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**APPLICATIONS OF MULTICOMPONENT CHEMICAL EQUILIBRIA TO
VOLCANIC GASES AT AUGUSTINE VOLCANO, VOLCANIC HALOGEN
EMISSIONS, AND VOLCANOLOGICAL STUDIES OF GAS-PHASE
TRANSPORT**

By

Robert Bruce Symonds

A DISSERTATION

Submitted in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

(Geology)

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ABSTRACT

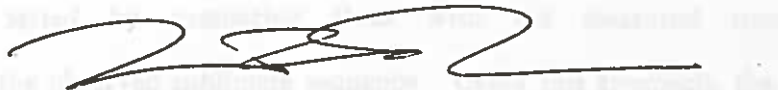
APPLICATIONS OF MULTICOMPONENT CHEMICAL EQUILIBRIA TO VOLCANIC
GASES AT AUGUSTINE VOLCANO, VOLCANIC HALOGEN EMISSIONS, AND

This dissertation, "Applications of Multicomponent Chemical Equilibria to Volcanic Gases at Augustine Volcano, Volcanic Halogen Emissions, and Volcanological Studies of Gas-phase Transport", is hereby approved in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in the field of Geology.

DEPARTMENT Geological Engineering, Geology, and Geophysics



Thesis Advisor



Head of Department

Date 1 NOV 1990

ABSTRACT**APPLICATIONS OF MULTICOMPONENT CHEMICAL EQUILIBRIA TO VOLCANIC GASES AT AUGUSTINE VOLCANO, VOLCANIC HALOGEN EMISSIONS, AND VOLCANOLOGICAL STUDIES OF GAS-PHASE TRANSPORT**

Dynamic chemical processes in multicomponent volcanic-gas systems were studied using a thermodynamic modeling approach by changing the bulk composition, temperature, or pressure in small increments. To constrain the calculations, a thermochemical data base of >1000 species of gases, solids, and liquids in a 42 element system was compiled. This data base interfaces with computer programs (modified from Reed, 1982) that calculate multicomponent homogeneous and heterogeneous chemical equilibrium in gas-solid-liquid systems.

Applications of the modeling to the 9/81 Mount St. Helens volcanic gases are shown. Constraining the model with samples of gases, sublimates, and magmas from the volcano, the model computes: (1) the amounts of trace elements degassed from magma, and (2) the solids that fractionate from the gas upon cooling. Then the model's predictions were tested by comparing them with the measured trace-element concentrations and the observed sublimate sequence. Using this approach, the following conclusions are reached: (1) most trace elements are volatilized from dacite magma as simple chlorides (e.g., CuCl, AgCl, CsCl) or other types of gas species (e.g., H₂MoO₄, AuS, Fe(OH)₂, Hg, H₂Se); (2) some elements (e.g., Al, Si) exist as rock particles-not gases-in the gas stream; (3) near-surface cooling of the gases triggers sublimation of oxides (e.g., magnetite), sulfides (e.g., molybdenite), halides (e.g., halite), tungstates (e.g., ferberite), and native elements (e.g., gold); (4) equilibrium cooling of the gases to 100°C causes most trace elements, except for Hg, Sb, and Se, to fractionate from the gas by sublimation.

The thermochemical modeling approach was also used to study volcanic halogen emissions. This work shows that HCl and HF are the overwhelmingly dominant species of Cl and F in volcanic gases. It also shows that large explosive volcanic eruptions may inject significant amounts of HCl and HF into the stratosphere and that passively degassing volcanoes are a major source of tropospheric HF.

Finally, the thermochemical models were used to understand the origin and speciation of trace elements in high-temperature, HCl-rich gases collected from Augustine volcano after the spring-1986 eruptions. The study shows that the HCl-rich Augustine gases are very favorable for volatilizing metal chlorides (e.g., FeCl_2 , NaCl , KCl , MnCl_2 , CuCl) from magma.

Acknowledgements

The seed for this project was planted eight years ago when I was employed by Tom Casadevall to help study the SO₂ emissions from Mount St. Helens. Fifteen months of work on an active volcano changed the direction of my life. Thanks Tom for introducing me to a great field of research.

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Thermochemical Data and Applications to Studies of High-Temperature Volcanic

Cases with Examples from Mount St. Helens

ABSTRACT

A thermochemical data base, GASTHERM, has been compiled to interface with an Algebraic program (GAS and LIQUID, 1981) that calculates multicomponent chemical equilibria in gas-solid-liquid systems. GASTHERM contains coefficients for the calculation of the equilibrium constant, K , from 25°-1200°C for various species reactions that are defined by a choice of thermodynamic components. GASTHERM includes 1000 species of gases, solids, and liquids in the 42 element system.

Chapter 1

Detailed chemical equilibria in 2-3 component systems will be provided with our program and data base by using the following:

**Calculation of Multicomponent Chemical Equilibria in Gas-Solid-Liquid Systems:
Thermochemical Data and Applications to Studies of High-temperature Volcanic
Gases with Examples from Mount St. Helens.**

Dynamic chemical equilibria in 2-3 component systems will be provided with our program and data base by using the following:

1. A choice of thermodynamic components for the calculation of the equilibrium constant, K , from 25°-1200°C for various species reactions that are defined by a choice of thermodynamic components.

2. A choice of thermodynamic components for the calculation of the equilibrium constant, K , from 25°-1200°C for various species reactions that are defined by a choice of thermodynamic components.

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9. A choice of thermodynamic components for the calculation of the equilibrium constant, K , from 25°-1200°C for various species reactions that are defined by a choice of thermodynamic components.

10. A choice of thermodynamic components for the calculation of the equilibrium constant, K , from 25°-1200°C for various species reactions that are defined by a choice of thermodynamic components.

ABSTRACT

A thermochemical data base, GASTHERM, has been compiled to interface with our computer programs (Reed and Symonds, 1990) that calculate multicomponent chemical equilibrium in gas-solid-liquid systems. GASTHERM contains coefficients for calculation of the equilibrium constants, K , from 25⁰-1200⁰C for derived-species reactions that are defined by a chosen set of thermodynamic components. GASTHERM includes >1000 species of gases, solids, and liquids in the 42 element system.

Dynamic chemical processes in 30-40 component volcanic-gas systems can be modeled with our programs and data base by changing the bulk composition, temperature, or pressure in small increments. Examples of such calculations for the 9/81 Mount St. Helens volcanic gases are shown. Constraining our model with samples of gases, sublimates, and magmas from the volcano, we predict: (1) the amounts of trace elements degassed from magma, and (2) the solids that fractionate from the gas upon cooling. We then test the model's predictions by comparing them with the measured trace-element concentrations and the observed sublimate sequence. Using this approach, we reach the following conclusions: (1) most trace elements are volatilized from dacite magma as simple chlorides (e.g., CuCl, AgCl, CsCl) or other types of gas species (e.g., H₂MoO₄, AuS, Fe(OH)₂, Hg, H₂Se); (2) some elements (e.g., Al, Si) exist as rock particles-not gases-in the gas stream; (3) near-surface cooling of the gases triggers sublimation of oxides (e.g., magnetite), sulfides (e.g., molybdenite), halides (e.g., halite), tungstates (e.g., ferberite), and native elements (e.g., gold); (4) equilibrium cooling of the gases to 100⁰C causes most trace elements, except for Hg, Sb, and Se, to fractionate from the gas by sublimation.

INTRODUCTION

High-temperature volcanic gas systems are chemically and physically complex; they contain significant concentrations of 30 to 60 elements that are subjected to a wide range of temperature and pressure conditions. Most high-temperature volcanic gases originate from degassing magma. In route to the surface, however, these magmatic gases may cool, erode and entrain rock particles, react with the wall rock, and mix with crustal gases such as boiled meteoric water, seawater, or metamorphic fluids. As the volcanic gases cool and mix with other gases, sublimates and acid droplets form; they may nucleate on the walls of the vent or in the gas stream as particles. Incrustations may also form by gas-rock or liquid-rock reactions if this gas-solid-liquid mixture reacts with the wall rock. Finally, this complex solution of gases and particles escapes from volcanic fumaroles where the gases are shocked by additional cooling and mixing with atmospheric gases.

At present, it is only possible to sample volcanic gases or their reaction products after they have reached volcanic fumaroles or mixed with the atmosphere; even then, sampling methods only allow incomplete snapshots of the ensuing chemical reactions. These natural samples provide direct information on the major gas species (H_2O , CO_2 , CO , SO_2 , H_2S , H_2 , HCl , HF), the concentrations of trace elements (e.g., Cu , Zn , Pb , Ir , Se), the speciation and zoning of sublimates (e.g., halite, sylvite, molybdenite, native S) and other types of incrustations (e.g., gypsum, hematite) around volcanic vents, and the speciation of particles in volcanic plumes.

Without further analysis, however, such data do not tell us (A) whether the sampled gases are direct products of magma degassing or whether the gases come from some other source, (B) if the gases were once in equilibrium, (C) the molecular form of the trace gases, or (D) the chemical reactions that occur in volcanic gas systems. Thermochemical modeling can be used to (1) determine whether the concentrations of trace elements in volcanic gases can be explained by the predicted concentrations of

trace elements volatilized from magma; (2) test the equilibrium hypothesis; (3) predict the distribution of trace species (e.g., COS, NaCl, AsS) in the volcanic gas; (4) identify the reactions which control the origin and zoning of sublimates and other types of incrustations; and (5) predict the reactions that control the origin of particles in volcanic plumes.

The ideal thermochemical model would consider every possible reaction between gases, solids, and liquids in 30- to 60-component volcanic gas systems; it would incorporate the thermochemical properties of all possible species. Although limited by available thermochemical data, it is possible to approximate such a comprehensive model by compiling the large amount of modern thermochemical data, attempting to include the most abundant or probable species of every component under consideration. Many of the first thermochemical models of volcanic gases (Ellis, 1957; Heald, Naughton, and Barnes, 1963; Gerlach and Nordlie, 1975) were limited to chemical equilibrium of gases in the C-O-H-S or C-O-H-S-Cl-F systems, the dominant elements in terrestrial volcanic gases. Early modeling studies that did include more components (Krauskopf, 1957; Krauskopf, 1964; Naughton and others, 1974), were hampered by now-obsolete thermochemical data and relatively simple computer models.

Recent studies (Symonds and others, 1987; Le Guern 1988; Quisefit and others, 1989) use more versatile models that consider hundreds of gas, solid, and liquid species in 30-40 component systems; they also take advantage of the vastly improved quality and quantity of recent thermochemical data. Most of these studies, however, have used thermochemical modeling as a small part of their overall study; details of the modeling and documentation of the large thermochemical data bases have not been included in past communications. The purposes of this work are three-fold: (1) document the thermochemical data base; (2) describe the many applications of multicomponent thermochemical models to volcanic gas systems; and (3) evaluate the quality of our

modeling results. A companion paper (Reed and Symonds, 1990) describes the computer programs, SOLVGAS and GASWORKS, used for these calculations.

NUMERICAL MODELS

Numerical calculation were done with SOLVGAS and GASWORKS, computer codes for calculating homogeneous and heterogeneous equilibrium, respectively, in ideal gases. A complete description of these programs is given elsewhere (Reed and Symonds, 1990). Both programs accommodate minor and trace components (transition metals, etc.) and species in addition to the major ones (those in the C-O-H-S-Cl-F system), and provide for strict oxygen mass balance, allowing calculation of the oxygen fugacity at any pressure and temperature. The programs consider hundreds of gas, solid, and liquid species in systems of up to 42 components as a function of temperature and pressure using the basic formulations of equilibrium calculations of Reed (1982) modified by Reed and Symonds (1990) for gases. The calculations are constrained by thermochemical data (below) and consist of solving simultaneously a series of mass balance and mass action equations using a Newton-Raphson method.

Both the homogeneous and heterogeneous equilibrium models calculate the distribution of all possible gas species (of those included in our data base) for a given set of components. In contrast of homogeneous equilibrium, computing heterogeneous equilibrium involves a selection process whereby only supersaturated solids and liquids are equilibrated with the gas. To choose the supersaturated solids and liquids from many possible ones, GASWORKS calculates for each solid and liquid a saturation index, $\log(Q/K)$, where Q is the calculated activity quotient and K is the appropriate equilibrium constant (Reed, 1982; Symonds and others, 1987). After incorporating any supersaturated ($\log(Q/K) > 0.0$) solids and liquids, GASWORKS computes heterogeneous equilibrium and then, once again, tests for supersaturated phases. This process is repeated until the overall equilibrium assemblage is identified. Therefore, the computed

gas, solid, and liquid species are truly the most stable ones of those considered given the various input parameters.

These models have been applied previously to the volcanic gases, condensates, and sublimates at Merapi Volcano, Indonesia (Symonds and others, 1987); the speciation of Cl and F in volcanic gases (Symonds and others, 1988); the possible gas-phase transport of Hg, As, and Sb in geothermal systems (Spycher and Reed, 1989); the restoration of the 1979-1987 Augustine gas samples (Symonds and others, 1990; Kodosky, Motyka, and Symonds, 1990); the speciation of Mo, W, and Re in magmatic fluids (Bernard, Symonds, and Rose, 1990); and to the speciation and origin of trace elements in Augustine volcanic gases (Symonds, Reed, and Rose, 1990).

Assumptions and Uncertainties.—The thermodynamic calculations are done assuming equilibrium, although the extent to which equilibrium applies to volcanic gases is not entirely known. Another uncertainty is whether the quality and quantity of thermochemical data is sufficient to predict the most stable gas, mineral, or liquid species. One reason for doing these calculations is to test these assumptions.

Thermodynamic evaluations of high-temperature ($> 500^{\circ}\text{C}$) volcanic gases are consistent with initial equilibrium for the major gas species (H_2O , H_2 , CO_2 , CO , H_2S , SO_2 , HCl , HF) at or above the measured temperature at the collection site (Gerlach, 1980a, 1980b; Gerlach and Casadevall, 1986a). The relevance of the equilibrium to trace species in high-temperature volcanic gases can be also evaluated thermodynamically by comparing numerical calculations with the observed fumarole sublimates and the measured contents of trace elements in volcanic gases (Symonds and others, 1987). Since the models can be used to predict the speciation and zoning of solids, a good match with the observed sublimate sequence is evidence for the validity of the equilibrium model. A good agreement between calculated volatilities and the analyzed concentrations of trace elements in the volcanic gases also supports the equilibrium degassing model. Such comparisons at Merapi Volcano suggest that the equilibrium calculations do provide a

means to understand the natural process, even though the calculations do not exactly reproduce the observed results (Symonds and others, 1987).

THERMOCHEMICAL DATA

The validity of numerical calculations from SOLVGAS and GASWORKS depend on the quality and quantity of the thermochemical data. Large uncertainties or missing species in the thermochemical data base can lead to erroneous computations of the distribution of gas species. By testing the models on well-constrained systems, we can identify imperfections in the thermochemical data.

Reference States and Conventions.—We chose 298.15^oK and 1 atmosphere pressure as the standard state for the thermochemical data. For each species, we obtained values for the standard enthalpy of formation from the elements, $\Delta_f H^o$, and the standard entropy, S^o , both at 298.15^oK and 1 atmosphere pressure; for some solid species (from Robie, Hemingway, and Fisher, 1978; Helgeson and others, 1978; Berman, 1988), we used the reported values at 298.15^oK and 1 bar pressure. We also obtained a constant-pressure heat capacity equation, generally of the form:

$$C_p^o = a + bT + cT^{-2}, \quad (1)$$

where, C_p^o is the standard heat capacity at constant pressure, T is temperature (^oK), and a , b , and c are constants; for some species, a fourth term, dT^2 , was added to equation (1). Heat capacities for some solids (those from Berman and Brown, 1985, and Berman, 1989) were described by a different equation:

$$C_p^o = k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3}, \quad (2)$$

where k_0 , k_1 , k_2 , and k_3 are constants. When an appropriate heat capacity equation was not available, tabulated heat capacity data were fit to equation (1) using least-squares regression.

Thermochemical data for the elements were taken from Pankratz (1982). In general, we used the most stable form of each element at 298.15^oK and 1 atmosphere

pressure as the reference state; exceptions are S, Se, and Te for which we used the nonstandard reference states of $S_2(g)$, $Se_2(g)$, and $Te_2(g)$ for convenience because they are used by Pankratz (1982).

Finally, we calculated the standard Gibbs free energy of formation from the elements, $\Delta_f G^0$, at 298.15^oK and 1 atmosphere pressure using the equation:

$$\Delta_f G^0 = \Delta_f H^0 - T\Delta_f S, \quad (3)$$

where $\Delta_f S$ was calculated using S^0 data for the elements from Pankratz (1982).

Sources of data.-For each gas, liquid, and solid species included in the calculations, we attempted to use the most recent thermochemical data. Thermochemical data for gas, solid, and liquid species were obtained from the U.S. Bureau of Mines (Decock, 1982; Pankratz, 1982, 1984; Pankratz, Stuve, and Gokcen, 1984; Pankratz, Mah, and Watson, 1987); the JANAF thermochemical tables (Stull and Prophet, 1971; Chase and others, 1974, 1975, 1978, 1982); Barin and Knacke (1973); Barin, Knacke, and Kubaschewski (1977); Berman and Brown (1985); Berman (1988); Robie, Hemingway and Fisher (1978); Helgeson and others (1978); and Anovitz and others (1985). The specific source for each species is listed in Table 1 and in the Appendix.

Methods.-For each of the 42 elements included in the calculations, it is necessary to choose a component gas species. In theory, the choice of component gas species is arbitrary; regardless of the component species chosen, the final calculated distribution of species will be the same if the equations can be solved. With the numerical limitations of modern computers (e.g., precision shortcomings, constraints on the size of exponents), however, the choice of component gas species makes a difference in the computer's ability to solve the equations with speed and accuracy. Therefore, we chose the dominant, or at least one of the more abundant, gas species of each element in high-temperature volcanic gases as the component species (Table 1). Our component species (Table 1) are best suited for computations involving reduced volcanic gases; equilibrium calculations involving oxidized or halogen-poor systems (e.g., underground coal fires),

Table 1. Component gas species presently used in GASTHERM. Listed in order of increasing atomic number.

Element	Component Gas Species	Reference
1 H	H ₂	Pankrantz (1982)
2 Li	LiCl	Pankrantz (1984)
3 C	CO ₂	Pankrantz (1982)
4 N	N ₂	Pankrantz (1982)
5 O	H ₂ O	Pankrantz (1982)
6 F	HF	Pankrantz (1984)
7 Na	NaCl	Pankrantz (1984)
8 Mg	MgCl ₂	Pankrantz (1984)
9 Al	AlF ₃	Pankrantz (1984)
10 Si	SiF ₄	Pankrantz (1984)
11 S	H ₂ S	Pankrantz, Mah, and Watson (1987)
12 Cl	HCl	Pankrantz (1984)
13 K	KCl	Pankrantz (1984)
14 Ca	CaCl ₂	Pankrantz (1984)
15 Ti	TiF ₄	Pankrantz (1984)
16 V	VCl ₄	Pankrantz (1984)
17 Cr	CrCl ₄	Pankrantz (1984)
18 Mn	MnCl ₂	Barin and Knack (1973)
19 Fe	FeCl ₂	Pankrantz (1984)
20 Co	CoCl ₂	Pankrantz (1984)
21 Ni	NiCl ₂	Pankrantz (1984)
22 Cu	CuCl	Pankrantz (1984)
23 Zn	ZnCl ₂	Barin and Knack (1973)
24 Ga	GaCl ₃	Pankrantz (1984)
25 As	AsCl ₃	Pankrantz (1984)
26 Se	H ₂ Se	Barin, Knack, and Kubaschewski (1973)
27 Br	HBr	Pankrantz (1984)
28 Rb	RbCl	Pankrantz (1984)
29 Sr	SrCl ₂	Pankrantz (1984)
30 Mo	H ₂ MoO ₄	Stull and Prophet (1971)
31 Ag	AgCl	Barin and Knack (1973)
32 Cd	Cd	Pankrantz (1982)
33 Sn	SnCl ₂	Pankrantz (1984)
34 Sb	SbCl ₃	Pankrantz (1984)
35 Te	H ₂ Te	Barin, Knack, and Kubaschewski (1973)
36 Cs	CsCl	Pankrantz (1984)
37 W	H ₂ WO ₄	Stull and Prophet (1971)
38 Ir	Ir	Pankrantz (1982)
39 Au	Au	Pankrantz (1982)
40 Hg	Hg	Pankrantz (1982)
41 Pb	PbCl ₂	Pankrantz (1984)
42 Bi	BiCl ₃	Pankrantz (1984)

might require different component species. Changing component species is accomplished by simply combining the appropriate log K equations (below), although additional modification of SOLVGAS and GASWORKS are required to change the components species for H (H₂) and O (H₂O) since they are used to fix the O₂ fugacity (see Reed and Symonds, 1990).

For every component, we have included all the derived gas species for which we could find thermochemical data at the time of this compilation. Our compilation of solid and liquid species, although very substantial, is somewhat less comprehensive as we have not included every possible species. The data base, GASTHERM, presently incorporates 627 gas species and 398 solids and liquids in the 42 component system (Appendix).

To calculate the distribution of gas, solid, and liquid species, we need the equilibrium constant, K, for the reaction between each derived species and its respective component species. First, we calculated the apparent standard Gibbs free energy of formation from the elements, $\Delta_a G^T$, of the *i*th species involved in each reaction at one atmosphere pressure and at a given temperature, T (°K), using the equation:

$$\Delta_a G^T = \Delta_f G^0 - (T - T_r) \Delta_f S + \int_{T_r}^T C_p^0 dT - \int_{T_r}^T (C_p^0/T) dT, \quad (4)$$

where T_r is 298.15°K and C_p^0 is described using equations (1) or (2). Then, we calculated the standard Gibbs free energy for the reaction, $\Delta_r G^T$, at the same temperature, T, with the equation:

$$\Delta_r G^T = \sum \nu_i \Delta_a G^T, \quad (5)$$

where $\Delta_a G^T$ is given in equation (4) and ν_i is the stoichiometric coefficient of *i*th species in the reaction. Finally, we calculated the logarithm of the equilibrium constant for the reaction, log K_T , at the temperature, T, with the equation:

$$\log K_T = -\Delta_r G^T / (2.303RT), \quad (6)$$

where R is the gas constant.

Values for $\log K_T$ calculated at 298.15^oK (25^oC) and from 373.15^oK (100^oC) to 1473.15^oK (1200^oC) at 100^oK (100^oC) increments are stored in a data file, GASTHERM, for use in our programs. To obtain $\log K_T$ values at any arbitrary temperature over the range of data validity, it is most convenient (requires fewer calculations) to use a function for $\log K_T$ rather than calculating them each time using equations (4) through (6). Substituting equation (1), our dominant heat capacity equation, for C_p^o into equation (4) and combining terms in equations (4) through (6), results in an expression for $\log K_T$ of the form:

$$\log K_T = l_0 + l_1 T^{-1} + l_2 T + l_3 T^{-2} + l_4 \log(T) \quad (7),$$

where l_0 , l_1 , l_2 , l_3 , and l_4 are constants. To fit the computed $\log K_T$ values to equation (7), we used least-squares regression. The coefficients for equation (7), l_0 , l_1 , l_2 , l_3 , and l_4 , for each derived species reaction in GASTHERM are tabulated in the Appendix.

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APPENDIX
 Calculations for calculating log V_g values with eqn (7)

DATA SPECIFICS

log V _g	log V _g	log V _g	log V _g
0.000	0.000	0.000	0.000
0.001	0.001	0.001	0.001
0.002	0.002	0.002	0.002
0.003	0.003	0.003	0.003
0.004	0.004	0.004	0.004
0.005	0.005	0.005	0.005
0.006	0.006	0.006	0.006
0.007	0.007	0.007	0.007
0.008	0.008	0.008	0.008
0.009	0.009	0.009	0.009
0.010	0.010	0.010	0.010
0.011	0.011	0.011	0.011
0.012	0.012	0.012	0.012
0.013	0.013	0.013	0.013
0.014	0.014	0.014	0.014
0.015	0.015	0.015	0.015
0.016	0.016	0.016	0.016
0.017	0.017	0.017	0.017
0.018	0.018	0.018	0.018
0.019	0.019	0.019	0.019
0.020	0.020	0.020	0.020
0.021	0.021	0.021	0.021
0.022	0.022	0.022	0.022
0.023	0.023	0.023	0.023
0.024	0.024	0.024	0.024
0.025	0.025	0.025	0.025
0.026	0.026	0.026	0.026
0.027	0.027	0.027	0.027
0.028	0.028	0.028	0.028
0.029	0.029	0.029	0.029
0.030	0.030	0.030	0.030
0.031	0.031	0.031	0.031
0.032	0.032	0.032	0.032
0.033	0.033	0.033	0.033
0.034	0.034	0.034	0.034
0.035	0.035	0.035	0.035
0.036	0.036	0.036	0.036
0.037	0.037	0.037	0.037
0.038	0.038	0.038	0.038
0.039	0.039	0.039	0.039
0.040	0.040	0.040	0.040
0.041	0.041	0.041	0.041
0.042	0.042	0.042	0.042
0.043	0.043	0.043	0.043
0.044	0.044	0.044	0.044
0.045	0.045	0.045	0.045
0.046	0.046	0.046	0.046
0.047	0.047	0.047	0.047
0.048	0.048	0.048	0.048
0.049	0.049	0.049	0.049
0.050	0.050	0.050	0.050
0.051	0.051	0.051	0.051
0.052	0.052	0.052	0.052
0.053	0.053	0.053	0.053
0.054	0.054	0.054	0.054
0.055	0.055	0.055	0.055
0.056	0.056	0.056	0.056
0.057	0.057	0.057	0.057
0.058	0.058	0.058	0.058
0.059	0.059	0.059	0.059
0.060	0.060	0.060	0.060
0.061	0.061	0.061	0.061
0.062	0.062	0.062	0.062
0.063	0.063	0.063	0.063
0.064	0.064	0.064	0.064
0.065	0.065	0.065	0.065
0.066	0.066	0.066	0.066
0.067	0.067	0.067	0.067
0.068	0.068	0.068	0.068
0.069	0.069	0.069	0.069
0.070	0.070	0.070	0.070
0.071	0.071	0.071	0.071
0.072	0.072	0.072	0.072
0.073	0.073	0.073	0.073
0.074	0.074	0.074	0.074
0.075	0.075	0.075	0.075
0.076	0.076	0.076	0.076
0.077	0.077	0.077	0.077
0.078	0.078	0.078	0.078
0.079	0.079	0.079	0.079
0.080	0.080	0.080	0.080
0.081	0.081	0.081	0.081
0.082	0.082	0.082	0.082
0.083	0.083	0.083	0.083
0.084	0.084	0.084	0.084
0.085	0.085	0.085	0.085
0.086	0.086	0.086	0.086
0.087	0.087	0.087	0.087
0.088	0.088	0.088	0.088
0.089	0.089	0.089	0.089
0.090	0.090	0.090	0.090
0.091	0.091	0.091	0.091
0.092	0.092	0.092	0.092
0.093	0.093	0.093	0.093
0.094	0.094	0.094	0.094
0.095	0.095	0.095	0.095
0.096	0.096	0.096	0.096
0.097	0.097	0.097	0.097
0.098	0.098	0.098	0.098
0.099	0.099	0.099	0.099
0.100	0.100	0.100	0.100