **Table 3**. The melting enthalpy value equal to $H_{m2MnO\cdot SiO_2} = 116,475$ J/mol at the melting temperature 1618 Kwas accepted for thermodynamic calculations [18, 19].

The graph of the relationship between the Bjerrum-Guggenheim osmotic coefficient Φ''_{op} and activity correlation $a^L_{Mn_2SiO_4}/a^S_{Mn_2SiO_4}$ for the ideal state of liquid and solid phases is presented on the **Fig. 3**.

The initial data were processes via the least squares method for a straight relationship, and the values of the osmotic coefficient were obtained as the following expression (3):

$$\Phi''_{calc} = 5.527 - 5.5271 \cdot a^L_{2MnO\cdot SiO_2}/a^S_{2MnO\cdot SiO_2},$$
$$R_{xy} = -0.9998 \quad (3)$$

The obtained calculated values were compared with the experimental ones. The results are presented in the **Table 4**.

Mathematical expression of the Mn_2SiO_4 crystallization line in the system $2MnO\cdot SiO_2-MnO$ is presented in the form of the following formula (4):

$\ln X^{L}_{Mn_2SiO_4} =$

$$= \frac{\frac{116475}{8.3143}\left(\frac{1}{1618}-\frac{1}{T}\right)+\int\limits_{T}^{Tm}\left[\frac{1}{RT^2}\int\limits_{T}^{Tm}C_p dT\right]dT}{5.527-5.5271\cdot exp\left[\frac{116475}{8.3143}\left(\frac{1}{1618}-\frac{1}{T}\right)+\int\limits_{T}^{Tm}\left[\frac{1}{RT^2}\int\limits_{T}^{Tm}C_p dT\right]dT\right]} \quad (4)$$
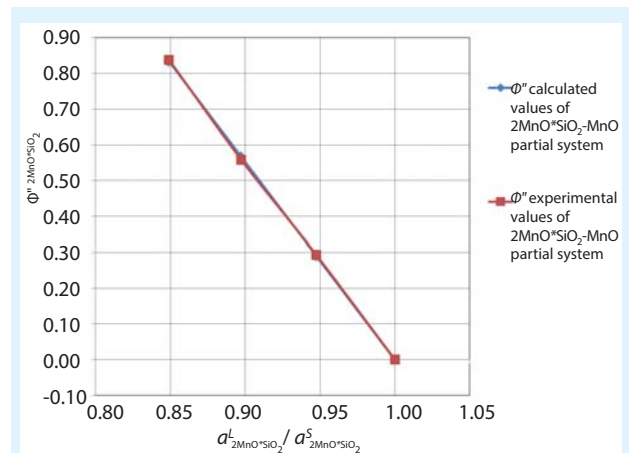

Fig. 3. Relationship between the Bjerrum-Guggenheim osmotic coefficient Φ''_{op} and activity correlation of $2MnO\cdot SiO_2$ for the quasi-system $2MnO\cdot SiO_2$-MnO

Table 4. Comparative analysis of the calculated and experimental data for the Mn_2SiO_4 crystallization area in the system $2MnO\cdot SiO_2$ – MnO

T, K	X^S_{exp}	X^S_{calc}	Φ''_{exp}	Φ''_{calc}	X^L_{exp}	X^L_{calc}
1618	1.0060	1	0	-0.0006	1.006	1
1608	1.0060	1.0059	0.2926	0.2891	0.8319	0.8301
1598	1.0060	1.0060	0.5578	0.5670	0.8235	0.8260
1588	1.0060	1.0061	0.8384	0.8334	0.8228	0.8218

Table 5. Initial data for the Mn_2SiO_4 crystallization area in the system $2MnO\cdot SiO_2$ – SiO_2

t, °C	T, K	X^L_{MnO}	X^S_{MnO}	$\ln X_{MnO}/X_{MnO}$	$a^L_{2MnO\cdot SiO_2}/a^S_{2MnO\cdot SiO_2}$	$\ln a^L_{2MnO\cdot SiO_2}/a^S_{2MnO\cdot SiO_2}$	$\Phi''_{2MnO\cdot SiO_2}$
1	2	3	4	5	6	7	8
1345	1618	0.667	0.667	0	1	0	0
1335	1608	0.62	0.667	-0.0731	0.9476	-0.0538	0.2645
1325	1598	0.616	0.667	-0.0795	0.8973	-0.1084	0.4913
1315	1588	0.612	0.667	-0.0861	0.8491	-0.1636	0.6889
1300	1573	0.605	0.667	-0.0976	0.7806	-0.2477	0.9284
1290	1563	0.598	0.667	-0.1092	0.7374	-0.3047	1.0293
1280	1553	0.59	0.667	-0.1227	0.6960	-0.3624	1.1009
1270	1543	0.58	0.667	-0.1398	0.6565	-0.4208	1.1363
1260	1533	0.57	0.667	-0.1572	0.6187	-0.4801	1.1672
1251	1524	0.56	0.667	-0.1749	0.5862	-0.5340	1.1815

Then let's consider the Mn_2SiO_4 crystallization area in the system $2MnO \cdot SiO_2 - SiO_2$. $H_{m2MnO*SiO_2} = 116,474$ J/mol for the melting temperature 1618 K [8, 9].

The massif of initial data depending on the melting temperature and corresponding composition was created (**Table 5**) [22, 23].

The graph of relationship between Φ''_{op} and $a^L_{Mn_2SiO_4}/a^S_{Mn_2SiO_4}$ was built. Small dissociation degree can be seen here, the graph is characterized by small convexity (**Fig. 4**).

As soon as the graph is curvilinear, the value of the osmotic coefficient was calculated vie the least squares method for curvilinear relationship. The initial data were processed and the values of osmotic coefficient were obtained in the form of expression (5) [24-26]:

$$\Phi''_{calc} = 466.91 - 243.11 \cdot a^L_{Mn_2SiO_4}/a^S_{Mn_2SiO_4} + $$
$$+ 223.84/(0 - a^L_{Mn_2SiO_4}/a^S_{Mn_2SiO_4}), \sigma = 0.019 \qquad (5)$$

Mathematical expression of the Mn_2SiO_4 crystallization line in the system $2MnO \cdot SiO_2 - SiO_2$ is presented in the form of semi-empiric relationship of the Schroeder-Le Chatelier equation (6).
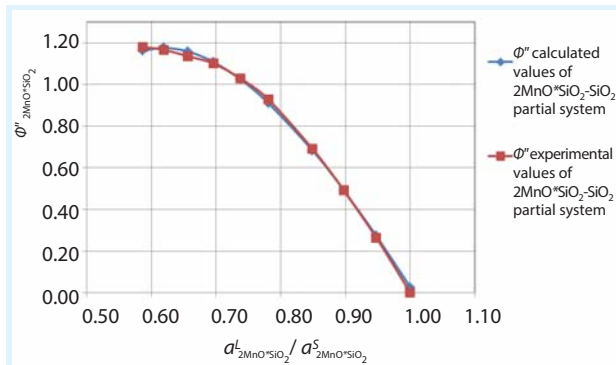

Fig. 4. Relationship between the Bjerrum-Guggenheim osmotic coefficient Φ''_{op} and activity correlation of $2MnO \cdot SiO_2$ for the quasi-system $2MnO \cdot SiO_2 - SiO_2$

$$\ln X^L_{Mn_2SiO_4} =$$

$$= \frac{\frac{116475}{8.3143}\left(\frac{1}{1618} - \frac{1}{T}\right) + \int_T^{Tm}\left[\frac{1}{RT^2}\int_T^{Tm}C_p dT\right]dT}{466.91 - 243.11 + 223.84 \cdot \exp\left[\frac{116475}{8.3143}\left(\frac{1}{1618} - \frac{1}{T}\right) + \int_T^{Tm}\left[\frac{1}{RT^2}\int_T^{Tm}C_p dT\right]dT\right]} \qquad (6)$$

The obtained results on convergence of the calculated and experimental data are displayed in the **Table 6.**

Conclusion

The theoretically substantiated calculating and experimental method for mathematical description of phase equilibrium diagrams using the Bjerrum-Guggenheim osmotic coefficient is developed. Universal features of this technique in solving the mathematical task of phase equilibrium diagrams were displayed, as well as its efficiency for reveal of the features of behaviour of solvent and solved components in equilibrium phases. To describe analytically the solidus and liquidus lines of $MnO-SiO_2$ phase equilibrium diagram, generalized mathematical expressions in the form of semi-empiric Schroeder-Le Chatelier equation were suggested.

The obtained theoretical results on the properties of the Bjerrum-Guggenheim osmotic coefficient ($\Phi_i <>1$) of the $MnO-SiO_2$ system make the scientific base for searching the rational charge compositions that are used in processing of various low-melting manganese and other raw materials; it means that it will be possible to optimize the production technology of manganese and silicon alloys and alloying compositions from different kinds of raw materials. At the same time, theoretical investigations will expand the application area of the model for mathematical description of the phase equilibrium lines on the base of the Bjerrum-Guggenheim concept and will allow to create the general algorithm of theoretical studies of physical-chemical interactions in complicated iron ore and ferroalloy raw materials in high temperature conditions. **CIS**

Table 6. Comparative analysis of the calculated and experimental data for the Mn_2SiO_4 crystallization area in the system $2MnO \cdot SiO_2 - SiO_2$

T, K	$\Phi'_{for\ p.c., exp.}$	Φ'_{calc}	X^S_{exp}	X^S_{calc}	$\Phi''_{exp,}$	$\Phi''_{calc,}$	X^L_{exp}	X^L_{calc}
1618	0	0.0257	1.0015	1	0	0.0266	1.0015	1
1608	0.2625	0.2713	1.0015	1.0016	0.2645	0.2735	0.8158	0.8213
1598	0.4880	0.4887	1.0015	1.0015	0.4913	0.4919	0.8021	0.8023
1588	0.6846	0.6774	1.0015	1.0015	0.6889	0.6815	0.7887	0.7866
1573	0.9232	0.9054	1.0015	1.0015	0.9284	0.9103	0.7658	0.7618
1563	1.0241	1.0197	1.0015	1.0015	1.0293	1.0249	0.7438	0.7428
1553	1.0959	1.1030	1.0015	1.0015	1.1009	1.1081	0.7195	0.7211
1543	1.1317	1.1541	1.0015	1.0015	1.1363	1.1590	0.6905	0.6955
1533	1.1630	1.1721	1.0015	1.0015	1.1672	1.1765	0.6628	0.6649
1524	1.1776	1.1589	1.0015	1.0014	1.1815	1.1625	0.6364	0.6317

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