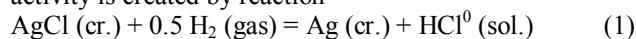


Kovalenko N.I., Ryzhenko B.N. Experimental determination of the redox potential of the “rock-water” systems

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Hydrogen fugacity in the systems “rock (granite, basalt, dunite-water)” at 400-450°C, 1 kbar by activity of HCl⁰ is experimentally measured. The cell “Ag/AgCl, aqueous solution // rock powder + water”, separated by a platinum membrane, permeable for hydrogen [1-4], is used. Due to the interaction of the studied material (i.e. rock powders) with water, the fixed hydrogen fugacity appears in the autoclave. Due to the diffusion of hydrogen through membrane (walls of the platinum ampoule “AgCl/Ag, H₂O or aqueous solution of HCl”), similar hydrogen fugacity appears in it. Consequently, a fixed HCl⁰ activity is created by reaction



$$K_1 = a_{\text{HCl}}/f_{\text{H}_2}^{0.5}$$

$f_{\text{H}_2} = (a_{\text{HCl}}/K_1)^2 = [\alpha m_{\text{HCl}}(T,P)/K_1]^2 = [\alpha m_{\text{HCl}}(25^\circ\text{C})/K_1]^2$
where α is a fraction of associated HCl⁰ in total HCl at T, P. Concentration m_{HCl} at T, P (total content of HCl in the platinum ampoule after the experiment) is taken to be equal to $m_{\text{HCl}}(25^\circ\text{C})$, measured by the potentiometric analysis of quenched probes.

Experimental procedure. Electrode “Ag/AgCl, H₂O or aqueous solution of HCl” was sealed in the platinum ampoule. Volume of solution, in dependence on T, P conditions of the experiment, was 0.3-0.35 ml. In order to achieve the equilibrium, from both sides of the cell “Ag/AgCl, aqueous solution”, H₂O or 0.1-0.5 M HCl were placed. The sealed platinum ampoules (5x0.1x40 mm) with the buffer Ag-AgCl and aqueous solutions of HCl or water were placed into heat-proof autoclaves fettled by gold (V = 20 ml or 7 ml). The studied material (rock powder with water in ratio 1:4 or 1:10 by mass) were placed

into the autoclave as well. Pressure in the autoclave was created by means of filling of free volume by water according to the coefficient of filling, determined from the P-V-T diagram of water. Autoclaves were put into the electric stove equipped with nichrome heaters. Temperature was controlled with the accuracy 5°C. Run duration was 20-90 days. The autoclaves were quenched by running water. The platinum ampoules were weighted before and after the run. The hermetical ampoules were opened, solution was extracted and emplaced into the microcell for pH measurements. The volume of the solution (0.3-0.35 ml) allowed measuring the dilution of the solution. The pH measurements were carried out by the universal ionmeter EV-74. Glass electrodes were calibrated by the standard method. Reproducibility of the measurements was 0.03 log(m_{HCl}). As the calibration showed, the equilibrium with the Ni-NiO buffer was stabilized during 0-12 days in the whole studied temperature interval (400-450°C). For reversal experiments, H₂O and 0.1-0.5 M HCl solutions were used. In all runs, the agreement between the value of HCl concentration was satisfactory. That correspond to equilibrium. The principal influence of duration of rock-water interaction on the value of the equilibrium concentration of acid was not established (within the interval week-three months).

Hydrogen fugacity, f_{H_2} (gas), in the experimental ampoules (at experimental t and P) was calculated by means of comparing of HCl (25°C) concentration for the standard Ni/NiO buffer and the experimental mixture “rock powder+water”. Measured during calibration (400, 450 and 500°C, 1 kbar) equilibrium HCl concentrations were 0.24 M, 0.28 M, 0.32 M. The H₂ fugacities of 0.69 bar, 1.07 bar and 1.52 bar correspond to these values. Practically, concentration of HCl⁰ was measured at run conditions at the equilibrium state of the system (1) with experimental m_{HCl} (25). The values of free Gibbs energies for Ag⁺, Cl⁻, AgCl⁰, AgCl₂⁻, AgCl₃²⁻, Ni, NiO, H₂O, H₂, and HCl⁰, used in calculations, are taken from [5-6]. The experimental results are shown in Table. The higher equilibrium concentrations of HCl for some runs in the system “granite-water” and two groups of data points for the system “dunite-water” should be noted.

Table. Results of the experimental determination of hydrogen fugacity in the systems “rock-water” at 400, 450°C and total pressure 1000 bars.

Initial m_{HCl}	pH (25°C), after run	log f_{H_2} (bar)	Initial m_{HCl}	pH (25°C), after run	lg f_{H_2} (bar)	Initial m_{HCl}	pH (25°C), after run	lg f_{H_2} (bar)
Granite, 400°C						Dunite, 400°C		
H ₂ O	0.45		H ₂ O	1.00		H ₂ O	0.64	
0.1	0.45	+0.44	0.1	0.98	-0.79	0.1	0.60	+0.06
0.3	0.45		0.3	0.92		0.4	0.61	
H ₂ O	0.97		H ₂ O	0.30		H ₂ O	0.42	
0.1	0.95	-0.71	0.1	0.30	+0.71	0.1	0.41	+0.52
0.3	0.92		0.3	0.30		0.4	0.42	
H ₂ O	0.95		H ₂ O	0.70		H ₂ O	0.65	
0.1	0.95	-0.74	0.1	0.71	-0.14	0.1	0.64	+0.07
0.3	0.97		0.3	0.70		0.3	0.61	

H ₂ O	1.00				H ₂ O	0.65		
0.1	0.94	-0.75	Basalt, 400°C			0.1	0.60	+0.09
0.3	0.92				0.4	0.62		
H ₂ O	0.95		H ₂ O	1.01		H ₂ O	0.42	
0.1	0.95	-0.77	0.1	0.92	-0.78	0.1	0.35	+0.66
0.3	1.00		0.5	0.90		0.4	0.24	
H ₂ O	0.72		H ₂ O	0.90		H ₂ O	0.45	
0.1	0.84	-0.27	0.1	0.85	-0.60	0.1	0.40	+0.53
0.3	0.73		0.3	0.92		0.4	0.36	
H ₂ O	0.87		H ₂ O	0.95		Granite		
0.1	0.87	-0.52	0.1	0.95	-0.80	H ₂ O	0.88	
0.3	0.87					H ₂ O	0.85	
						0.1	0.85	-0.48
						0.2	0.90	

The experimental values of hydrogen fugacity for mixtures "rock powder+water" quantitatively support the results of the computer modeling at the experimental parameters. An increase of reducing properties of pore fluids from acid rocks to ultrabasic rocks is found.

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References:

1. I-Ming Chou. Hydrothermal experimental techniques / ed. G.C. Ulmer and H.L. Barnes, NY: John Wiley & Sons. 1987. pp. 61-99.
2. Korzhinskii M.A. // Ocherki fizico-khimicheskoi petrologii. 1980. Issue 9. pp. 41-51.
3. Korzhinskii M.A. // Geokhimiya. 1981. no. 5. pp. 689-706.
4. Korzhinskii M.A. // Geokhimiya. 1991. no. 6. pp. 755-768.
5. Ryzhenko B.N., Kovalenko N.I. // Geokhimiya. 2000. no. 3. pp. 329-333.
6. Kovalenko N.I., Ryzhenko B.N. // Geokhimiya. 2001. in press