

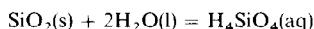
## The kinetics of silica-water reactions

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**Abstract** A differential rate equation for silica-water reactions from 0–300°C has been derived based on stoichiometry and activities of the reactants in the reaction



$$(\partial a_{\text{H}_4\text{SiO}_4} / \partial t)_{P,T,M,\dots} = (A/M)(\gamma_{\text{H}_4\text{SiO}_4})(k_+ a_{\text{SiO}_2} a_{\text{H}_2\text{O}}^2 - k_- a_{\text{H}_4\text{SiO}_4})$$

where  $(A/M)$  = (the relative interfacial area between the solid and aqueous phases/the relative mass of water in the system), and  $k_+$  and  $k_-$  are the rate constants for, respectively, dissolution and precipitation. The rate constant for precipitation of all silica phases is

$$\log k_- = -0.707 - 2598/T \quad (T, \text{K})$$

and  $E_{\text{act}}$  for this reaction is 49.8 kJ mol<sup>-1</sup>. Corresponding equilibrium constants for this reaction with quartz, cristobalite, or amorphous silica were expressed as  $\log K = a + bT + c/T$ . Using  $K = k_+/k_-$ ,  $k_+$  was expressed as  $\log k_+ = a + bT + c/T$  and a corresponding activation energy calculated:

	a	b	c	$E_{\text{act}}(\text{kJ mol}^{-1})$
Quartz	1.174	$-2.028 \times 10^{-3}$	-4158	67.4–76.6
$\alpha$ -Cristobalite	-0.739	0	-3586	68.7
$\beta$ -Cristobalite	-0.936	0	-3392	65.0
Amorphous silica	-0.369	$-7.890 \times 10^{-4}$	-3438	60.9–64.9

Upon cooling a silica-saturated solution below the equilibrium temperature, the decreasing solubility of silica causes increasing super saturation, which tends to raise the precipitation rate, but the rate constants rapidly decrease, which tends to lower the precipitation rate. These competing effects cause a maximum rate of precipitation 25–50°C below the saturation temperature. At temperatures below that of the maximum rate, silica is often quenched into solution by very slow reaction rates. Consequently, the quartz geothermometer will give the most accurate results if samples are taken from the hottest, highest flow rate, thermal springs which occur above highly fractured areas.

### NOMENCLATURE

A	interfacial area (m <sup>2</sup> )	$\gamma_i$	activity coefficient of i
A'	frequency factor in Arrhenius equation	h	Planck's constant ( $6.63 \times 10^{-34}$ J sec)
A	relative interfacial area (= $A/A^0$ where $A^0 = 1 \text{ m}^2$ )	k	Boltzman's constant ( $1.38 \times 10^{-23}$ J mol <sup>-1</sup> K <sup>-1</sup> )
A <sub>sp</sub>	specific surface area (m <sup>2</sup> gm <sup>-1</sup> )	k <sub>+</sub>	dissolution rate constant (sec <sup>-1</sup> )
E <sub>act</sub>	activation energy (kJ mol <sup>-1</sup> )	k <sub>a</sub>	apparent dissolution rate constant (sec <sup>-1</sup> )
$\Delta G_f^0$	free energy of formation (kJ mol <sup>-1</sup> )	k <sub>-</sub>	precipitation rate constant (sec <sup>-1</sup> )
$\Delta G_r$	free energy of reaction (kJ mol <sup>-1</sup> )	k <sub>-</sub>	apparent precipitation rate constant (sec <sup>-1</sup> )
$\Delta G^*$	free energy of activation (kJ mol <sup>-1</sup> )	l	liquid
K	equilibrium constant	m <sub>i</sub>	concentration of i (molal)
K*	equilibrium constant for the formation of the activated complex	n <sub>i</sub>	amount of i (moles)
K <sup>‡</sup>	equilibrium constant for the formation of the activated complex with a degree of translational freedom removed	qtz	quartz
M	mass of water in the system (kg)	r	radius (m)
M	relative mass of water in the system (= $M/M^0$ where $M^0 = 1 \text{ kg}$ )	r <sub>i</sub>	net rate of change of a <sub>i</sub> with time (sec <sup>-1</sup> )
P	pressure (bars)	r' <sub>i</sub>	net rate of change of m <sub>i</sub> with time (m sec <sup>-1</sup> )
Q	activity product	r <sub>afc</sub>	rate of change of thickness of a layer of material on a surface (m sec <sup>-1</sup> )
R	gas constant (8.318 J mol <sup>-1</sup> K <sup>-1</sup> )	s	solid
S	degree of saturation (= $Q/K$ )	t	time (sec)
T	temperature (K)	t <sub>c</sub>	time constant (sec)
V	volume (m <sup>3</sup> )		
V <sub>i</sub>	molar volume of i (m <sup>3</sup> mol <sup>-1</sup> )		
V <sub>sp</sub>	specific volume of water (cm <sup>3</sup> gm <sup>-1</sup> )		
a <sub>i</sub>	activity of i		
aq	aqueous		
am sil	amorphous silica		
crist	cristobalite		

### INTRODUCTION

THIS STUDY was undertaken to develop a basis for reaction kinetics that is consistent with the thermodynamic approach commonly used in geochemistry. Thermodynamics is a powerful tool for elucidating geological phenomena where equilibrium is normally attained; however, many geological processes are controlled by reaction rates so that they can only be