

Biochemistry of Silicon and Related Problems

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Preface

Silicon chemistry was initiated in 1823 by Berzelius who prepared elemental silicon. In many ways silicon was considered a typical opposite of carbon, although the two elements are closely related as to their electronic structure, both having four valence electrons. The properties of their compounds are, however, extremely different. Both form extended structures, but in different ways - carbon by covalent carbon-carbon bonds; silicon by polar silicon-oxygen-silicon bonds. The complex carbon compounds are integral parts of all living matter, plants and animals. The corresponding silicon compounds build up a major part of dead matter, soils and minerals.

As recently as twenty years ago the title of this Symposium, "Biochemistry of Silicon", would have been considered as contradictio in adjecto. However, the development in the field has, during the past fifteen years, been overwhelming and has convinced us that silicon is a necessary element in the life processes, for animals as well as for plants. Interesting therapeutical uses have been suggested, but we have also become increasingly aware of serious occupational diseases - asbestosis and silicosis - and of possible cancerogenic effects.

It is our hope that this volume will give some idea about various aspects of silicon compounds which were discussed during the Symposium.

We would like to express our thanks to all participants for their excellent cooperation in writing their discussion contributions and delivering their manuscripts so promptly. Our thanks are also due to the secretaries for their efficient work. A grant from the Bank of Sweden Tercentenary Fund to the Nobel Foundation enabled us to organize this Symposium. We also owe gratitude to the Royal Academy of Sciences and its Nobel Institute for Chemistry for generous economic support and hospitality during one day of sessions when Professor C-G Bernhard and Dr W. Odelberg also oriented us about the history and activities of the Academy. To the pharmaceutical companies AB Kabi and AB Astra we would like to express our appreciation of their generous financial contribution.

The Symposium took place on the premises of the Nordic Education Center of IBM at Elfviksudde, Lidingö. We are most grateful to the directors and staff members of IBM who helped making the meeting so successful.

Finally we wish to thank other members of the Organizing Committee - particularly Professor Fredga who initiated this Symposium - for advice and pleasant collaboration.

Uppsala
September, 1977

Gerd Bendz
Ingvar Lindqvist

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General Chemistry of Silicon

AQUEOUS SILICIC ACID, SILICATES AND SILICATE COMPLEXES

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SUMMARY

The paper aims at giving a brief review of the aqueous chemistry of silicic acid, silicates and silicate complexes. In particular, problems concerning equilibria and structures are discussed. In addition geochemical data of silicon and silicon distribution on the earth crust will be briefly presented.

GEOCHEMICAL DATA FOR SILICON, ITS DISTRIBUTION ON THE EARTH'S CRUST AND IN THE HYDROSPHERE

First some geological facts about the earth's crust. Fig. 1 shows a schematic cross section of the upper earth's crust. We can see 1. that 147×10^6 km² are continents, whereas 361×10^6 km² of the earth is covered with water; 2. that the oceans have an average depth of around 4 km (thus of the same order of magnitude as the highest mountains on the continents); 3. that the earth's crust is thinnest under the oceans, and here consists of an upper sediment layer (1 km) and a lower igneous rock layer of basalt type (5-6 km); 4. that the sediment package increases near a continent and is thickest in the continental mountainous regions; 5. that under the continents the earth's crust is considerably thicker (up to 40 km) than under the oceans and the predominant igneous rock is here mainly granodiorite, an acid type of igneous rock.

We may conclude that the layer above the mantle of the earth consists of igneous rocks, sedimentary rocks and the hydrosphere (+ atmosphere). The three dominating elements in this upper layer of the earth are oxygen, silicon and hydrogen, with 55.1, 16.3 and 15.4 atom%, respectively (2).

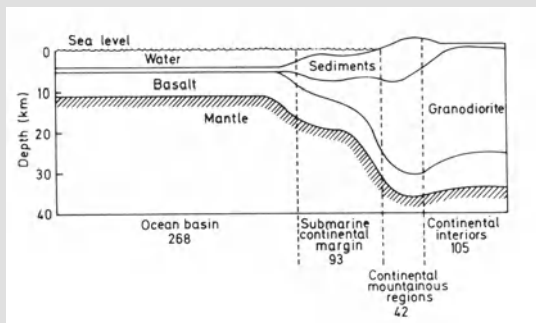


Fig. 1. Schematic cross section of the upper earth's crust. Redrawn from a figure in Garrels & Mackenzie (1). The values refer to approximate areas in units of 10^6 km^2 of ocean waters and continental regions.

Silicon in Igneous Rocks

Igneous rocks are rocks which have been formed from a melt under high temperature and pressure. Fig. 2a is a diagram showing the average compositions of the most commonly occurring igneous rock types. The lowest strip is concerned with rock type granite; then follows quartz monzonite, granodiorite and so on up to diorite and gabbro. In this order the SiO_2 content successively decreases from 77.66 mol % for granite down to 50.55 mol % in gabbro. It is further apparent that silicon is the predominant element in all igneous rock types. The major silicon bearing minerals in igneous rocks are quartz (SiO_2), potassium feldspar (KAlSi_3O_8), plagioclase ($\text{NaAlSi}_3\text{O}_8 + \text{CaAl}_2\text{Si}_2\text{O}_8$), pyroxenes and amphiboles. The most silicon-rich rocks are designated as acidic, whereas those poor in silicon and which also contain much MgO and CaO , are denoted as basic rocks. The use of the terms "acidic" and "basic" for igneous rock is an extension of the general acid-base concept (2). Fig. 2a shows the composition of an igneous rock, calculated so that it corresponds to an average value for all igneous rocks in the upper solid crust. This composition has been obtained by geochemical balance calculations.

Silicon in Sedimentary Rocks

There are three main types of sedimentary rocks, limestone, shale and sandstone, all of the average compositions indicated in the strips, Fig. 2b. Values for a representative average sediment (upper strip) are also given. These values may be considered as a good estimate for the chemical composition of all sediments on the earth's crust. The typical minerals of sedimentary rocks are albite feldspar, K-feldspar, quartz, calcite, dolomite, hematite, illite, chlorite and montmorillonite. We may note that the silicon content in sedimentary rocks as a whole is also high. A sedimentary rock differs, however, from an igneous rock in the way that H_2O ,

a)

Average igneous rock	SiO ₂		Al ₂ O ₃	K ₂ O + Na ₂ O	CaO	MgO	
Gabbro	SiO ₂		Al ₂ O ₃		CaO	MgO	FeO
Diorite	SiO ₂		Al ₂ O ₃		CaO	MgO	FeO
Monzonite	SiO ₂		Al ₂ O ₃	K ₂ O + Na ₂ O	CaO + MgO		
Syenite	SiO ₂		Al ₂ O ₃	K ₂ O + Na ₂ O	CaO + MgO		
Granodiorite	SiO ₂			Al ₂ O ₃	K ₂ O + Na ₂ O	CaO + MgO	
Quartz-monzonite	SiO ₂			Al ₂ O ₃	K ₂ O + Na ₂ O	CaO + MgO	
Granite	SiO ₂			Al ₂ O ₃	K ₂ O + Na ₂ O		

b)

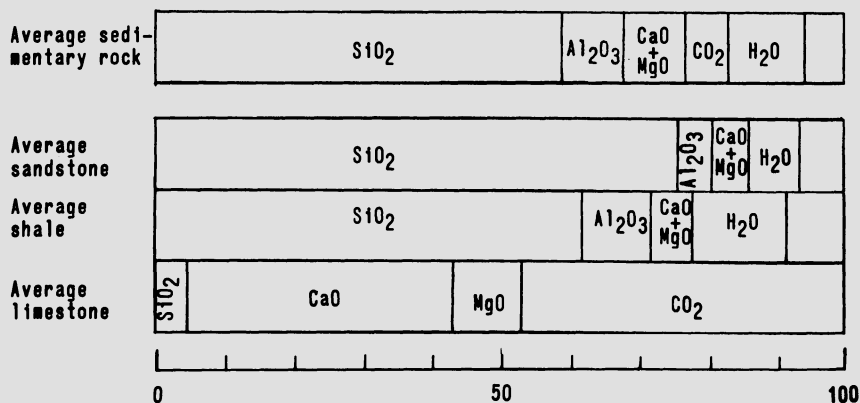
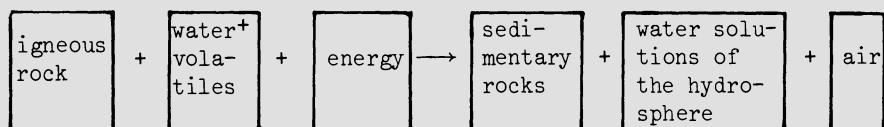


Fig. 2. Average chemical compositions in mole-% of igneous and sedimentary rocks. Data for the igneous rocks (intrusive) from Ernst (3); average values for igneous rocks of the earth's crust as a whole from Sibley et al. (4); and data for sedimentary rocks from Garrels & Mackenzie (1).

CO₂ and HCl seem to have been added, and a rearrangement of the igneous minerals to typical sedimentary minerals has occurred. In Nature this transformation is achieved by chemical weathering and leaching of igneous rocks. There is a chemical weathering balance between the igneous rocks and the sediments on the earth's crust, a balance, which may be written as follows:



Silicon in the Hydrosphere

The hydrosphere can be considered to comprise the subsystems, oceans (13 700, 80.0), pore water in sediments (3 300, 18.8), ice (200, 1.2), rivers-lakes (0.3, 0.002) and atmosphere (0.13, 0.0008), where the figures in parentheses are total mass (units of 10²⁰ g) and percentage of total hydrosphere, respectively. From these figures the predominance of the ocean water is apparent. Table 1 gives the chemical compositions of an ocean water and a river water. We can see from Table 1 that the total concentration of silicon is 0.1 mM (millimolarity) in sea water and about twice that value in river waters, 0.22 mM. The major part of the silica in the hydrosphere is in the form of silicic acid, Si(OH)₄, with small amounts of the monosilicate ion SiO(OH)₃⁻ (particularly in sea water). From these figures we may conclude that the silicon contribution in the hydrosphere term of the chemical balance equation is small.

The Cycling of Silicon in the Upper Earth's Crust

The hydrosphere acts as a link between the igneous rocks and the sedimentary rocks, and thus transports silicon from the igneous rocks of the continents through rivers and streams out to the oceans, where the sediments are formed. As the sediments grow in thickness they sink deeper and deeper into the sea bottom. The temperature increases successively and the sediment becomes metamorphosized and finally melted. This melt is perhaps mixed with magma from the mantle and may come up to the surface forming new mountain ridges and new continents. The process is then repeated with weathering, river transportation, sedimentation and so on. We have in this way a cycle for the silicon transport on the upper earth's crust. A scheme of this geological cycle for silicon is shown in Fig. 3.

We have hitherto treated this cycle as being composed of purely physical, geological and inorganic chemical processes. However, in the hydrological part of the cycle, the biological activities certainly play an important role. The main contribution from these biological activities in the Si cycle are indicated in Fig. 3.

Table 1. Major constituents of river and sea water. (From Garrels & Mackenzie (1), p. 101.)

Constituents	River water		Sea water	
	ppm	mmoles/l	ppm	mmoles/l
Cl ⁻	7.8	0.220	19 000	535.2
Na ⁺	6.3	0.270	10 500	456.2
Mg ²⁺	4.1	0.171	1 300	54.2
SO ₄ ²⁻	11.2	0.117	2 650	27.6
K ⁺	2.3	0.059	380	9.7
Ca ²⁺	15	0.375	400	10.0
HCO ₃ ⁻	58.4	0.958	140	2.3
SiO ₂	13.1	0.218	6	0.1
NO ₃ ⁻	1	0.016	-	-
Fe ²⁺	0.67	0.012	-	-
Al	0.01	-	0.001	-
Br ⁻	-	-	65	0.8
CO ₃ ²⁻	-	-	18	0.3
Sr ²⁺	-	-	8	0.1
Dissolved org. C.	9.6	-	0.5	-
Total	129.5	-	34 467	-

Model Calculations for Weathering Processes

It is important to try to determine how the weathering processes in Nature take place chemically. One possible approach is to perform laboratory experiments. A drastic proposal for such an experiment has been given by Garrels & Mackenzie (1), details of which are given in Fig. 4. However, in practice it is impossible to carry out this experiment. It will take geologic eras before an equilibrium is attained. A better way for reaching the goal would be to collect systematically experimental thermodynamic data, e.g. free energy data (equilibrium constants) for all steps in the weathering cycle, and on the basis of such data, successively

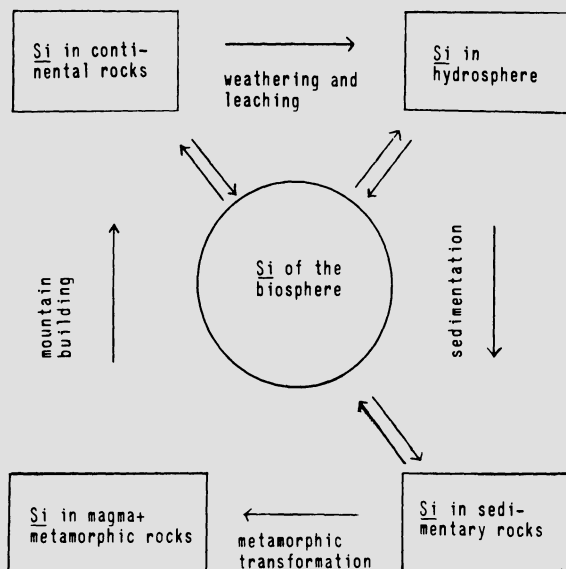


Fig. 3. Cycling of silicon in Nature. Data have been taken from Garrels & Mackenzie (1) and from Wollast (5).

make models of how the system might function. Nowadays, with good access to high speed computers, this seems to be feasible. However, the restricted number of accurate thermodynamic data available at present constitutes a difficulty.

Results of Some Computer Calculations

In order to illustrate the possibilities for such a simulation procedure, we have used the thermodynamic data available in literature and performed a computer calculation for "a simple case" - the chemical weathering of a feldspar. A scheme of the general procedure for such a calculation is shown in Fig. 5. The data input, with definition of species and equilibrium constants used, is shown in Table 2 and the result of the calculation is given in Table 3. From Table 3, we can read the concentration of the prevailing aqueous species, as well as moles of each solid phase present if equilibrium is attained. We may note that the silicon concentration at pH around 8.2 lies in the order of magnitude actually found in Nature. The presented calculation makes no claim to be anything else than an illustration of how a complicated equilibrium system can be resolved by using electronic high speed computer calculations. The still more complicated case of Garrels' weathering model has also been computed and a part of this calculation is shown in Table 4 (in abbreviated form). More detailed discussions of this type of computer calculation and its possibilities will be given in a forthcoming paper by Ingri, Eriksson & Sjöberg (10).

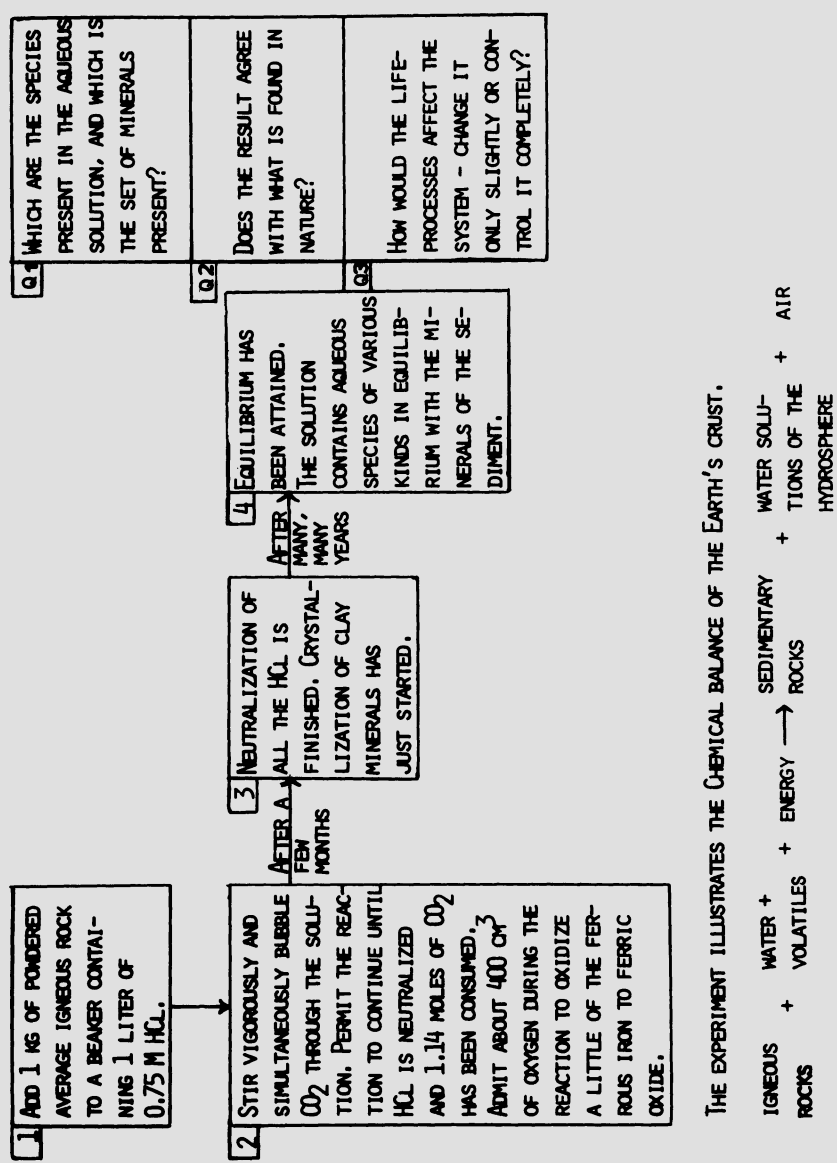


Fig. 4 A weathering experiment in laboratory scale, a proposal given by Garrels & Mackenzie (1)

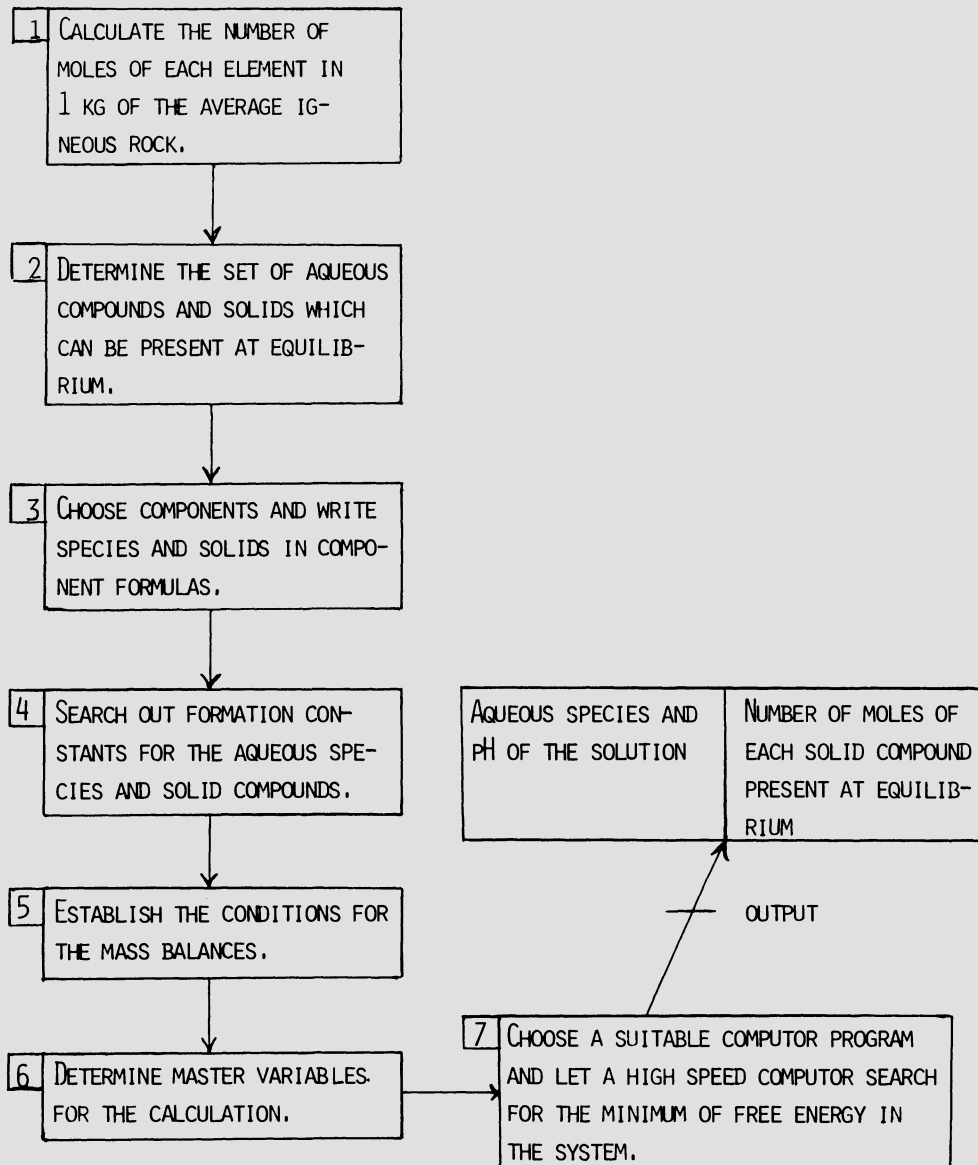


Fig. 5. "Weathering experiments" using thermodynamic data and high speed computer calculations. How computation can be performed and what results can be obtained. Scheme adopted to the computer program SOLGASWATER, developed by Eriksson (9).

Table 2. Thermodynamic data for computer calculation II -
Weathering of a feldspar KAlSi_3O_8

The equilibrium constants used are defined according to the equilibria $pA + qB + rC + sD \rightleftharpoons A_pB_qC_rD_s$, where $A = \text{H}^+$, $B = \text{Si}(\text{OH})_4$, $C = \text{Al}^{3+}$ and $D = \text{K}^+$. Values for the constants have been taken from Stability Constants (6), Baes & Mesmer (7) and Helgeson (8). Temperature 25°C. Medium: dilute solutions

	Species and solids	pqrs	$\log \beta_{pqrs}$
1	H^+	1000	0
2	$\text{Si}(\text{OH})_4$	0100	0
3	$\text{SiO}(\text{OH})_3^-$	$\bar{1}000$	-9.41
4	$\text{SiO}_2(\text{OH})_2^{2-}$	$\bar{2}100$	-22.12
5	$\text{Si}_4\text{O}_6(\text{OH})_6$	$\bar{2}400$	-12.37
6	Al^{3+}	0010	0
7	AlOH^{2+}	$\bar{1}010$	-5.48
8	$\text{Al}(\text{OH})_2^+$	$\bar{2}010$	-9.98
9	$\text{Al}(\text{OH})_3$	$\bar{3}010$	-15.6
10	$\text{Al}(\text{OH})_4^-$	$\bar{4}010$	-23.0
11	$\text{Al}_2(\text{OH})_2$	$\bar{2}020$	-8.0
12	$\text{Al}_3(\text{OH})_4^{5+}$	$\bar{4}030$	-13.47
13	$\text{Al}_{13}(\text{OH})_{32}^{7+}$	$\bar{3}2\ 0\ 13\ 0$	-104.87
14	K^+	0001	0
15	OH^-	$\bar{1}000$	-13.70
16	$\text{SiO}_2(\text{am.})$	0100	2.74
17	$\text{Al}(\text{OH})_3(\text{s})$	$\bar{3}010$	-7.96
18	$\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5(\text{s})$	$\bar{6}220$	-7.63
19	$\text{Al}_2\text{OSiO}_4(\text{s})$	$\bar{6}120$	-14.70
20	$\text{KAlSi}_3\text{O}_8(\text{s})$	$\bar{4}311$	-1.29
21	$\text{KAl}_2(\text{OH})_2\text{Si}_3\text{AlO}_{10}(\text{s})$	$\bar{1}0\ 3\ 3\ 1$	-17.05

Table 3. Results of computer calculation II - Weathering of a feldspar KAlSi_3O_8

Thermodynamic data, aqueous species and solid compounds assumed are given in Table 2. The calculation is based on 1 mole KAlSi_3O_8 (microcline) and 1 l of water. Species with concentration less than 10^{-6} M are left out. The computation has been performed using the computer program SOLGASWATER, constructed by Eriksson (9). Species and solids are numbered as in Table 2.

-log c_i					-log n_i			
1	2	3	10	14	16	18	20	21
4.00	2.74	8.15	12.45	1.05	0.75	1.35	0.04	-
4.40	2.74	7.75	12.01	1.45	1.16	1.75	0.02	-
4.80	2.74	7.35	11.65	1.85	1.57	2.15	0.01	-
5.20	2.74	6.95	11.25	2.25	2.02	2.55	0.00	-
5.60	2.74	6.55	10.85	2.65	2.57	2.95	0.00	-
6.00	2.74	6.15	10.44	3.04	-	2.34	0.00	-
6.40	2.87	5.88	9.91	3.18	-	3.48	0.00	-
6.80	3.01	5.62	9.38	3.31	-	3.61	0.00	-
7.20	3.14	5.35	8.84	3.44	-	3.74	0.00	-
7.60	3.28	5.09	8.31	3.57	-	3.87	0.00	-
8.00	3.41	4.82	7.77	3.70	-	4.00	0.00	-
8.40	3.55	4.56	7.23	3.82	-	4.12	0.00	-
8.80	3.71	4.32	6.68	3.91	-	4.21	0.00	-
9.20	3.88	4.09	6.11	3.97	-	4.28	0.00	-
9.60	4.07	3.88	5.52	4.00	-	4.38	0.00	5.15
10.00	4.20	3.61	5.12	3.99	-	-	0.00	4.32