COMPONENTS:	EVALUATOR:
(1) Copper; Cu; [7440-50-8] Zinc; Zn; [7440-66-6] Silver; Ag; [7440-22-4] Lead; Pb; [7439-92-1] (2) Water; H_2O; [7732-18-5]	Appendix I The Solubility of Some Metallic Elements in Water

CRITICAL EVALUATION:

Those interested in the solubility of metallic mercury in water may want to compare the solubility of mercury with other metals in water. There are only a few papers that report studies of the solubility of unionized metallic elements in water. The results of two of these studies are given here (ref. 1, 2).

The determination of the solubility of an oxide-free pure metal in distilled, degassed, neutral water is a difficult experiment. The following data sheets report metallic element solubiliies in water of silver, copper, zinc, and lead. From the experiments of Krepelka and Toul (ref. 1), we conclude that when oxygen and carbon dioxide are rigoroursly excluded in experiments carried out in metallic vessels (which avoids alkali contamination from glass) the solubility of unionized silver in water is below the limit of detection of about 0.000002 g dm^{-3} used by the authors. We believe that the solubility values on the following data sheets are upper limits and the true metal atom solubility in water may be much smaller.

Reliable values of the solubility of the metallic elements in water would be of interest. New studies using modern analytical methods along with techniques to prepare ultra-pure oxide-free metals and bring them in contact with pure degassed neutral water would be desirable.

There are a number of papers in the literature that report metal solubilities in natural systems. Many of these are summarized in the Seidell-Linke Handbook (ref. 3), or can be found in *Chemical Abstracts*. These papers usually report the total metal in solution from a variety of sources after reaction with oxygen, carbon dioxide, and/or electrolyte. The reactions result in the metal surface coated with a mixture of solid oxides, hydroxides, and carbonates. The total metal concentration is the sum of the metal atom, metal ion, and metal ion complexes in solution. Various models are proposed to explain the total metal ion concentration relationship to the multiple equilibriums among the surface solids and the solution components. These studies are of great practical use for corrosion and enviromental problems. However, they take us to far from the scope of the present volume to consider further.

REFERENCES:

1. Krepelka, H.; Toul, F. *Coll. Czech. Chem. Comm.* 1929, *1*, 155.

2. Pariaud, J.; Archinard, P. *Bull. Soc. Chim. France* 1952, 454; *J. Chim. Phys.* 1956, *53*, 765.

3. Seidell, A.; Linke, W. F. *Solubilities of Inorganic and Metal Organic Compounds*, American Chemical Society, Washington, DC, Vol. I. 1958, Vol. II. 1965.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper; Cu; [7440-50-8] (2) Water; H_2O; [7732-18-5]	Pariaud, J.; Archinard, P. *Bull. Soc. Chim. France* <u>1952</u>, 454 - 6. *J. Chim. Phys.* <u>1956</u>, *53*, 765 - 9.
VARIABLES: T/K = 303.15	PREPARED BY: M. Iwamoto H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Time of Mixing	Mercury in[a] Solution	Copper Solubility		
				Concentration[b]	Mole[b] Fraction	Molality[b]
t/°C	T/K[b]	t/days	$10^6 c_1$/g dm^{-3}	$10^6 c_1$/mol dm^{-3}	$10^8 x_1$	$10^6 m_1$/mol kg^{-1}
30	303.15	6	170			
			160			
			165			
			170			
		29	175			
			180			
			180			
			170 ± 12[c]	1.89	3.42	1.90

[a] All of the experimental values are given with an uncertainty of ±12.

[b] Calculated by compilers.

[c] The solubility and its uncertainty given in the authors' second paper.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Colorimetric method with dithizone. Copper and triply distilled degassed water were equilibrated for up to 24 days to insure saturation.

The copper was oxidized to copper (II) and complexed with dithizone. The silver dithizonate complex absorption was measured at 490 nm.

SOURCE AND PURITY OF MATERIALS:

(1) Copper. Electroanalytically pure.

(2) Water. Triply distilled and degassed.

ESTIMATED ERROR:

See uncertainty in table above.

REFERENCES:

COMPONENTS:

(1) Zinc; Zn; [7440-66-6]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Pariaud, J.; Archinard, P.

Bull. Soc. Chim. France 1952, 454 - 6.

J. Chim. Phys. 1956, *53*, 765 - 9.

VARIABLES:

$T/K = 305.15$

PREPARED BY:

M. Iwamoto
H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Time of Mixing	Mercury in[a] Solution	Zinc Solubility		
				Concentration[b]	Mole[b] Fraction	Molality[b]
$t/°C$	T/K[b]	t/days	$10^6 c_1/\mathrm{g\ dm^{-3}}$	$10^5 c_1/\mathrm{mol\ dm^{-3}}$	$10^7 x_1$	$10^5 m_1/\mathrm{mol\ kg^{-1}}$
25	298.15	17	710 725 715			
24	297.15	32	700 710 710			
32[d]	305.15	32	700 ± 50[c]	1.07	1.94	1.08

[a] All of the experimental values are given with an uncertainty of ±50.

[b] Calculated by compilers.

[c] The solubility and its uncertainty given in the authors' second paper.

[d] [sic.]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Colorimetric method with dithizone. Zinc and triply distilled degassed water were equilibrated for up to 24 days to insure saturation.

The zinc was oxidized to zinc(II) and complexed with dithizone. The mercury dithizonate complex absorption was measured at 490 nm.

SOURCE AND PURITY OF MATERIALS:

(1) Zinc. Electroanalytically pure.

(2) Water. Triply distilled and degassed.

ESTIMATED ERROR:

See uncertainty in table above.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver; Ag; [7440-22-4] (2) Water; H_2O; [7732-18-5]	Krepelka, H.; Toul, F. *Coll. Czech. Chem. Comm.* 1929, *1*, 155 - 64.

EXPERIMENTAL VALUES:

Temperature		Time	Mass of Silver Found $10^6 c_1/g\ dm^{-3}$			Method
$t/°C$	T/K	t/days	Exp. I	Exp. II	Avg.	

I. Thi silver leaves were brought into contact with freshly distilled water in heavy walled, hard glass, Erlenmeyer flasks filled to the top with water and sealed with parafin. The water contained only traces of air and carbon dioxide. The flasks were shaken in the dark at 18 to 20°C for the days stated below, then analyzed for silver by nephelometry.

$t/°C$	T/K	t/days	Exp. I	Exp. II	Avg.	Method
18 - 20	291.15 - 293.15	7	15	9	12	Nephelometry
		14	22	20	21	"
		21	37	33	35	"
		180	37	35	36	"

II. The water in contact with silver was analyzed for Ag^+ by an emf method. The cell used was

$$Ag/H_2O//KCl\ (sat.)//KCl\ (1\ mol\ dm^{-3})(Hg_2Cl_2)/Hg.$$

The Nernst equation was used to calculate the Ag^+ concentration at the Ag/H_2O electrode. The water was freshly distilled before use. The atmosphere was carbon dioxide free air. The time of contact between the silver and water was not stated. Average results are given below, the complete set of emf data are given in the paper.

$t/°C$	T/K	t/days	Exp. I	Exp. II	Avg.	Method
18.95	292.10				6.3(4)[a]	Emf
18.22	291.37				6.0(9)[a]	"
18.95	292.10				5.3(4)[a]	"
18.85	292.00				15. (7)[a]	"

III. Experiments similar to I above, but carried out in silver vessels with silver powder prepared by reduction of ammonical silver solution by sulfur dioxide. The experiments were done to avoid the effect of alkali leached from glass surfaces. Oxygen and carbon dioxide were rigorously excluded. All silver surfaces were treated with steam followed by reduction with hydrogen gas to insure an oxide free silver surface. The silver dissolved was below the limit of detection of the nephelometry method.

$t/°C$	T/K	t/days	Exp. I	Exp. II	Avg.	Method
18 - 20[b]	291.15 - 293.15	7	-	-	-	Nephelometry
		14	-	-	-	"
		21	-	-	-	"

IV. Same as III above, but without the hydrogen reduction step to make sure silver surface is oxide free.

$t/°C$	T/K	t/days	Exp. I	Exp. II	Avg.	Method
18 - 20[b]	291.15 - 293.15	7	10	10	10	Nephelometry
		14	21	20	20	"
		21	34	33	33	"

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[a] Numbers in ( ) are the number of determinations. Standard deviations are 0, 0.1, 0.7, and 1. interval.

[b] Temperature not stated by authors. Values assumed by compiler because of temperatures used in first experiment.

COMPONENTS:

(1) Silver; Ag; [7440-22-4]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Krepelka, H.; Toul, F.

Coll. Czech. Chem. Comm. 1929, *1*, 155 - 64.

VARIABLES:

T/K = 291.15 - 293.15

PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

See comments above each set of experiments reported on the previous page.

Nephelometry. The water, separated from the silver leaves, was evaporated from a quartz dish to a volume of 60 - 80 cm^3, made up to a volume of 100 cm^3, then compared with a known standard containing a similar amount of silver in the presence of KBr.

Emf. Method of Beans and Oakes (ref. 2).

SOURCE AND PURITY OF MATERIALS:

(1) Silver. Standard sample (ref. 1) prepared for atomic weight work. Melted again on pure CaO in an atmosphere of dry, pure hydrogen. Silver etched with HNO_3, H_2O, and NH_3 to increase surface area. Thoroughly washed with H_2O, and dried at 110°C. Then rolled into thin leaves between well cleaned steel rollers. Surface etched again after each rolling.

(2) Water. Distilled water freed from organic material by action of $KMnO_4$, then twice distilled, the second time in Pt directly into the container used in the experiment.

ESTIMATED ERROR:

The lower limit of detection by nephelometry is about 10×10^{-6} g dm^{-3}.

REFERENCES:

1. Krepelke, H. *J. Am. Chem. Soc.* 1920, *42*, 925.
2. Beans, H. T.; Oakes, E. T. *J. Am. Chem. Soc.* 1920, *42*, 2116.

COMPONENTS:

(1) Silver; Ag; [7440-22-4]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Pariaud, J.; Archinard, P.

Bull. Soc. Chim. France 1952, 454 - 6.

J. Chim. Phys. 1956, *53*, 765 - 9.

VARIABLES:

$T/K = 301.15$

PREPARED BY:

M. Iwamoto
H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Time of Mixing	Mercury in[a] Solution	Silver Solubility		
				Concentration[b]	Mole[b] Fraction	Molality[b]
$t/°C$	T/K[b]	t/days	$10^6 c_1/g\ dm^{-3}$	$10^7 c_1/mol\ dm^{-3}$	$10^9 x_1$	$10^7 m_1/mol\ kg^{-1}$
25	298.15	1	0			
		3	10, 15, 10			
		8	25, 20, 20			
28	301.15	18	28, 25, 25			
		24	28, 30			
			26 ± 7[c]	2.41	4.36	2.42

[a] All of the experimental values are given with an uncertainty of ±7.

[b] Calculated by compilers.

[c] The solubility and its uncertainty given in the authors' second paper.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Colorimetric method with dithizone. Silver and triply distilled degassed water were equilibrated for up to 24 days to insure saturation.

The silver was oxidized to silver(I) and complexed with dithizone. The silver dithizonate complex absorption was measured at 490 nm.

SOURCE AND PURITY OF MATERIALS:

(1) Silver. Electroanalytically pure.

(2) Water. Triply distilled and degassed.

ESTIMATED ERROR:

See uncertainty in table above.

REFERENCES:

COMPONENTS:

(1) Lead; Pb; [7439-92-1]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Pariaud, J.; Archinard, P.

Bull. Soc. Chim. France 1952, 454 - 6.

J. Chim. Phys. 1956, *53*, 765 - 9.

VARIABLES:

$T/K = 297.15$

PREPARED BY:

M. Iwamoto
H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Time of Mixing	Mercury in[a] Solution	Lead Solubility		
				Concentration[b]	Mole[b] Fraction	Molality[b]
$t/°C$	T/K[b]	t/days	$10^6 c_1/\text{g dm}^{-3}$	$10^7 c_1/\text{mol dm}^{-3}$	$10^9 x_1$	$10^7 m_1/\text{mol kg}^{-1}$
24	297.15	15	310 310			
		30	310 315			
			310 ± 18[c]	1.50	2.71	1.50

[a] All of the experimental values are given with an uncertainty of ±18.

[b] Calculated by compilers.

[c] The solubility and its uncertainty given in the authors' second paper.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Colorimetric method with dithizone. Lead and triply distilled degassed water were equilibrated for up to 24 days to insure saturation.

The lead was oxidized to lead(V) and complexed with dithizone. The mercury dithizonate complex absorption was measured at 490 nm.

SOURCE AND PURITY OF MATERIALS:

(1) Lead. Electroanalytically pure.

(2) Water. Triply distilled and degassed.

ESTIMATED ERROR:

See uncertainty in table above.

REFERENCES: