COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Water; H_2O; [7732-18-5]	Kozlov, K.; Kuznetsov, V. N.; Khodakovskii, I. L. *Geokhimiya* 1983, 215-27; *Geochem. Int. (Engl. transl.)* 1983, 137-49.
VARIABLES: Concentration of sodium hydroxide, total ionic strength, and temperature.	**PREPARED BY:** T. P. Dirkse

EXPERIMENTAL VALUES: Table I. Equilibrium values for the reaction:[a]

$$AgCl(s) + OH^- = 1/2\ Ag_2O(s) + 1/2\ H_2O + Cl^-$$

t/°C	C_{Cl^-}/mol kg^{-1}	I/mol kg^{-1}	Solid phase	C_{Cl^-}/C_{OH^-}
25	0.007	0.20	Ag_2O + AgCl	0.0222
25	0.007	0.20	Ag_2O + AgCl	0.00888 [b]
25	0.007	0.20	Ag_2O + AgCl	0.00821 [b]
25	0.007	0.30	AgCl	0.0218
25	0.007	1.0	AgCl	0.0214
60	0.01	0.30	Ag_2O	0.0366 [b]
60	0.01	0.30	AgCl	0.0360 [b]
60	0.01	0.70	AgCl	0.0362 [b]
60	0.01	1.00	AgCl	0.0341
60	0.01	0.30	AgCl	0.0763

[a] The solid phase was allowed to equilibrate isothermally with a 0.200 mol kg^{-1} solution of NaOH.

[b] The Ag_2O present is said to be an active form rather than the crystalline form.

K_{so} for AgOH was calculated from log K_{so} = -9.75 + log C_{Cl^-}/C_{OH^-}, where -9.75 is log K_{so} for AgCl.

The authors report a value of log K^o_{so} = -8.08 $\pm$ 0.02 at 25°C, but this appears to be a concentration product rather than a thermodynamic value.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Two methods were used. In one method, solid Ag_2O and/or AgCl was added to a 0.200 mol kg^{-1} solution of NaOH and allowed to equilibrate. Then the concentration ratio of Cl^-/OH^- was measured and used with the solubility product value for AgCl to obtain the solubility product value for Ag_2O. In the second method, mixtures of solid Ag_2O and aqueous NaOH solutions were allowed to equilibrate isothermally in an O_2 atmosphere. This was done to prevent the decomposition of the Ag_2O. A jet of O_2 was used to stir the mixtures occasionally. The analyses were made by potentiometric titration: with HCl to determine OH^- ion; with $AgNO_3$ to determine Cl^- ion; and with KI to determine Ag^+ ion. The silver content was also determined by atomic absorption spectrometry. Total ionic strength was attained by the addition of $NaClO_4$.

SOURCE AND PURITY OF MATERIALS:

Chemically pure materials were used and were recrystallized several times. Ag_2O was prepared by a method described earlier (1). The water was double-distilled and was boiled to remove CO_2.

ESTIMATED ERROR:

The temperature was controlled to within 0.05°C. The analytical uncertainties were less than 6%.

REFERENCES:

1. Johnston, H. L.; Cuta, F.; Garrett, A. B. *J. Am. Chem. Soc.* 1933, 55, 2311.

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EXPERIMENTAL VALUES, contd:

Table II. Solubility of Ag_2O in NaOH solutions.

T/K	I/mol kg^{-1}	C_{NaOH}/mol kg^{-1}	$10^6 C_{Ag^+}$/mol kg^{-1}
298.15	2.65	0.00835	2.16
"	"	0.0209	2.55
"	"	0.0342	4.35
"	"	0.0523	6.65
"	"	0.0838	8.40
"	"	0.0839	8.36
"	"	0.115	10.3
"	"	0.370	27.6
333.15	"	0.00809	2.60
"	"	0.0202	3.53
"	"	0.0523	4.03
"	"	0.115	13.6
"	"	0.206	19.7
"	"	0.370	23.7
298.15	1.14	0.00719	2.30
"	"	0.00719	2.13
"	"	0.0116	2.27
"	"	0.0180	2.48
"	"	0.177	9.67
"	"	0.177	9.49
333.15	"	0.0119	2.86
"	"	0.0180	3.19
"	"	0.0310	4.35
"	"	0.0452	4.60
"	"	0.177	14.2
"	"	0.233	17.5
363.15	"	0.00700	6.57
"	"	0.00719	5.78
"	"	0.0452	7.97
"	"	0.177	27.3
298.15	0.53	0.0168	2.54
"	"	0.0422	2.57
"	"	0.106	4.44
"	"	0.166	8.27
333.15	"	0.329	21.7
"	"	0.00672	6.16
"	"	0.0422	11.0
"	"	0.166	29.6
"	"	0.329	66.0
"	"	0.00672	12.5
363.15	"	0.0422	19.3
"	"	0.106	39.1
"	"	0.166	82.9
"	"	0.329	121

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EXPERIMENTAL VALUES, contd:

Table III. Calculated constants [a]

t/°C	I/mol kg^{-1}	-log K_{s1} [b]	-log K_{s2} [c]
25	0.53	5.80	4.37
25	1.14	5.75	4.36
25	2.65	5.77	4.16
60	0.53	5.44	3.82
60	1.14	5.78	4.13
60	2.65	5.82	4.13
90	0.53	5.20	3.46
90	1.14	5.55	3.85
25	0	5.79 ± 0.10	4.37 ± 0.05
60	0	5.46 ± 0.15	3.86 ± 0.10
90	0	5.38 ± 0.15	3.66 ± 0.15

[a] The constants were calculated from the results in Table II. An equation was written for the total concentration of Ag in terms of Ag^+, AgOH and $Ag(OH)_2^-$. This equation was solved by successive approximations to minimize the sum of the squares of the differences in experimental and calculated values. The values at zero ionic strength were calculated on the assumption that the constants have a linear dependence on ionic strength.

[b] For the equation: $1/2\ Ag_2O(s) + 1/2\ H_2O = AgOH\ (aq)$

[c] For the reaction: $1/2\ Ag_2O(s) + 1/2\ H_2O + OH^- = Ag(OH)_2^-(aq)$