COMPONENTS:	EVALUATOR:
(1) Mercury; Hg; [7439-97-6] (2) Water; H <sub>2</sub> O; [7732-18-5]	H. Lawrence Clever Chemistry Department Emory University Atlanta, Georgia 30322 USA
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### CRITICAL EVALUATION:

An Evaluation of the Solubility of Mercury in Water from 273 to 773 K.

Christoff (ref. 1) was the first to show that metallic mercury is soluble in water. He passed ten liters of water slowly over a mercury sample and measured the amount dissolved by weight loss of the mercury. The solubility values he reported are only about 30 percent of the values accepted today. Since Christoff's pioneering work the solubility of mercury in water has been reported in at least seventeen papers from fifteen laboratories. The reported solubility values were measured over the 273 to 773 K temperature interval and the 0.1 to 100 MPa pressure range. The molal (mol kg<sup>-1</sup>) solubility increases with increasing temperature, and decreases with increasing total pressure. However, when expressed as Henry's constant the solubility shows a maximum, and as the Ostwald coefficient the solubility shows a minimum as a function of temperature. These inflections vary with the total pressure and occur between 473 K and 512 K.

There are two earlier evaluations of the solubility of mercury in water. They are Khodakovskii et al. (ref. 19) and Clever et al. (ref. 20). The present work uses additional data not available at the time of the earlier evaluations.

Table 1 summarizes the analytical methods used by various workers to determine the amount of dissolved mercury. Some workers used more than one method.

Table 1. Analytical methods used to determine dissolved mercury.

Method		References		
1.	Mercury weight loss	1		
	Ultraviolet absorption			
	(253.7 nm, 256.0 nm, 236.5 nm)	2, 7, 11		
3.	Weight increase on amalgamation with gold	2, 10, 13		
4.	Electrodeposition	3		
5.	Colorimetry with dithizone	4, 10, 13		
6.	Radioactive Hg-203	5, 8, 18		
7.	Neutron activation	6		
8.	Cold vapor atomic absorption	9, 12, 14, 15, 16, 17		
9.	Titration with ammonium thiocyanate	10, 13		

Most of the workers equilibrated liquid mercury directly with the water. Sanemasa (ref. 12) and Hursh (ref. 18) equilibrated mercury vapor with the water. Sanemasa controlled the mercury pressure by controlling the temperature of a sample of pure liquid mercury. He tested Henry's law by doing experiments with the mercury at several temperatures below the temperature of the solubility measurement. When both the mercury and the water were at the same temperature the result was the equivalent of the liquid mercury in contact with the water. The Henry law test is shown Hursh (ref. 18) equilibrated at an unknown mercury presonly on graphs. sure at less than the equilibrium vapor pressure of mercury. He experimentally measured the concentration of the mercury in both vapor and solution phase to obtain an Ostwald coefficient. By using the equilibrium vapor pressure of mercury to calculate the vapor concentration at the temperature of the solubility determination one can obtain the solubility of liquid mercury in water. The value agrees satisfactorily with the results of those who equilibrated with liquid mercury. The Sanemasa solubility values at room temperature also agree satisfactorily with the liquid mercury solubility values. The Sanemasa values at other temperatures are discussed in more detail below.

Voigt and co-workers (ref. 5 and 8) used radioactive mercury-203. They found it was necessary to add a small amount of reducing agent, hypophosphorous acid, to prevent the oxidation of mercury by the products of radiolysis. Hursh (ref. 18) also used mercury-203. He used either an oxygen free carrier gas or added ethanol (to blood, plasma, and hemoglobin solutions) to prevent mercury oxidation.

Most workers have agreed with Reichardt and Bonhoeffer (ref. 2) that mercury dissolved in air-free water is monatomic and unionized with the zero-valent mercury in the spherically symmetric <sup>1</sup>S<sub>0</sub> ground state. Glew and Hames (ref. 9) have been the most careful to insure a non-oxidizing environment. They avoided the use of radioactive mercury, they rigorously excluded oxygen, and they added trace amounts of reducing agent. Most other workers have tried to keep their systems air-free. Recently Sanemasa (ref. 12) has carried out experiments in which he obtains the same solubility in the presence and in the absence of air. In Sanemasa's experiment either air or nitrogen is circulated over liquid mercury and water in separate compartments. Mercury liquid-vapor equilibrium and mercury vapor-aqueous solution equilibrium are stated to be established within thirty minutes.

When the solubility values from the two laboratories are compared it is observed that at 278 K Sanemasa's values are smaller than Glew and Hames, near 298 K there is a cross-over and the values agree within a few percent, but by 333 K Sanemasa's values are three times larger than Glew and Hames. It is the evaluator's opinion that the Glew and Hames values are too large below 293 K and that Sanemasa's values are too small below 293 K and too large above 303 K. The evaluator has tried to test several models for the air oxidation of mercury in aqueous solution with available thermodynamic data. It is not possible to obtain a definitive answer, but the possibility of air oxidation of the mercury appears to be real. We suspect that the Sanemasa solubility values at the higher temperatures are too large because of air oxidation. Some of the solubility results of Choi and Tuck (ref. 6) and of Onat (ref. 11) agree with the higher Sanemasa results.

The problem of possible air oxidation of aqueous metallic mercury is not settled. The Sanemasa results may fall on a different line from the other values because pure liquid mercury may have different properties than liquid mercury in contact with water. However, this seems unlikely to us. We are concerned by the short time used by Sanemasa to establish both pure mercury liquid-vapor equilibrium and mercury vapor-saturated aqueous solution equilibrium. The short time could lead to undersaturation and the low solubility values at 278 and 283 K. The air oxidation may have a kinetic component, and be important at only the higher temperatures where the Sanemasa values are higher than others. We do not want to be overly critical of the Sanemasa experiment. Future work may show he is correct and all the other values are wrong. However, in this work the evaluator prefers the lower solubility results from air-free systems.

At temperatures of 473 K and above all of the data are from Sorokin and co-workers (ref. 10 and 13). The experiments reported in the two papers clearly show that the molal and mole fraction solubility decrease with increasing total pressure at 473, 573, 673, and 773 K. The solubilities at 573, 673 and 773 K (ref. 10) fall on a curve that is a reasonable extension of the lower temperature data (Figure 2). The solubilities at 473 K (ref. 13) show a greater variation with pressure than the values at the higher temperatures and do not fit the overall pattern as well as might be expected. It is possible that the solubility shows a different pressure dependence below and above the water critical temperature. It would take more experiments to clarify the matter.

Table 2 summarizes the available experimental mercury solubility values. The literature values have been calculated as concentration,  $c_1/\text{mol} \text{ dm}^{-3}$ , molality,  $m_1/\text{mol} \text{ kg}^{-1}$ , mole fraction,  $x_1$ , Henry's constant in the two units  $(p_1/\text{kPa})/(m_1/\text{mol} \text{ kg}^{-1})$  and  $(p_1/\text{kPa})/(x_1)$ , and the Ostwald coefficient,  $(c_1(\text{liq})/\text{mol} \text{ dm}^{-3})/(c_1(\text{gas})/\text{mol} \text{ dm}^{-3})$ . The last two columns of the table give mercury liquid-vapor equilibrium properties. There is the equilibrium vapor pressure,  $p_1/\text{kPa}$ , and concentration in the vapor,  $c_1/\text{mol} \text{ dm}^{-3}$ . The mercury vapor pressure and vapor concentration were calculated from the evaluation of mercury vapor pressure of Ambrose and Sprake (ref. 21). The equilibrium mercury vapor pressure was corrected for any excess external pressure by (d ln f/dp)<sub>T</sub> = V/RT and assuming ideal gas behavior.

							Mercury	Vapor	
T/K	107 c <sub>1</sub> /mo1 dm <sup>-3</sup>	107 m <sub>1</sub> /mo1 kg-1	10° x <sub>1</sub>	$\frac{10^{-3}H = p_1/m_1}{$	$\frac{10^{-4}H = p_1/x_1}{}$	$\frac{L = c_1(1)/c_1(g)}{-}$	p <sub>1</sub> /kPa	c <sub>1</sub> /mo1 dm-3	Re
393.15	50	53	95	20	105	0.163	1.002 x 10 <sup>-1</sup>	3.066 x 10 <sup>-5</sup>	2
803.15	1.0 - 1.5	1.3	2.3	3.0	17	0.820	3.857 x 10 <sup>-4</sup>	1.53 x 10-7	3
358.15	15	15	28	11	57	0.280	1.595 x 10 <sup>-2</sup>	5.36 x 10-6	
73.15	30	31	56	12	66	0.253	3.690 x 10 <sup>-2</sup>	1.189 x 10-s	
01.15	1,5	1.5	2.7	2.2	12	1.15	3.280 x 10-4	1.310 x 10-7	4
98.15	3.0	3.0	5.4	0.85	4.7	2.90	2.562 x 10 <sup>-4</sup>	1.034 x 10 <sup>-7</sup>	5
	2.9	2.9	5.2	0.88	4.9	2.80			
	3.0	3.0	5.4	0.85	4.7	2.90			
98.15	3.14	3.15	5.67	0.813	4.52	3.04	2.562 x 10 <sup>-4</sup>	1.034 x 10 <sup>-7</sup>	
08.15	5.40	5.43	9.79	1.055	5.85	2.41	5.731 x 10 <sup>-4</sup>	2,237 x 10-7	
23.15	8.72	8.82	15.9	1.98	11.0	1.34	1.744 x 10 <sup>-3</sup>	6.491 x 10-7	
38.15	10.6	10.8	19.5	4.44	24.6	0.621	$4.798 \times 10^{-3}$	$1.707 \times 10^{-6}$	
53.15	12.6	13.0	23.4	9.31	51.7	0.306	$1.210 \times 10^{-2}$	$4.121 \times 10^{-6}$	
63.15	16.1	16.7	30.0	12.9	71.5	0.227	2.146 x 10 <sup>-2</sup>	7.107 x 10 <sup>-6</sup>	
98.15	1	1	1.8	2.6	14	0.97	2.562 x 10 <sup>-4</sup>	1.034 x 10 <sup>-7</sup>	7
73.15	1.2	1.2	2.2	0.22	1.2	10.35	2.632 x 10 <sup>-5</sup>	1.159 x 10-8	1
88.65	2.1	2.1	3.8	0.54	3.0	4.46	$1.131 \times 10^{-4}$	4.713 x 10 <sup>-8</sup>	
93.15	2.4	2.4	4.3	0.70	3.9	3.48	$1.677 \times 10^{-4}$	$6.880 \times 10^{-8}$	
98.15	2.8	2.8	5.1	0.92	5.0	2.71	2.562 x 10-4	1.034 x 10-7	
03.15	2.9	2.9	5.2	1.3	7.4	1.89	$3.857 \times 10^{-4}$	1.530 x 10 <sup>-7</sup>	
08.15	3.4	3.4	6.2	1.7	9.2	1.52	5.731 x 10 <sup>-4</sup>	2.237 x 10 <sup>-7</sup>	
77.45	2.33	2.33	4.19	0.172	0.957	13.40	4.01 x 10 <sup>-5</sup>	1.738 x 10-8	9
	2.21	2.21	3.99	0.181	1.005	12.72			
84.56	2.37	2.38	4.28	0.329	1.83	7.18	7.82 x 10-5	3.305 x 10 <sup>-8</sup>	
	2.31	2.31	4.17	0.339	1.88	6.99			
	2.22	2.23	4.01	0.351	1.95	6.72			
88.12	2.14	2.14	3.86	0.504	2.80	4.75	$1.079 \times 10^{-4}$	$4.504 \times 10^{-8}$	
92.95	2.39	2.39	4.31	0.690	3.82	3.53	$1.648 \times 10^{-4}$	6.766 x 10 <sup>-8</sup>	
	2.49	2.49	4.49	0.661	3.67	3.68			
98.17	2.98	2.99	5.39	0.858	4.76	2.88	$2.566 \times 10^{-4}$	1.035 x 10-7	
03.17	3.58	3 <b>.5</b> 9	6.47	1.076	5.97	2.34	$3.864 \times 10^{-4}$	1.533 x 10 <sup>-7</sup>	

Table 2	. (continued)						Mercury	Vapor	
T/K	107 c <sub>1</sub> /mo1 dm <sup>-3</sup>	107 m <sub>1</sub> /mol kg <sup>-1</sup>	10° x <sub>1</sub>	$\frac{10^{-3}H = p_1/m_1}{}$	$\frac{10^{-4}H = p_1/x_1}{}$	$L = c_1(1)/c_1(g)$	p <sub>1</sub> /kPa	c <sub>1</sub> /mo1 dm <sup>-3</sup>	Ref
303.24	3.43	3.44	6.20	1.129	6.27	2.23	3.885 x 10 <sup>-4</sup>	1.541 x 10 <sup>-7</sup>	9
	3.48	3.49	6.29	1.113	6.18	2,26			
312.31	4.35	4.39	7.90	1.73	9.62	1.49	$7.600 \times 10^{-4}$	2.927 x 10 <sup>-7</sup>	
18.22	4.58	4.62	8.33	2.65	14.69	0.990	$1.224 \times 10^{-3}$	$4.626 \times 10^{-7}$	
	4.40	4.45	8.01	2.75	15.28	0.951			
22.95	5.42	5.48	9.88	3.04	16.88	0.873	1.668 x 10 <sup>-3</sup>	$6.212 \times 10^{-7}$	
23.39	4.51	4.56	8.22	3.88	21.5	0.684			
	5.32	5.38	9.70	3.33	18.2	0.806			
	4.85	4.91	8.85	3.60	20.0	0.735			
26.86	5.31	5.38	9.70	4.08	22.6	0.657	$2.197 \times 10^{-3}$	$8.084 \pm 10^{-7}$	
33.13	6.77	6.88	12.4	5.02	27.9	0.543	$3.455 \times 10^{-3}$	1.247 x 10-6	
	6.06	6.16	11.1	5,61	31.1	0.486			
35.43	7.25	7.38	13.3	5.32	29,5	0.515	3.927 x 10 <sup>-3</sup>	1.408 x 10-6	9
41.34	8.75	8.94	16.1	6.58	36.5	0.422	5.882 x 10 <sup>-3</sup>	2.073 x 10 <sup>-6</sup>	
	8.31	8.49	15.3	6.93	38.4	0.401			
45.59	9.48	9.71	17.5	7.75	43.0	0.362	$7.524 \times 10^{-8}$	2.619 x 10-6	
	c <sub>1</sub> /mo1 dm <sup>-</sup>	m <sub>1</sub> /mol kg <sup>-1</sup>	10° x <sub>1</sub>						
73,15	0.0010	0.0014	0.026	27.8	150	0.123	38.88	8.159 x 10 <sup>-3</sup>	10
73.13	0.0010	0.0014	0.028	33.9	185	0.123	40.71	8.543 x 10 <sup>-3</sup>	10
71,15	0.00064	0.0012	0.022	47.3	250	0.033	42.53	8.956 x 10 <sup>-3</sup>	
11.13	0.00004	0,0009	0.017	47.5	230	0.071	42.33	8.930 1 10	
73.15	0.00884	0.0168	0.302	14.0	77.9	0.210	235.4	$4.206 \times 10^{-2}$	10
	0.00800	0.0138	0.248	17.6	97.7	0.185	242.3	$4.329 \times 10^{-2}$	
	0.00932	0.0161	0.289	15.0	83.7	0.216	242.0	4.324 x 10 <sup>-2</sup>	
	0.00786	0.0123	0.222	20.9	116	0.171	256.6	$4.585 \times 10^{-2}$	
	0.00895	0.0140	0.251	18.3	102	0.195	256.6	$4.885 \times 10^{-2}$	
71.15	0.00758	0.0111	0.200	23.9	133	0.160	265.1	$4.751 \times 10^{-2}$	
74.15	0.00722	0.0106	0.191	26.1	145	0.146	276.8	4.938 x 10 <sup>-2</sup>	
73.15	0.03161	0.1202	2.162	7.76	43.1	0.218	932.7	0.1450	10
75.15	0.03191	0.1182	2.125	8.09	45.0	0.215	956.7	0.1484	
73.15	0.02812	0.1008	1.812	9.29	51.7	0.193	936.9	0.1457	
68.15	0.04048	0.0920	1.654	10.2	56.7	0.276	938.4	0.1469	
80.15	0.0407	0.0992	1.784	10.7	59.6	0.248	1064.0	0.1640	
71.15	0.0432	0.0816	1.467	12,6	70.4	0.268	1032.1	0.1610	

Table 2.	(continued)						Mercury	Vapor	
T/K	c <sub>1</sub> /mol dm <sup>-1</sup>	m <sub>1</sub> /mo1 kg <sup>-1</sup>	10° x <sub>1</sub>	$10^{-3}H = p_1/m_1$	$\frac{10^{-4}H = p_1/x_1}{}$	$L = c_1(1)/c_1(g)$	p <sub>1</sub> /kPa	c <sub>1</sub> /mo1 dm <sup>-3</sup>	Re
776.15	0.0347	0.0667	1.202	16.3	90.3	0.206	1085.0	0.1681	10
	107 c <sub>1</sub> /mo1 dm <sup>-2</sup>	107 m <sub>1</sub> /mol kg <sup>-1</sup>	10° x <sub>1</sub>						
298.15	3.05	3.06	5.51	0.837	4.65	2.95	2.562 x 10 <sup>-4</sup>	1.034 x 10 <sup>-7</sup>	11
313.15	5.12	5.16	9.30	1.63	9.04	1.59	$8.405 \times 10^{-4}$	3.228 x 10-7	
323.15	7.43	7.52	13.5	2.32	12.9	1.14	$1.744 \times 10^{-3}$	6.491 x 10 <sup>-7</sup>	
333.15	10.78	11.0	19.8	3.15	17.5	0.863	$3.460 \times 10^{-3}$	$1.249 \times 10^{-6}$	
343,15	13.33	13.6	24.6	4.85	26.8	0.577	$6.591 \times 10^{-3}$	2.310 x 10-6	
353.15	16.37	16.8	30.3	7.20	39.9	0.397	$1.210 \times 10^{-3}$	4.121 x 10 <sup>-6</sup>	
278.15	0.957	0.96	1.72	0.447	2.49	5.16	4.289 x 10 <sup>-5</sup>	1.855 x 10-8	12
283.15	1.37	1.37	2.46	0.501	2.79	4.70	6.869 x 10 <sup>-5</sup>	2.918 x 10-8	
293.15	2.24	2.25	4.04	0.745	4.15	3.14	$1.677 \times 10^{-4}$	7.123 x 10 <sup>-8</sup>	
303.15	4.05	4.07	7.33	0.948	5.26	2.65	$3.857 \times 10^{-4}$	1.530 x 10-7	
313.15	6.83	6.88	12.4	1.221	6.78	2.12	$8.405 \times 10^{-4}$	3.228 x 10 <sup>-7</sup>	
323.15	10.7	11.0	19.8	1.585	8.81	1.68	$1.744 \times 10^{-3}$	6.491 x 10 <sup>-7</sup>	
333.15	18.3	18.7	33.6	1.85	10.30	1.47	$3.460 \times 10^{-3}$	1.249 x 10 <sup>-6</sup>	
378.15		22.3	40.2	34.8	193	0.086	0.0777	2.471 x 10-s	13
473.15		2580	4650	8.98	49.8	0.379	2.317	5.890 x 10-4	
		1220	2200	23.3	129	0.146	2.838	$7.214 \times 10^{-4}$	
475.15		608	1100	60.0	332	0.057	3.650	9.239 x 10 <sup>-4</sup>	
310.15	4.4	4.4	8.0	1.52	8.36	1.70	6.689 x 10 <sup>-4</sup>	2.594 x 10 <sup>-7</sup>	14
303.15	3.14	3.15	5.68	1.22	6.79	2.05	$3.857 \times 10^{-4}$	1.530 x 10 <sup>-7</sup>	15
278.15	2.2	2.2	3.9	0.20	1.1	11.9	4.289 x 10-s	1.855 x 10-*	16
283.15	2.3	2.3	4.2	0.30	1.6	7.9	$6.869 \times 10^{-5}$	2.918 x 10-8	
293.15	2.7	2.7	4.8	0.62	3.5	3.8	$1.677 \times 10^{-4}$	7.123 x 10 <sup>-8</sup>	
298.15	3.0	3.0	5.4	0.85	4.7	2.9	$2.562 \times 10^{-4}$	1.034 x 10-7	
303.15	3.2	3.2	5.8	1.21	6.7	2.1	$3.857 \times 10^{-4}$	$1.530 \times 10^{-7}$	
313.15	4.1	4.1	7.4	2.05	11.4	1.27	$8.405 \times 10^{-4}$	3.228 x 10 <sup>-7</sup>	
Room	0.4	0.4	0.7						1
298.15	2.88	2.89	5.21	0.887	4.92	2.78	2.562 x 10 <sup>-4</sup>	1.034 x 10 <sup>-7</sup>	1

Table 3. Ostwald coefficents at elevated total pressures.

T/K	Total	Total Pure Mercury Pressure Vapor Pressure	Mercury Vapor	Mercury Co	ncentration	Ostwald	Water
	Plessule		Pressure At Total Pressure	In Vapor	In Liquid	Coefficient	Density
	p <sub>t</sub> /MPa	p <sub>1</sub> /kPa	p <sub>1</sub> /kPa	$c_1(g)/mol dm^{-3}$	$c_1(1)/mol dm^{-3}$	L	ρ <sub>2</sub> /Mg m <sup>-1</sup>
378	101.3	0.0479	0.0777	2.47 x 10 <sup>-5</sup>	2.13 x 10 <sup>-6</sup>	0.086	0.9547
473	1.6	2.303	2.317	5.89 x 10-4	2.23 x 10 <sup>-4</sup>	0.379	0.8649
n	53.7	2.303	2.838	7.21 x 10 <sup>-4</sup>	1.06 x 10 <sup>-4</sup>	0.146	#
475	102.3	2.456	3.650	9.24 x 10-4	0.524 x 10-4	0.057	0.8625
573	50.7	32.94	38.88	8.16 x 10 <sup>-3</sup>	1.00 x 10 <sup>-3</sup>	0.123	0.7127
Ħ	64.8	32.94	40.71	$8.54 \times 10^{-3}$	$0.85 \times 10^{-3}$	0.100	Ħ
571	91.2	31.53	42.53	8.96 x 10 <sup>-3</sup>	0.64 x 10 <sup>-3</sup>	0.071	0.7166
647.14	Critical '	Temperature of Pu	re Water.				
673	40.5	210.0	235.4	4.21 x 10-2	8.84 x 10 <sup>-3</sup>	0.210	0.526
11	50.7	n	242.3	$4.33 \times 10^{-2}$	8.00 x 10 <sup>-3</sup>	0.185	0.580
Ħ	50.2	n	242.0	$4.32 \times 10^{-2}$	$9.32 \times 10^{-3}$	0.193	0.579
Ħ	70.9	Ħ	256.6	4.59 x 10 <sup>-2</sup>	$7.86 \times 10^{-3}$	0.171	0.639
n	70.9	n	n	m	8.95 x 10 <sup>-3</sup>	0.195	п
671	93.2	203.5	265.1	4.75 x 10 <sup>-2</sup>	7.58 x 10 <sup>-3</sup>	0.160	0.683
674	92.2	213.3	276.8	4.94 x 10 <sup>-2</sup>	7.22 x 10 <sup>-3</sup>	0.146	0.681
773	50.7	822.1	932.2	0.1450	0.0316	0.218	0.263
775	51.7	841.8	956.7	0.1485	0.0319	0.215	0.270
773	52.7	822.1	936.9	0.1457	0.0281	0.193	0.279
768	76.5	774.5	938.4	0.1469	0.0405	0.276	0.440
780	70.9	892.7	1064.0	0.1640	0.0407	0.248	0.410
771	100.3	802.8	1032.1	0.1610	0.0432	0.268	0.529
776	97.3	851.8	1085.0	0.1681	0.0347	0.206	0.520

The equilibrium vapor pressures of pure mercury were calculated from equations in the evaluation of Ambrose and Spraake (ref. 21).

The equilibrium vapor pressure of mercury at the total pressure of the solubility measurements was calculated from the thermodynamic equation (dln f/dp)<sub>T</sub> = V/RT assuming f = p.

The concentration of mercury in the vapor phase was calculated from the vapor pressure of mercury at the total pressure of the solubility measurement assuming ideal vapor behavior of the mercury.

Density of pure liquid water. Values below the critical temperature were taken from handbook tables, values above the critical temperature were taken from Sengers and Kamgar-Parsi (ref. 22).

COMPONENTS:	EVALUATOR:
(1) Mercury; Hg; [7439-97-6] (2) Water; H <sub>2</sub> O; [7732-18-5]	H. Lawrence Clever Chemistry Department Emory University Atlanta, Georgia 30322 USA
	1986, July

### CRITICAL EVALUATION:

The concentration (mol dm<sup>-3</sup>), molality (mol kg<sup>-1</sup>), and mole fraction solubilities.

The experimental values of solubility are given in either volume (mol dm<sup>-3</sup>) or weight (mol kg<sup>-1</sup>) units. The concentration and molal values differ negligibly from 273 to 323 K. Between 323 and 393 K the difference increases from 1 to 6 percent. At higher temperatures and into the water supercritical region the difference is much larger. The concentration, molal, and mole fraction values in Table 2 can be converted from one to another assuming the pure water density is a measure of the solution density. The assumption seems well justified for the dilute mercury solutions with the possible exception of the water supercritical region. The density of pure liquid water was taken from standard sources. The supercritical pure water density was taken from Sengers and Kamgar-Parsi (ref. 22). The densities have been used to calculate the solubility in the three units of concentration, molal, and mole fraction which are given in columns 2, 3, and 4 of Table 2. The molal values are shown in Figure 1 and 2. In the supercritical region the solubility decreases with increasing total pressure (increasing water density). Table 3 gives the water densities used in the calculations of solubility in the various units in the supercritical region. It also gives the mercury vapor pressures corrected for the total pressure.

Only the molal and mole fraction values are smoothed in this section. Between 273 and 393 K one can use the concentration and molal values interchangeably and probably be within the experimental error.

The molal solubility. There are eight experimental values of the solubility of mercury in water at 298.15 K. They are:

~~~~~~~	
10 7 m <sub>1</sub> /mol kg -1	(ref.)
2.81	(ref. 8)
2.89	(ref. 18)
2.99	(ref. 9)
3.00	(ref. 16)
3.00	(ref. 5)
3.06	(ref. 11)
3.15	(ref. 6)
3.18	(ref. 12)
~~~~~~~~~~	

Av.  $(3.01 \pm 0.12) \times 10^{-7} \text{ mol kg}^{-1}$ 

We take the value as the recommended solubility of mercury in water at 298.15 K. The smoothed curves for the temperature dependence of the solubility of mercury do not go exactly through the recommended value, but the curve is within a standard deviation of the value.

In an earlier evaluation (ref. 20) 36 experimental mercury molal solubility values were treated by a linear regression to obtain the tentative solubility values between 273 and 393 K. We have added about 10 values from (ref. 14, 15, 16, and 18) to the data base and repeated the linear regression. Both three and four constant equations were tried. The four constant equation gave unacceptable curvature and was not satisfactory. The three constant equation agrees well our earlier result (ref. 20), although it gives slightly higher results from 273.15 to about 303.15 K.

All of the molal solubility values between 273 and 773 K were treated in one linear regression. This ignores the pressure dependence of the solubility at 473 K and higher temperatures. The pressure dependence is taken into account in the treatment of Henry's constant and the Ostwald coefficient later in the evaluation. The equation gives values which are probably reliable to within 50 % at the higher temperatures. Although the

equation is intended for use over the 423 to 773 K temperature interval it gives results within 2 % of the three constant linear regression over the 298.15 to 343.15 K temperature interval and could be used over the 298 to 773 K temperature interval to give values that are probably within the range of experimental error.

The linear regression constants for an equation of the type

 $\ln (m_1/\text{mol kg}^{-1}) = A_1 + A_2/(T/100 \text{ K}) + A_3 \ln(T/100 \text{ K}) + A_4(T/100 \text{ K})$ 

are in Table 4. Smoothed values of molal solubility are in Tables 5 and 6. The line drawn in Figure 1 is from the three constant equation, and the line drawn in Figure 2 is from the four constant equation.

Table 4. Regression parameters for the molal solubility of mercury in water.

Temperature interval	A <sub>1</sub>	A <sub>2</sub>	. A <sub>3</sub>	A <sub>4</sub>
273.15 to 393.15	-42.4014	25.6254	17.1591	
423 to 773	-112.8354	126.4586	62.9768	-4.4945

Table 5. Tentative values of the molal solubility of mercury in water between 273.15 and 393.15 K.

<i>T/</i> K	10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>	<i>T</i> /K	10' m <sub>1</sub> /mol kg <sup>-1</sup>
273.15	1.41	333.15	7.83
278.15	1.62	338.15	9.03
283.15	1.87	343.15	10.40
288.15	2.16	348.15	11.97
293.15	2.49	353.15	13.8
298.15	2.88	358.15	15.9
303.15	3.30	363.15	18.2
308.15	3.83	368.15	20.9
313.15	4.42	373.15	24.0
318.15	5.11	378.15	27.6
323.15	5.89	383.15	31.6
328.15	6.79	388.15	36.2
		393.15	41.5

Table 6. Tentative values of the molal solubility of mercury in water between 423 and 773 K. No account taken of total pressure.

T/K	m <sub>1</sub> /mol kg <sup>-1</sup>	<i>T</i> /K	$m_1/\text{mol kg}^{-1}$
423	0.0000148	598	0.00264
448	0.0000336	623	0.00486
473	0.0000754	648	0.00858
498	0.000163	673	0.0147
523	0.000346	698	0.0242
548	0.000704	723	0.0386
573	0.00139	748	0.0594
		773	0.0887

The mole fraction solubility. A linear regression of the mole fraction solubilities from the same data set as used for the molal solubilities was carried out. For the 273.15 to 393.15 K temperature interval the three constant equation is

 $\ln x_1 = -46.0770 + 25.1284/(T/100 K) + 16.9998 \ln(T/100 K)$ .

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

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1986, July

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Smoothed values from the equation are given below in Table 7.

Table 7. Tentative values of the mole fraction solubility of mercury in water between 273.15 and 393.15 K.

T/K	10°x <sub>1</sub>	T/K	$10  ^{s}x_{1}$
273.15	2.53	333.15	14.1
278.15	2.92	338.15	16.3
283.15	3.37	343.15	18.7
288.15	3.89	348.15	21.6
293.15	4.49	353.15	24.8
298.15	5.18	358.15	28.5
303.15	5.98	363.15	32.8
308.15	6.91	368.15	37.6
313.15	7.97	373.15	43.2
318.15	9.20	378.15	49.6
323.15	10.6	383.15	56.8
328.15	12.2	388.15	65.1
		393.15	74.5

The mole fraction solubility data were not treated further in this evaluation. Total pressure has an effect on the solubility of mercury in the supercritical region of water. There is a suggestion of a pressure effect, perhaps of somewhat different character, below the water critical temperature. The effect of total pressure on the solubility of mercury seems to be better treated with the Henry's constant or the Ostwald coefficient which is done in the following two sections. Both the Henry's constant and the Ostwald coefficient can be used at mercury vapor pressures less than the saturation pressure of mercury. When they are used at the saturation vapor pressure they also represent the solubility when in equilibrium with liquid mercury. It is assumed that the solubility of water in mercury is negligible and does not effect the properties of pure mercury.

### II. Henry's Constant.

Columns 5 and 6 of Table 2 contain values of Henry's constant. The constant is given in both molal and mole fraction forms. They are  $(K/(kPa kg mol^{-1})) = (p_1/kPa)/(m_1/mol kg^{-1})$  and  $(K'/kPa) = (p_1/kPa)/x_1$ . The two values differ by a factor of 55.508, the number of moles of water in 1 kg. Thus, K = K'/55.508. Only the molal form has been plotted and fitted to smoothing equations. Figure 3 displays the values as  $ln(K/kPa kg mol^{-1})$  vs. 1000/(T/K). The values go through a maximum and show the effect of total external pressure above 473 K. Figure 6 show the pressure dependence of the Henry's constant. The values are linear in pressure within experimental error, but the values below the water critical temperature (473, 573 K) have a much larger slope than the values above the critical temperature (673, 773 K). There are not enough experimental data to tell whether or not this is a significant difference. It is an area that deserves further experimental investigation. The curves on Figure 3 are reproduced by the equation

 $\ln(K/kPa \ kg \ mol^{-1}) = A_1 + A_2/(T/100 \ K) + A_3 \ln(T/100 \ K) + A_4(T/100 \ K)$ .

with the parameters given in Table 8. The 273 to 393 K equation does not merge as smoothly as one might like with the 473 to 773 K equations. It is believed this is an indication of the larger uncertainty in the higher temperature solubility values.

Table 8. Linear regression parameters for Henry's constant.

Temperature Interval, T/K	Total Pressure p <sub>t</sub> /MPa	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>
273.15 - 393.15	0.1	254.1649	-372.8229	-167.0119	20.1528
473 - 773	50	126.5286	-196.9318	- 60.0986	3.9986
473 - 773	75	107.8775	-170.5553	- 47.5540	2.6886
473 - 773	100	94.1291	-151.5763	- 37.8481	1.6065

The maximums at 50, 75, and 100 MPa total pressure occur at 483, 500, and 512 K, respectively.

Smoothed values of the Henry's constant are in the following two tables. For Henry's constant in the form (pressure/mole fraction) see the earlier evaluation (ref. 20). More care was taken to evaluate the effect of total pressure in the supercritical region in the present evaluation.

Table 9. Tentative values of Henry's constant.

~~~			
T/K	K/kPa kg mol-1	T/K	K/kPa kg mol <sup>-1</sup>
273.15	134	323.15	3045
283.15	308	333.15	4490
293.15	627	343.15	6290
		353.15	8443
298.15	860	363.15	10,940
		373.15	13,760
303.15	1152	383.15	16,910
313.15	1942	393.15	20,395

Table 10. Tentative values of Henry's constant.

T/K	Henry's cons	stant, K/kPa	kg mol <sup>-1</sup> , at
	50 MPa	75 MPa	100 MPa
473	33,480	41,830	52,560
483	33,630 max	-	-
500	-	43,210 max	-
512	-		56,270 max
523	31,530	42,350	55 <b>,</b> 980
573	25 <b>,</b> 750	36,370	49,460
623	19,650	28,450	38,890
673	14,680	21,230	28,490
723	11,050	15,550	20,050
773	8,540	11,410	13,820

The values from 473 to 773 K are based on somewhat scattered data from one laboratory and should be used with caution.

### III. The Ostwald [Partition] Coefficient.

The Ostwald coefficient is the ratio of the equilibrium concentrations of solute in the liquid phase to the concentration in the gas phase. Thus, L =  $(c_1(\text{liq})/\text{mol dm}^{-3})/(c_1(\text{gas})/\text{mol dm}^{-3})$ .

Liquid phase concentration. The liquid phase concentrations were calculated from papers reporting molal or mole fraction solubilities using the density of pure water. The densities of subcritical pure water were taken from standard compilations. The densities of supercritical water were taken from (ref. 22). In the water supercritical region we do not have a true Ostwald coefficient, but a number that is the ratio of the concentra-

COMPONENTS:	EVALUATOR:
(1) Mercury; Hg; [7439-97-6] (2) Water; H <sub>2</sub> O; [7732-18-5]	H. Lawrence Clever Chemistry Department Emory University Atlanta, Georgia 30322 USA
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tion of mercury in the supercritical water to the concentration of mercury vapor above pure liquid mercury at the same total hydrostatic pressure.

Gas phase concentration. The concentration of mercury in the gas phase was calculated assuming ideal behavior of the vapor pressure of pure liquid mercury calculated from a literature evaluation (ref. 21). At elevated total pressures the Poynting correction was applied assuming fugacity and pressure to be equal. Some details of the calculation at the elevated pressures are shown in Table 3. Column 7 of Table 2 contains all of the Ostwald coefficient values. Figures 4 and 5 give two representations of the Ostwald coefficient as a function of temperature.

The Ostwald coefficients were fitted to four constant equations of the type

$$\ln L = A_1 + A_2/(T/100 \text{ K}) + A_3 \ln(T/100 \text{ K}) + A_4(T/100 \text{ K}).$$

The constants for the equation over the 273.15 to 393.15 and 473 to 773 K temperature intervals are in the table below. Figure 4 shows the Ostwald coefficient as a function of temperature. The 350 to 785 K region is shown with an expanded scale for the Ostwald coefficient. Figure 5 shows the logarithm of the Ostwald coefficient as a function of the inverse Kelvin temperature. The lines are generated from the constants in Table 11.

Table 11. Linear regression parameters for the Ostwald coefficient.

Temperature Interval, T/K	Total Pressure p <sub>t</sub> /MPa	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>
273.15 - 393.15	0.1	-236.5852	358.1516	158.1918	-18.5469
473 - 773	50	-127.9489	208.0691	68.3318	- 5.1724
473 - 773	75	-116.4886	192.0615	60.3112	- 4.2749
473 - 773	100	- 94.3479	161.3909	44.4468	- 2.4351

The minimums at 50, 75, and 100 MPa occur at temperatures of 476, 486, and 500 K, respectively.

Some smoothed values of the Ostwald coefficient at selected temperatures are given in the Tables 12 and 13 below.

Table 12. Tentative values of the Ostwald coefficient between 273.15 and 393.15 K.

		*************	
T/K	L	T/K	L
	~		
273.15	16.98	319.9	1.000
278.15	11.21	323.15	0.971
283.15	7.65	333.15	0.608
288.15	5.37	343.15	0.446
293.15	3.879	353.15	0.342
298.15	2.871	363.15	0.272
303.15	2.175	373.15	0.222
308.15	1.683	383.15	0.186
313.15	1.328	393.15	0.159

T/K	Ostwald co	efficient at p	pressures of
	50 MPa	75 MPa	100 MPa
423	0.123	0.112	0.0912
473	0.106	0.0921	0.0687
476	0.106 min	_	_
486	-	0.0915 min	-
500	-	-	0.0665 min
523	0.114	0.0960	0.0678
573	0.137	0.113	0.0786
623	0.170	0.141	0.100
673	0.210	0.177	0.134
723	0.249	0.218	0.182

Table 13. Tentative values of Ostwald coefficient from 423 to 773 K at total pressures of 50, 75 and 100 MPa.

Figure 7 shows the change of the experimental values of the Ostwald coefficient with pressure below (473, 573 K) and above (673, 773 K) the water critical temperature of 647 K. As noted with the Henry's constant there may be a difference in the pressure dependence of the Ostwald coefficient in the sub- and super-critical water regions. However, the case for the different pressure dependence is not as compelling for the Ostwald coefficient as for Henry's constant. See Figures 6 and 7.

0.269

0.248

### IV. Thermodynamic changes for the dissolution of mercury in water.

0.281

773

The parameters of the fitted equations can be used to calculate the Gibbs energy, enthalpy, entropy and heat capacity changes on dissolving mercury in water. Figure 8 shows these changes calculated from the parameters for the Ostwald coefficient. These values were chosen because they represent the simplest standard state change. They are for the transfer on one mole of mercury from the gas to the solution at the hypothetical concentrations of one mole per liter in each phase. The temperatures at which the Ostwald coefficients equals unity (equal equilibrium concentration in both phases), the temperature range at which the Ostwald coefficient goes through a minimum at the three total pressures, and the water critical temperature are marked on the figure. Table 14 gives the values as calculated from the Ostwald coefficient fit at 50 MPa total pressure.

Table 14. Standard thermodynamic changes for the transfer of one mole of mercury from the vapor to the solution at a hypothetical concentration of one mole per liter. Values calculated from the 50 MPa equation.

T/K	Gibbs Energy kJ mol <sup>-1</sup>	Enthalpy Change kJ mol <sup>-1</sup>	Entropy Change J K <sup>-1</sup> mol <sup>-1</sup>	Heat Capacity Change J K <sup>-1</sup> mol <sup>-1</sup>
273	-6.27	-49.9	-160	333
323	+0.34	-34.3	-107	290
373	4.68	-20.9	- 68.5	247
423	7.36	- 9.59	- 40.1	204
473	8.82	- 0.46	- 19.6	161
523	9.43	+ 6.52	- 5.6	118
573	9.46	11.4	+ 3.3	75
623	9.17	14.0	7.8	32
673	8.74	14.6	8.7	- 11
723	8.36	13.0	6.4	- 54
773	8.15	9.2	1.3	- 97

At 273 K the equilibrium concentration of mercury is ten times larger in the water than the gas phase. This indicates a strong interaction between water and mercury which is reflected in the exothermic enthalpy change at

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

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the lower temperatures. At all temperatures above 320 K the Ostwald coefficient is less than unity. Thus the mercury equilibrium concentration is larger in the vapor phase than in the liquid water. This indicates a change from a dominate attractive interaction between mercury and water to a repulsion as the temperature increases. This is reflected in an endothermic enthalpy of solution at temperatures of 473 and above. Some further comments about the thermodynamic changes on dissolution follow below.

Standard Gibbs Energy change. Negative over the temperature interval of 273 to 320 K where the Ostwald coefficient is greater than one, positive at the higher temperatures where the Ostwald coefficient is less than one, and zero at the 320 K where the Ostwald coefficient equals unity.

Standard Heat Capacity change. The linear decrease in the heat capacity change follows from the four constant equation which on taking two temperature derivates gives an equation linear in temperature. The important point is the decrease from a large positive value to a negative value as the temperature increases. The heat capacities at 298 K of the pure components are liquid water 75.0 J K<sup>-1</sup> mol<sup>-1</sup> and mercury vapor 20.8 J K<sup>-1</sup> mol<sup>-1</sup>. The heat capacity change in the room temperature range on dissolving the mercury indicates a loosening of the water structure when the mercury atom enters the solution and interacts with the water. The effect decreases with temperature and the heat capacity change become negative at about the critical temperature of water. It is probably only a coincidence that the change in sign occurs near the water critical temperature.

Entropy change. The large negative entropy change at low temperature appears to be consistent with a loosening of the water structure indicated by the large positive heat capacity change. However, there appears to be a strong attractive interaction between the mercury and water in the 273 to 320 K range, thus the effect may be a large cooperative loosening of the water structure even though the mercury-water interaction is large with the effect in the water primarily an entropy effect. At the higher temperatures the mercury-water interaction changes to a net repulsion and order is restored in the water structure.

Enthalpy change. The large exothermic enthalpy change at 273 K is a measure of the strong interaction between mercury and water. The effect decreases rapidly with increasing temperature. Above about 480 K the change is endothermic which is consistent with a repulsion between the mercury and water dominating at the higher temperatures.

### ADDED NOTE:

Dr. V. I. Sorokin, Institute of Experimental Mineralogy, Academy of Sciences, Moscow, USSR, has informed the IUPAC Solubility Commission that he has prepared a new critical evaluation of the Hg + H $_2$ O system. The evaluation takes into account the partial molar volumes and pressure dependence of solubility up to 773 K and 152 MPa (1500 atm). The evaluation will be published in 1987.

Dr. G. Kolonin, Institute of Geology and Geophysics, Academy of Sciences (Siberian Branch), Novosibirsk-90, USSR, has informed the IUPAC Solubility Commission that he has new measurements in progress on the solubility of mercury in water by UV spectrophotometry over the 423 to 523 K temperature interval.

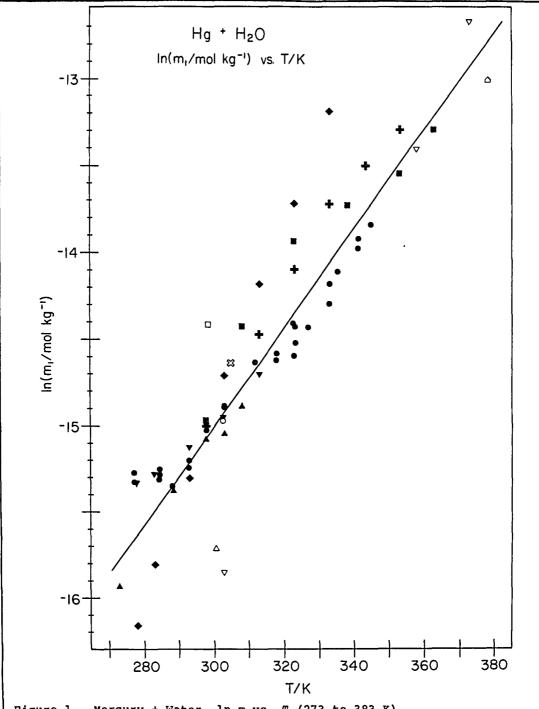


Figure 1. Mercury + Water, ln m vs. T (273 to 383 K).

- Reichardt and Bonhoeffer (ref. 2)
- Stock et al. (ref. 3)
- △ Pariaud and Archinard (ref. 4)
- Choi and Tuck (ref. 6)
- □ Kuntz and Mains (ref. 7)
- ▲ Spencer and Voigt (ref. 8)
- O Baltisberger et al. (ref. 15)

- Glew and Hames (ref. 9)
- + Onat (ref. 11)
- Sanemasa (ref. 12)
- △ Sorokin et al. (ref. 13)
- X Kawakara et al. (ref. 14)
- ▼ Okouchi and Sasaki (ref. 16)

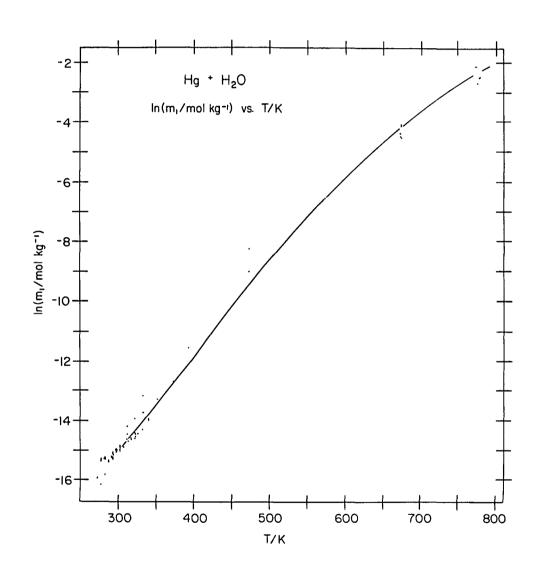
- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

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Mercury + Water, ln m vs. T (273 to 773 K).

From top to bottom the total pressures were:

473 K 1.6, 54, 102 MPa

573 K 673 K 41,

65, 91 MPa 50, 51, 71, 71, 92, 93 MPa 52, 53, 71, 76.5, 100, 97 MPa. 41, 773 K 51,

The curve was drawn from 298 to 773 K from the parameters of the four constant linear regression (Table 4).

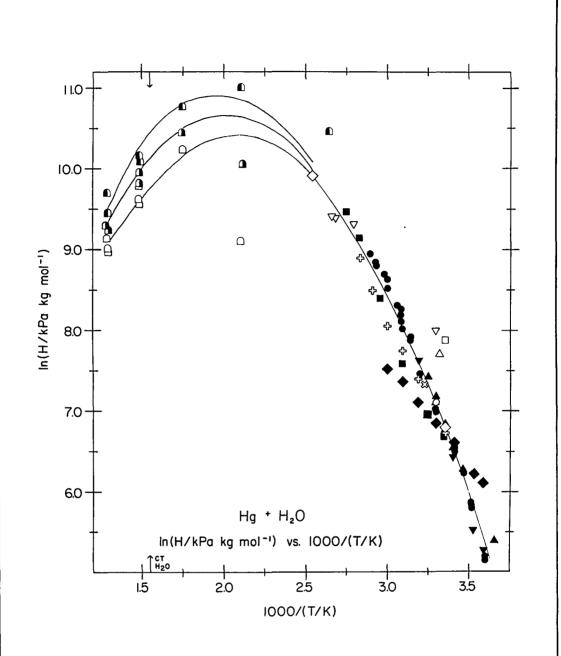


Figure 3. Mercury + Water, Henry's constant. ln(K/(kPa kg mol<sup>-1</sup>) vs. 1000/(T/K).

Curves drawn from linear regression constants in Table 8. The three curves represent 100, 75, and 50 MPa total pressure as one goes from top to bottom.

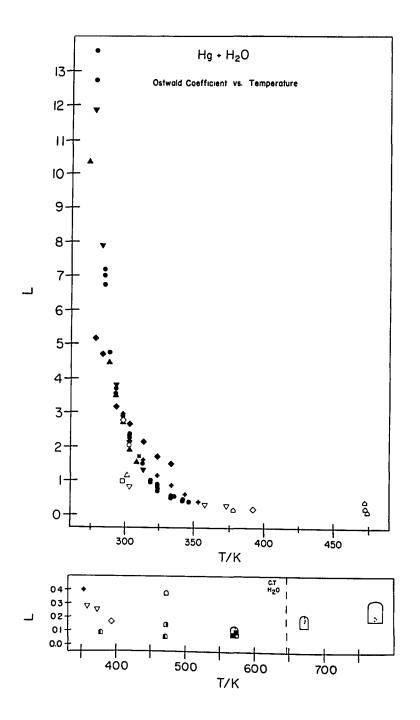
- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

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Mercury + Water, Ostwald coefficient, L vs. Temperature, T/K. Figure 4. The 350 to 773 K temperature range is shown on an expanded scale. Same symbol key as Figure 1.

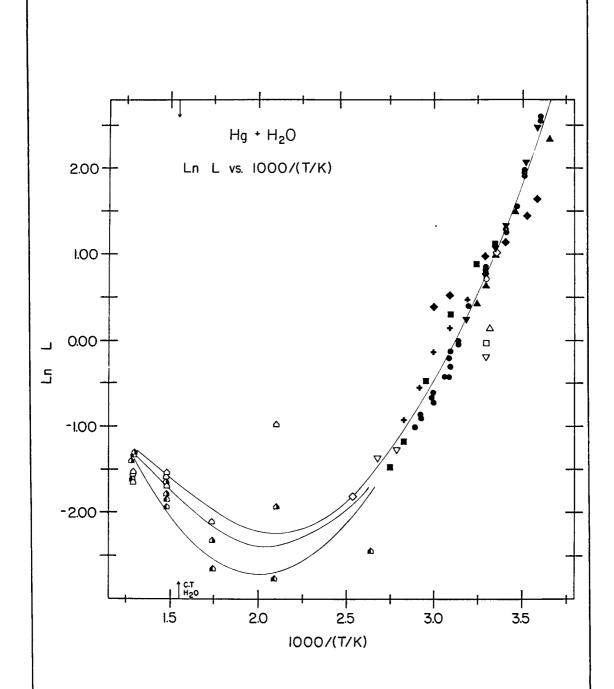


Figure 5. Mercury + Water, ln L vs. 1000/(T/K).

Same symbol key as Figure 1. The three curves represent total pressures of 50, 75 and 100 MPa as one goes from top to bottom.

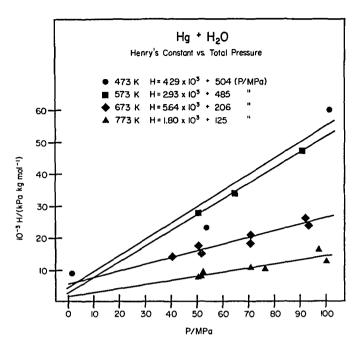


Figure 6. Mercury + Water, Henry's constant vs. Total pressure.

Evidence of a different pressure dependence of the Henry's constant above and below the water critical temperature of 647 K.

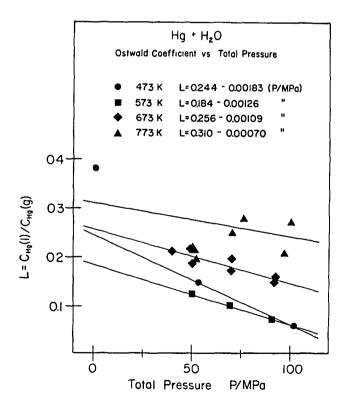


Figure 7. Mercury + Water, Ostwald coefficient vs. Total pressure.

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

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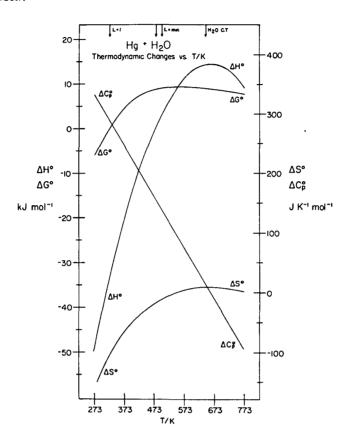


Figure 8. Mercury + Water.

Thermodynamic changes for the transfer on one mole of mercury from the gas phase at one mole per liter to the solution at one mole per liter. Calculated from the constants of the linear regression of the low temperature data plus the 50 MPa total pressure high temperature data.

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

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### CRITICAL EVALUATION:

- 1. Christoff, A. Z. Phys. Chem. Stoechiom. Verwandschaftsl. 1908, 63, 346 54.
- 2. Reichardt, H.; Bonhoeffer, K. F. Z. Phys. 1931, 67, 780 9.
- Stock, A.; Cucuel, F.; Gerstner, F.; Kohle, H.; Lux, H. Z. Anorg. Allgem. Chem. 1934, 217, 241 53.
- Pariaud, J.; Archinard, P. Bull. Soc. Chim. France <u>1952</u>, 454 6;
   J. Chim. Phys. <u>1956</u>, 53, 765 9.
- 5. Moser, H. C.; Voigt, A. F. J. Am. Chem. Soc. 1957, 79, 1837 9.
- 6. Choi, S. S.; Tuck, D. G. J. Chem. Soc. 1962, 4080 8.
- 7. Kuntz, R. R.; Mains, G. J. J. Phys. Chem. <u>1964</u>, 68, 408 10.
- Spencer, J. N.; Voigt, A. F. J. Phys. Chem. <u>1968</u>, 72, 464 70;
   Spencer, J. N. <u>Dissertation</u>, Iowa State University, <u>1967</u>.
- 9. Glew, D. N.; Hames, D. A. Can. J. Chem. 1971, 49, 3114 8.
- Sorokin, V. I. Dolk. Akad. Nauk SSSR <u>1973</u>, 213, 852 5; Dokl. Chem. (Engl. Transl.) <u>1973</u>, 213, 905 8.
- 11. Onat, E. J. Inorg. Nucl. Chem. 1974, 36, 2029 32.
- 12. Sanemasa, I. Bull. Chem. Soc. Jpn. 1975, 48, 1795 8.
- Sorokin, V. I.; Alekhin, Yu. V.; Dadze, T. P. Ocherki Fiz. Khim. Petrol. <u>1978</u>, 8, 133 - 49.
- Kawakara, H.; Nakamura, M.; Ishizaki, N.; Yamada, T.; Kawamoto, T.; Hikari, S.; Sogawa, K.; Maehara, S. Shika Rikogaku Zasshi 1979, 20, 137 - 41.
- Baltisberger, R. J.; Hildebrand, D. A.; Grieble, D.; Ballintine, T. A. Anal. Chim. Acta 1979, 111, 111 22.
- Okouchi, S.; Sasaki, S. Bull. Chem. Soc. Jpn. 1981, 54, 2513 4;
   Report of the College of Engineering of Hosei University 1983, (No. 22), 55 106.
- 17. Gjessing, E. T.; Rogne, A. K. G. Vatten 1982, 38, 406 8.
- 18. Hursh, J. B. JAT, J. Appl. Toxicol. 1985, 5, 327 32.
- Khodakovskii, I. L.; Popova, M. Ya.; Ozerova, N. A. Geokhim. Protsessov Migr. Rudn. Elem. <u>1977</u>, 86 118; Chem. Abstr. <u>1979</u>, 90, 57989s.
- Clever, H. L.; Johnson, S. A.; Derrick, M. E. J. Phys. Chem. Ref. Data <u>1985</u>, 14, 631 - 80.
- 21. Ambrose, D.; Sprake, C. H. S. J. Chem. Thermodynam. 1972, 4, 603 20.
- Sengers, J. V.; Kamgar Parsi, B. J. Phys. Chem. Ref. Data 1983, 13, 185 - 205.

### COMPONENTS: (1) Mercury; Hg; [7439-97-6]

### (2) Water; H<sub>2</sub>O; [7732-18-5]

### EVALUATOR:

Addendum I

Recommended solubility values at 298.15 K in several units.

### CRITICAL EVALUATION:

Experimental values of the solubility of mercury in water at 298.15 K have been taken from eight papers. The experimental values were converted from the original unit to concentration, molal, mole fraction, Ostwald coefficient, and several forms of Henry's constant. There appear to be some minor inconsistencies because some values were converted on the basis of two significant digits and some on the basis of three digits. Other inconsistencies arise because the conversions are not necessarily made in the same order because the original unit varies from paper to paper. The values are arranged below along with the average value, the standard deviation, and the units. In general the standard deviation amounts to about 4 per cent of the average value.

Molality, mole fraction, and Ostwald coefficient.

Molal	Mole Fraction	Ostwald coefficient
10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>	10°x <sub>1</sub>	$L = c_1(\text{liq})/c_1(\text{gas})$
2.81 (ref. 8) 2.89 (ref. 18) 2.99 (ref. 9) 3.00 (ref. 16) 3.00 (ref. 5) 3.06 (ref. 11) 3.15 (ref. 6) 3.18 (ref. 12)	5.1 (ref. 8) 5.21 (ref. 18) 5.33 (ref. 5) 5.39 (ref. 9) 5.40 (ref. 16) 5.51 (ref. 11) 5.67 (ref. 6) 5.76 (ref. 12)	2.71 (ref. 8) 2.78 (ref. 18) 2.84 (ref. 5) 2.88 (ref. 9) 2.90 (ref. 16) 2.95 (ref. 11) 3.04 (ref. 6) 3.09 (ref. 12)
(3.01 $\pm$ 0.12) x 10 <sup>-7</sup> mol kg <sup>-1</sup>	(5.42 ± 0.22) x 10 - mole fraction	(2.90 ± 0.13) Ostwald coef.

Henry's constants (several forms).

Pressure/Molal	Pressure/Mole Fraction	Pressure/Concentration
$K = p_1/m_1$	$K' = p_1/x_1$	$K^{\prime\prime} = p_1/c_1$
813 (ref. 6)	45200 (ref. 6)	816 (ref. 6)
837 (ref. 11)	46500 (ref. 11)	840 (ref. 11)
846 (ref. 12)	47000 (ref. 12)	850 (ref. 12)
850 (ref. 16)	47000 (ref. 16)	854 (ref. 16)
858 (ref. 9)	47600 (ref. 9)	861 (ref. 9)
860 (ref. 5)	48000 (ref. 5)	864 (ref. 5)
887 (ref. 18)	49200 (ref. 16)	890 (ref. 16)
920 (ref. 8)	50000 (ref. 8)	923 (ref. 8)
(859 <u>+</u> 30)	(47600 <u>+</u> 1500)	(862 ± 30)
kPa kg mol <sup>-1</sup>	kPa	kPa dm³ mol -1

It is of some concern that when all of the experimental data are fitted by a linear regression as a function of temperature the smoothed 298.15 K solubility value does not reproduce the recommended value above. In this evaluation the smoothed values from the linear regression are classed as tentative values. The tentative 298.15 K solubility value is within one standard deviation of the recommended value above.

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

### EVALUATOR:

Addendum II

Henry's constant in pressure and concentration.

### CRITICAL EVALUATION:

Henry's constant, (K''/kPa dm³ mol<sup>-1</sup>) =  $(p_1/kPa)/(c_1/mol dm^{-3})$ , is given here for comparison with the pressure/molal and pressure/mole fraction values given earlier in the evaluation. The pressure/concentration Henry's constant is larger than the pressure/molal constant by a percentage that reflect the difference in the mass of 1 kg and the mass of one dm³ of water in kg. At the lower temperatures this difference is negligible. For example at 298.15 K the recommended values are 862 kPa dm³ mol -¹ and 859 kPa kg mol -¹ which differ by 0.3 %. At the higher temperatures and especially in the water super critical region the differences are larger.

The feature that most distinguishes the pressure/concentration from the pressure/molal form of Henry's constant is the pressure dependence in the water supercritical region. The pressure/molal Henry's constant discussed earlier appears to be a continuous function of pressure through the water critical point and into the water super critical region (see Fig. 3, 6). In the super critical water region the pressure/concentration form of Henry's constant tends to be random with pressure. Average values of the constant are (31,100  $\pm$  4,500) and (28,200  $\pm$  3,800) kPa dm³ mol  $^{-1}$  at 673 and 773 K, respectively.

The pressure/concentration Henry's constant has been fitted by linear regression to four equations of the type

 $\ln(K'''/kPa\ dm^3\ mol^{-1}) = A_1 + A_2/(T/100\ K) + A_3\ \ln(T/100\ K) + A_4(T/100\ K)$ 

for 0.1 MPa and 273.15 to 393.15 K, 50 MPa and 423 to 647 K, 100 MPa and 423 to 647 K, and all pressures and 648 to 773 K.

The regression parameters are given in the Table below.

Table 1. Linear regression parameters for the pressure/concentration form of Henry's constant.

Temperatu Interval,		e A <sub>l</sub>	A <sub>2</sub>	A <sub>3</sub>	A4
273.15 - 39	3.15 0.1	71.9562 <u>+</u> 3.3697	-120.1691 ± 5.3714	-22.8021 <u>+</u> 1.4470	
423 - 64	7 50	137.3658 <u>+</u> 13.7699	-211.3420 <u>+</u> 19.7969	-69.9926 <u>+</u> 9.3807	5.6200 <u>+</u> 1.0528
423 - 64	7 100	63.3040 <u>+</u> 33.6868	-108.0239 <u>+</u> 47.3560	-16.3612 <u>+</u> 24.9924	-0.8248 ± 3.1950
648 - 77	3 all	9.6153 <u>+</u> 0.5429	4.8348 <u>+</u> 3.8948	-	-

T/K	K/kPa dm³ mol-1	T/K	K/kPa dm³ mol -1
273.15	154	323.15	3000
283.15	327	333.15	4480
293.15	633	343.15	6370
		353.15	8660
298.15	856	363.15	11300
		373.15	14200
303.15	1136	383.15	17400
313.15	1900	393.15	20600

Table 2. Tentative values of Henry's constant (pressure/concentration).

Table 3. Tentative values of Henry's constant (pressure/concentration).

T/K	Henry's	constant, K/kPa dm²	mol <sup>-1</sup> , at
171	50 MPa	100 MPa	All
423	27,800	3,600	-
443	32,200	55,000	_
463	35,300	64,900	-
483	37,300	72,300	•
503	38,200	76,800	-
523	38,300	78,200	-
543	37,700	76,800	_
563	36,800	73,000	-
583	35,600	67,600	_
603	34,400	61,000	-
623	33,300	53,900	-
643	32,200	46,800	_
663	-	-	31,100
683	-	-	30,400
703	-	-	29,800
723	_	-	29,300
743	_	-	28,700
763	-	-	28,200

The tentative values of Henry's constant in Tables 2 and 3 are generated from the linear regression parameters given in Table 1. The parameters for the 50 MPa total pressure equation will generate Henry's constant values within about 3 percent of the values above over the whole temperature interval of 273 to 773 K. The two sets of values are probably well within experimental error of each other.

The standard state change for the transfer of one mole of mercury is

$$Hg(aq, hyp 1 mol dm^{-3}) = Hg(g, 1 kPa) + H2O(liq)$$

Summarized in Table 4 are values of the standard thermodynamic changes calculated from the regression parameters of the  $50\ \text{MPa}$  total pressure equation.

Table 4. Standard thermodynamic changes in kJ mol<sup>-1</sup> and J K<sup>-1</sup> mol<sup>-1</sup> for the standard state change defined by the equation above.

T/K	Gibbs Energy	Enthalpy Change	Entropy . Change	Heat Capacity Change
273	-11.4	51.6	231	-327
298	-16.8	43.7	203	-303
373	-29.6	23.6	143	-233
473	-41.3	5.0	98	-140
573	-50.0	- 4.3	80	- 46
673	-57.9	- 4.3	80	+ 47

# COMPONENTS: (1) Mercury; Hg; [7439-97-6] (2) Water; H<sub>2</sub>O; [7732-18-5] VARIABLES: T/K = 281.15 - 3.15, 371.15 - 2.15 ORIGINAL MEASUREMENTS: Christoff, A. Z. Phys. Chem. 1908, 63, 346-54.

### EXPERIMENTAL VALUES:

Ter	mperature	Mercury Co	oncentration
t/°C	T/K	$10c_1/\text{mg dm}^{-3}$	10'c <sub>1</sub> /mol dm <sup>-2</sup>
8 - 10	281.15 - 3.15	0.1	0.5
98 - 99	371.15 - 2.15	0.93	4.6

The above results are of historical interest. Christoff was probably the first to show quantitatively that mercury dissolves in water and behaves as a "nonelectrolyte".

Christoff also showed that dissolved mercury could be detected in aqueous solutions of  $\rm H_2SO_4$  [7664-93-9] and of KOH [1310-58-3], and in the organic solvents benzene,  $\rm C_6H_6$ , [71-43-2], ethanol,  $\rm C_2H_6O$ , [64-17-5], and nitrobenzene,  $\rm C_6H_5NO_2$ , [98-95-3].

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

A pyknometer was partially filled with mercury and weighed. A supply of water was connected to the pyknometer and 10 liters of water slowly passed over the mercury surface. The pyknometer was dried and reweighed to find the mercury lost to the water.

Obviously the time of contact between water and mercury was not long enough to saturate the solution. However, the experiment did show that a measureable amount of mercury did dissolve in water. SOURCE AND PURITY OF MATERIALS:

No information given.

ESTIMATED ERROR:

# COMPONENTS: (1) Mercury; Hg; [7439-97-6] (2) Water; H<sub>2</sub>O; [7732-18-5] VARIABLES: PREPARED BY: H. L. Clever M. Iwamoto

### EXPERIMENTAL VALUES:

Tempe	erature	Mercury Solubility					
t/°C	<i>T</i> /K <sup>a</sup>	c <sub>1</sub> /mg dm <sup>-3</sup>	Concentration <sup>a</sup> 10 <sup>5</sup> ¢ <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>a</sup>	Molality <sup>a</sup> 10 <sup>5</sup> m <sub>1</sub> /mol kg <sup>-1</sup>		
120	393.15	1.0 <u>+</u> 0.2	0.5 ± 0.1	1.0 ± 0.2	0.5 <sub>3</sub> ± 0.1		

<sup>a</sup>Calculated by compilers.

Water density taken as 0.945 g cm -3.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

Some of these results are mentioned in two earlier papers (ref. 1 and 2), but the present paper discusses the solubility work in the most detail.

The solution is analyzed by weighing a gold foil before and after amalgamation with the mercury of the saturated solution. Ultraviolet absorption at 257.15 nm is also used.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. No information given.
- (2) Water. No information given.

### ESTIMATED ERROR:

 $\delta c_1/\text{mg dm}^{-3} = \pm (0.1 - 0.2)$ 

- Bonhoeffer, K. F.; Reichardt, H. Naturwissenshaften 1929, 17, 933.
- 2. Reichardt, H.; Bonhoeffer, K. F. 2. Electrochem. 1930, 36, 753.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6] (2) Water; H <sub>2</sub> O; [7732-18-5]	Stock, A.; Cucuel, F.; Gerstner, F.; Kohle, H.; Lux. H.  Z. Anorg. Allgem. Chem. 1934, 217, 241 - 53.
VARIABLES:	PREPARED BY:
T/K = 303.15 - 373.15	S. H. Johnson M. Iwamoto H. L. Clever
EXPERIMENTAL VALUES:	
Temperature	Mercury Solubility

Temp	erature		Mercury So	lubility	
t/°C	<i>T/</i> K	10 <sup>-1</sup> c <sub>1</sub> /mg dm <sup>-1</sup>	Concentration <sup>a</sup> 10'c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>a</sup> 10°x <sub>1</sub>	Molality <sup>a</sup> 10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
30	303.15	0.002 - 0.003	1.0 - 1.5	2.3	1.3
85	358.15	0.03	15	28	15
100	373.15	0.06	30	56	31

aCalculated by compilers.

# AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: Electrodeposition on a copper wire. (1) Mercury. (2) Water. Distilled. ESTIMATED ERROR: REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6]	Pariaud, J.; Archinard, P.
(2) Water; н <sub>2</sub> 0; [7732-18-5]	Bull. Soc. Chim. France <u>1952</u> , 454 - 6. J. Chim. Phys. <u>1956</u> , 53, 765 - 9.
VARIABLES:	PREPARED BY:
T/K = 301.15	S. H. Johnson M. Iwamoto H. L. Clever

		Mercury in <sup>a</sup> Solution	Mercury Solubility		
-	-		Concentration	Moleb	Molalityb
t/°C T/K <sup>D</sup>	t/days	10°c <sub>1</sub> /g dm <sup>-3</sup>	10 ° c 1 / mol dm - 3	Fraction 10°x1	10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
25 298.15	1 3 10	0 10, 15, 15 25, 20, 25			
28 301.15	18 24	30, 28 32, 30, 25 30 ± 10 <sup>c</sup>	1.5 + 0.5	2.7	1.5

<sup>&</sup>lt;sup>a</sup>All of the experimental values are given with an uncertainty of  $\pm 10$ .

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

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

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

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Electroanalytically pure.
- (2) Water. Triply distilled and degassed.

### ESTIMATED ERROR:

See uncertainty in table above.

bCalculated by compilers.

<sup>&</sup>lt;sup>C</sup>The solubility and its uncertainty given in the author's second paper.

### COMPONENTS: (1) Mercury; Hg; [7439-97-6] Mercury-203; 203Hg; [13982-78-0] (2) Hypophosphorus acid; H<sub>3</sub>PO<sub>2</sub>;

ORIGINAL MEASUREMENTS:

Moser, H. C.; Voigt, A. F.

J. Am. Chem. Soc. 1957, 79, 1837 - 9.

[6303-21-5]

(3) Nitric acid; HNO3; [7697-37-2] (4) Water; H<sub>2</sub>O; [7732-18-5]

### VARIABLES:

T/K = 298.15

### PREPARED BY:

S. H. Johnson

M. Iwamoto

H. L. Clever

### EXPERIMENTAL VALUES:

<b></b>			Mercury Solubility		
Temperature t/°C T/Ka	r <sub>3</sub> PO <sub>2</sub> c <sub>2</sub> /mol dm <sup>-3</sup>	HNO <sub>3</sub> c <sub>3</sub> /mol dm <sup>-2</sup>	Concentration  10'c <sub>1</sub> /mol dm <sup>-3</sup>	Fraction	Molality <sup>a</sup> 10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
25.0 298.15	0.1	0	3.0 ± 0.3	5.4	3.0
	0.01	0.01	$2.9 \pm 0.1$	5.2	2.9
	0.001	0.01	3.0 ± 0.1	5.4	3.0

<sup>&</sup>lt;sup>a</sup>Calculated by compilers.

The hypophosphorus acid,  ${\rm H_3PO}_2$ , and nitric acid,  ${\rm HNO}_3$ , were added to prevent oxidation of metallic mercury. The acids are assumed to be so dilute that they do not effect the solubility.

### ADDITIONAL DATA:

The authors used their solubility value along with literature values of the disproportionation of mercurous ion

 $Hg_{3}^{+}(aq) = Hg(1) + Hg^{2+}(aq)$ K = 0.0060 - 0.0120 (Literature) to estimate the disproportionation constant in aqueous solution of

Hg $3^+$  (aq) = Hg(aq) + Hg $2^+$  (aq) K = (1.9 - 3.6) x 10<sup>-3</sup>. The authors distribution study resulted in a slightly larger value of (5.3 - 5.6) x 10<sup>-3</sup>. No evidence of the dissociation of mercurous dimer, Hg $3^+$  (aq) = 2Hg $^+$ (aq), was found. It can be inferred that the dissociation K is < 1 x 10<sup>-7</sup>.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

The solubility of mercury in dilute aqueous acid solution was determined by shaking them with a drop of mercury of known specific activity.

The saturated solution was treated to obtain a precipitate of HgS which was deposited on a planchet and analyzed for mercury-203 with a thin window Geiger counter.

It was found necessary to add a small amount of hypophosphorus acid to prevent oxidation of metallic mercury by radiolysis.

More details may be found in (ref. 1).

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Oak Ridge National Lab. Obtained as a high specific activity solution of mercuric nitrate containing isotope 203.
- (2) Water. Distilled. Traces of hypophosphorus acid were added to prevent Hg oxidation by radiolysis.

### ESTIMATED ERROR:

$$\delta T/K = \pm 0.1$$

$$\delta c_1/c_1 = \pm 0.035$$

### REFERENCES:

Moser, H. C.; Voigt, A. F. USAEC Report <u>1957</u>, ISC-892.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6]	Choi, S. S.; Tuck, D. G.
(2) Water; H <sub>2</sub> O; [7732-18-5]	J. Chem. Soc. <u>1962</u> , 4080 - 8.
VARIABLES:	PREPARED BY:
T/K = 298.15 - 363.15	S. H. Johnson M. Iwamoto H. L. Clever

Temp	erature	Mercury Solubility				
t/°C	T/K	10 <sup>7</sup> w <sub>1</sub> /g g <sup>-1</sup>	Probable Error of Mean	Concentration <sup>a</sup> 10 <sup>7</sup> c <sub>1</sub> /mol dm <sup>-3</sup>		Molality <sup>a</sup> 10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
25	298.15	0.631	0.14	3.14	5.67	3.15
35	308.15	1.09	0.03	5.40	9.79	5.43
50	323.15	1.77	0.03	8.72	15.9	8.82
65	338.15	2.17	0.05	10.6	19.5	10.8
80	353.15	2.61	0.01	12.6	23.4	13.0
90	363.15	3.34	0.18	16.1	30.0	16.7

aCalculated by compilers.

The solubility values reported are mean values of two experiments (three at  $298.15~\mathrm{K}$ ) with duplicate samples taken in each experiment.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

A Neutron activation method was used. The method does not require other reagents in the solution such as H<sub>3</sub>PO<sub>2</sub>. The isotopes of mercury selected for analysis were <sup>1 \* 7</sup>mHg and <sup>1 \* 7</sup>Hg [13981-51-6].

Deoxygenated water and mercury were equilibrated 10 days without stirring to prevent suspended or colloidal Hg in the solution. Samples were taken and irradiated one week in a neutron source. Carrier Hg was added, the Hg reacted and precipitated as HgS for counting in a crystal spectrometer. The method can detect 2 x 10<sup>-9</sup> of Hg.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Johnson Matthey and Co. Spectroscopically pure, sodium impurity 1 ppm.
- (2) Water. Distilled three times, deoxygenated in an air free system.

### ESTIMATED ERROR:

See authors probable error on mean values in table above.

# COMPONENTS: (1) Mercury; Hg; [7439-97-6] (2) Water; H<sub>2</sub>O; [7732-18-5] VARIABLES: T/K = 298.15 ORIGINAL MEASUREMENTS: Kuntz, R. R.; Mains, G. J. J. Phys. Chem. 1964, 68, 408 - 10. PREPARED BY: S. H. Johnson M. Iwamoto H. L. Clever

### EXPERIMENTAL VALUES:

Temperature Mercury Solubility				
t/°C	<i>T</i> /K <sup>a</sup>	Concentration 10'c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>a</sup>	Molality <sup>a</sup> 10 <sup>7m</sup> 1/mol kg <sup>-1</sup>
25	298.15	1	1.8	1

aCalculated by compilers.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

spectrophotometric method. It was assumed that the optical density at 2560 A is a reliable measure of the solubility. It was further assumed that the extinction coefficient of mercury was the same in all hydrocarbon solvents. The optical density of a saturated solution of Hg in hexane was measured and, when combined with the solubility measured by Moser and Voigt (ref. 1), gives an extinction coefficient \$2.5 \cdot c. The value was used to calculate the solubility in the other solvents.

The Hg and solvent were equilibrated for 20 minutes and the optical density was measured by a Beckman DU Spectrophotometer.

The reliability of the results depends on the Moser and Voigt solubility value in hexane.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. No information given.
- (2) Water. No information given.

ESTIMATED ERROR:

### REFERENCES:

Moser, H. C.; Voigt, A. F. USAEC Report 1957, ISC-892, 65 pp.

### COMPONENTS: (1) Mercury; Hg; [7439-97-6]; Mercury-203; 20 Hg; [13982-78-0] (2) Water; H<sub>2</sub>O; [7732-18-5] VARIABLES: ORIGINAL MEASUREMENTS: Spencer, J. N.; Voigt, A. F. J. Phys. Chem. 1968, 72, 464 - 470. Spencer, J. N. Dissertation, Iowa State University, 1967. PREPARED BY: S. H. Johnson

M. Iwamoto H. L. Clever

### EXPERIMENTAL VALUES:

T/K = 273.15 - 308.15

Temperature		Mercury Solubility						
t/°C	T/K <sup>a</sup>	Concentration 10'c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>a</sup>	Molality <sup>a</sup> 10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>				
0	273.15	$1.2 \pm 0.2$	2.2	1.2				
15.5	288.65	$2.1 \pm 0.1$	3.8	2.1				
20	293.15	2.4 ± 0.2	4.3	2.4				
25	298.15	2.8 ± 0.1	5.1	2.8				
30	303.15	$2.9 \pm 0.1$	5.2	2.9				
35	308.15	3.4 ± 0.1	6.2	3.4				

aCalculated by compilers.

The authors smoothed their data according to the equation:  $\log x_1 = (8.600 \pm .575)\log(T/K) - 29.597$  for the 273.15 to 308.15 temperature interval.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

A radioactive tracer method was used. A high activity sample of mercury-203 nitrate was added to mercury(II) nitrate, reduced to metallic mercury by hypophosphorous acid, coagulated into a drop, washed and dried.

The mercury and solvent were shaken continuously in 25 ml glass stoppered flasks in a thermostat for 24 hours. Aliquots of the equilibrated solution were counted by a conventional single channel scintilation counter. The window width was set to count only the photopeak at 279 kev. The solubility values were the average of at least six determinations over a three day period.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury and Mercury-203. The isotope decays by emission of a beta particle at an energy of 210 kev, accompanied by a gamma ray of 279 kev. The isotope half-life is 47 days.
- (2) Water. Doubly distilled from alkaline permanganate solution.

### ESTIMATED ERROR:

 $\delta T/K = \pm 0.1$ ; See random error reported by authors with concentration values above.

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

### ORIGINAL MEASUREMENTS:

Glew, D. N.; Hames, D. A.

Can. J. Chem. 1971, 49, 3114 - 8.

EXPERTMENTA	T 1	7 A	T 11	DC.	
EXPERIMENTA	ь١	/ A	யப	LO.	ï

Temper	ature		ercury Solubility		Reducing
t/°C	<i>T</i> /K <sup>a</sup>	Concentration <sup>a</sup> 10 <sup>7</sup> c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction 10°x <sub>1</sub>	Molality <sup>a</sup> 10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>	Agent <sup>b</sup>
4.30 4.30	277.45 277.45	2.33 2.21	4.19 3.99	2.33 2.21	iv iv
11.41 11.41 11.41	284.56 284.56 284.56	2.37 2.31 2.22	4.28 4.17 4.01	2.38 2.31 2.23	ii ii ii
14.97	288.12	2.14	3.86	2.14	i
19.80 19.80	292.95 292.95	2.39 2.49	4.31 4.49	2.39 2.49	i
25.02	298.17	2.98	5.39	2.99	iv
30.02	303.17	3.58	6.47	3.59	iii
30.09 30.09	303.24 303.24	3.43 3.48	6.20 6.29	3.44 3.49	i
39.16	312.31	4.35	7.90	4.39	i
45.07 45.07	318.22 318.22	4.58 4.40	8.33 8.01	4.62 4.45	ii ii
49.80	322.95	5.42	9.88	5.48	i
50.24 50.24 50.24	323.39 323.39 323.39	4.51 5.32 4.85	8.22 9.70 8.85	4.56 5.38 4.91	i i i
53.71	326.86	5.31	9.70	5.38	ii
59.98 59.98	333.13 333.13	6.77 6.06	12.4 11.1	6.88 6.16	i i
62.28	335.43	7.25	13.3	7.38	ii
68.19 68.19	341.34 341.34	8.75 8.31	16.1 15.3	8.94 8.49	i i
72.44	345.59	9.48	17.5	9.71	ii

<sup>a</sup>Calculated by compilers.

The authors fit the data above by the method of least squares to obtain the equation:

 $\log x_1 = -122.811 + 4475.3/(T/K) + 40.2205 \log(T/K)$ 

The estimated standard error on a single measurement is 7.5 percent.

bi sodium sulfite

ii hydrazine hydrate

iii sodium borohydrate

iv none

and

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

### ORIGINAL MEASUREMENTS:

Glew, D. N.; Hames, D. A.

Can. J. Chem. 1971, 49, 3114 - 8.

### ADDITIONAL INFORMATION:

Author's smoothed data: Solubility of mercury in water.

The experimental solubility values of Glew and Hames between 4° and 72° (preceeding page), the value of Bonhoeffer and Reichart (ref. 1) at 120°C, the value of Stock et al. (ref. 2) at 85°C, the value of Moser and Voigt (ref. 3) at 25°C, and the values of Choi and Tuck (ref. 4) at 25°, 80° and 90°C were combined to obtain the equation and the smoothed values below. The Henry's constant,  $H/\text{atm} = (p_1/\text{atm})/x_1$ , were obtained from the same experimental solubility values and mercury vapor pressures from the equation of Douglas, Ball and Ginnings (ref. 5).

Temper	ature	Mole Fraction	Standard Deviation	Henry's Constant	Standard Deviation
t/°C	T/K	10°x <sub>1</sub>	σ	$H/atm = (p_1/atm)/x_1$	σ
0.0	273.2	3.73	0.14	70	3
5.0	278.2	3.91	0.11	109	3
10.0	283.2	4.15	0.10	165	4
15.0	288.2	4.46	0.08	242	5
20.0	293.2	4.83	0.08	346	6
25.0	298.2	5.28	0.08	482	3 4 5 6 7
30.0	303.2	5.83	0.08	658	10
35.0	308.2	6.48	0.10	878	13
40.0	313.2	7.27	0.11	1150	18
45.0	318.2	8.20	0.13	1470	23
50.0	323.2	9.31	0.15	1860	30
55.0	328.2	10.6	0.17	2300	38
60.0	333.2	12.2	0.20	2800	46
65.0	338.2	14.1	0.23	3370	56
70.0	343.2	16.4	0.28	3980	69
75.0	348.2	19.1	0.35	4640	85
80.0	353.2	22.4	0.44	5350	110
85.0	358.2	26.3	0.58	6080	140
90.0	363.2	31.0	0.78	6840	170
100.0	373.2	43.6	1.5	8360	280
110.0	383.2	62.1	2.7	9810	430
120.0	393.2	89.1	5.0	11100	630

Linear regression resulted in the equations for 0° to 120°C:

 $\log x_1 = -128.089 + 4715.2/(T/K) + 42.0288 \log(T/K)$ 

log(H/atm) = 135.636 - 8031.1/(T/K) - 42.8448 log(T/K).

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

### ORIGINAL MEASUREMENTS:

Glew, D. N.; Hames, D. A.

Can. J. Chem. 1971, 49, 3114 - 8.

### VARIABLES:

T/K = 277.45 - 345.59

### PREPARED BY:

- S. H. Johnson
- M. Iwamoto H. L. Clever

### EXPERIMENTAL VALUES:

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

About 300 cm<sup>3</sup> of water was distilled directly into a special solubility cell, then about 30 g of mercury was vacuum distilled into the cell. Atmospheric pressure was restored with helium. Reducing agent (see table) (0.001 M) was added to prevent oxidation of mercury by any The cell contents residual oxygen. were stirred continuously for up to a day and the temperature set to the operating level.

The stirrer was stopped two hours before sampling. A helium pressure 15 mmHg above atmospheric pressure was used to express a 10 - 20 g sample of saturated solution into a weighed flask containing 1 ml 4 percent  $KMnO_4$  and 1 ml 20 percent  $H_2SO_4$ . The flask was reweighed and the sample immediately analyzed for mercury by an atomic absorption Solubilities were apmethod. proached from both above and below saturation.

Further details are in the paper and in the authors later paper on mercury + sodium chloride + water (ref. 6).

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Technical electrolytic grade, washed with 10% NaOH in an air stream, washed with 5% HNO3, filtered through gold foil, rewashed with fresh 5% HNO3 and distilled three times.
- Distilled, degassed and (2) Water. purged several times with nitrogen at atmospheric pressure. Distilled under vacuum directly into the solubility vessel.

### **ESTIMATED ERROR:**

 $\delta T/K = \pm 0.01$ 

 $\delta x_1/x_1 = \pm 0.075$  Standared error of a single measurement (authors).

- Bonhoeffer, K. F.; Reichert, H. Z. Phys. <u>1931</u>, 67, 780.
- Stock, A.; Cucuel, F.; Gerstner, F.; Kohle, H.; Lux, H. Z. Anorg. Chem. 1934, 217, 241.
- Moser, H. C.; Voigt, A. F. J. Am. Chem. Soc. 1957, 79, 1837.
- 4. Choi, S. S.; Tuck, D. G. J. Chem. Soc. 1962, 4080.
- 5. Douglas, T. E Ginnings, D. C. B.; Ball, A. F.; J. Res. N. B. S. 1951, 46, 334.
- 6. Glew, D. N.; Hames, D. A. Can. J. Chem. 1972, 50, 3124 -

### ORIGINAL MEASUREMENTS: COMPONENTS: Sorokin, V. I. (1) Mercury; Hg; [7439-97-6] Dolk. Akad. Nauk SSSR 1973, (2) Water; H<sub>2</sub>O; [7732-18-5] 213(4), 852 - 5. \*Dok1. Chem. (Engl. Transl.) <u>1973</u>, 213, 905 - 8. VARIABLES: PREPARED BY: T/K = 571.15 - 780.15H. L. Clever

p/MPa = 40.5 - 100.3

M. Iwamoto

### EXPERIMENTAL VALUES:

Tempe	rature	Pressure	Equilibration	Mercury Solubility				
t/°C	T/K	p/atm	Time t/h	m <sub>1</sub> /g kg <sup>-1</sup>	Molality <sup>a</sup> m <sub>1</sub> /mol kg <sup>-1</sup>	Mole Fraction 10 3 x 1		
300 300 298	573.15 573.15 571.15	500 640 900	48 72 138	0.29 0.24 0.19	0.0014 0.0012 0.0009	0.0260 0.0216 0.0171		
400 400 400 400 400 398 401	673.15 673.15 673.15 673.15 673.15 671.15	400 500 495 700 700 920 910	24 24 24 24 48 24 48	3.37 2.76 3.22 2.47 2.80 2.23 2.13	0.0168 0.0138 0.0161 0.0123 0.0140 0.0111	0.302 0.248 0.289 0.222 0.251 0.200 0.191		
500 502 500 495 507 498 503	773.15 775.15 773.15 768.15 780.15 771.15 776.15	500 510 520 755 700 990 960	24 28 24 48 24 24 25	24.12 23.71 20.21 18.45 19.90 16.36 13.41	0.1202 0.1182 0.1008 0.0920 0.0992 0.0816 0.0667	2.16 2.12 1.81 1.65 1.78 1.47		

aCalculated by compiler.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

The 50 cm<sup>2</sup> reaction vessel and the 5 cm3 sample collector were constructed of VT-8 titanium alloy. solution was stirred by a magnetic stirrer. The apparatus was designed so that there was no change in temperature or pressure during sampling. Neither gas liberation from the sample nor the appearance of oxidized Hg or titanium were observed in the course of the work.

Three analytical methods were used with parallel samples:

- amalgamation with a gold cap, colorimetric titration with (i) (ii)
- dithizone, and (iii) volumetric titration with ammonium thiocyanate.

The author does not state what gas was used to pressure the system. It was probably argon.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Doubly distilled.
- (2) Water. Doubly distilled. Freed of dissolved gases by boiling and subsequent purging with pure argon. The pH of the water was 6.50 before and after the experiment.

ESTIMATED ERROR	E	SI	'II	'AA	ΤE	D	E	R	R	0	R	
-----------------	---	----	-----	-----	----	---	---	---	---	---	---	--

- (1) Mercury; Hg; [7439-97-6]
- (2) Water; H<sub>2</sub>O; [7732-18-5]

### ORIGINAL MEASUREMENTS:

Onat, E.

J. Inorg. Nucl. Chem. 1974, 36, 2029 - 32.

### VARIABLES:

T/K = 298.15 - 353.25

### PREPARED BY:

H. L. Clever

M. Iwamoto

### EXPERIMENTAL VALUES:

Tempe	 rature	No. of	Concentr	ation <sup>a</sup>	Avg.% Dev.	Mole Fraction <sup>b</sup>	Molalityb
t/°C	T/K	Detns.	10° c / mo.	1 dm -3	from	10°x <sub>1</sub>	10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
25	298.15	5	3.05	3.09	3.3	5.51	3.06
40	313.15	4	5.12	5.19	1.9	9.30	5.16
50	323.15	3	7.43	7.47	4.0	13.5	7.52
60	333.15	3	10.78	10.87	3.0	19.8	11.0
70	343.15	4	13.33	13.37	3.0	24.6	13.6
80	353.15	4	16.37	16.40	0.6	30.3	16.8

aThe two concentration values represent two ways of converting the experimental absorbance of Hg3 at 236.5 mm into a solubility value. The average values to the left are from the calibration curve. The average values to the right were calculated from Beer's law using the molar absorption of 2.8 x 10 (ref. 1).

The mole fraction and molality solubility values were calculated from the concentration in the left hand column.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

450 ml of water and 10 g of mercury were equilibrated with stirring for 24 hours in a thermostat. The system was oxygen free.

Duplicate 100 ml samples were taken and transferred to flasks containing 5 ml 0.001 M Hg(ClO)<sub>4</sub> and 0.837 g concentrated HClO<sub>4</sub>. The flask contents were shaken continuously, made oxygen free by bubbling N<sub>2</sub>, and brought to 25°C in a thermostat. The solution was left in the thermostat over night. The solution was analyzed for soluble Hg by measuring the absorbance of Hg<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> at 2 nm intervals over the 212 to 256 nm interval in a 10 cm cell on a Beckman DU spectrophotometer. The absorbance was compared with a calibration curve to obtain the Hg<sub>2</sub>\* concentration which was taken to be one-half the Hg concentration resulting from the reaction

ting from the reaction

Hg<sup>2+</sup>(aq) + Hg(aq) = Hg<sup>2+</sup>(aq),

which was complete under the analysis conditions.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Reagent grade. Purified chemically (ref. 2). Redistilled under reduced pressure.
- (2) Water. Triply distilled.

### ESTIMATED ERROR:

 $\delta T/K$  No information. See % average deviation from mean above.

- Higginson, W. C. E.
   Chem. Soc. <u>1951</u>, 1438.
- Palmer, W. G.
   Experimental Physical Chemistry,
   C. U. P., Cambridge, 1949, p. 203.

bCalculated by compilers.

# COMPONENTS: (1) Mercury; Hg; [7439-97-6] (2) Water; H<sub>2</sub>O; [7732-18-5] VARIABLES: T/K = 278.15 - 333.15 ORIGINAL MEASUREMENTS: Sanemasa, I. Bull. Chem. Soc. Jpn. 1975, 48, 1795 - 8. PREPARED BY: S. H. Johnson H. L. Clever

M. Iwamoto

### EXPERIMENTAL VALUES:

Temperature  t/°C T/K		Henry's	1	Mercury Solubility				
		constant	Concentration	Mole Fraction <sup>a</sup>	Molality <sup>a</sup> 10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>			
		K/atm	10°c <sub>1</sub> /g dm <sup>-3</sup>	10 * x 1				
5	278.15	233	19.2	1.72	0.957			
10	283.15	262	27.4	2.46	1.37			
20	293.15	391	45.0	4.04	2.25			
30	303.15	500	81.3	7.33	4.07			
40	313.15	650	137	12.4	6.88			
50	323.15	852	218	19.8	11.0			
60	333.15	1010	368	33.6	18.7			

aCalculated by compilers.

Values in the paper above 333.15K were extrapolated by the author.

Henry's constant:

 $\ln (K/atm) = \ln ((P_1/atm)/x_1)$ = -1078/(T/K) + 6.250

The enthalpy of solution:

 $\Delta H/\text{kcal mol}^{-1} = 5.3$ 

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

The solubility apparatus is a closed system which consists of several flasks connected by tubing. A 20 g portion of Hg is placed in one flask immersed in thermostat I, and up to 200 ml of water are placed in a second flask immersed in thermostat II. The Hg vapor pressure is controlled by the temperature of thermostat I. Nitrogen gas at atm pressure is circulated by the pump. The gas passes over the Hg and bubbles through the water (or solution). One hour circulation saturates both the gas space and water.

The Hg is determined by cold-vapor atomic absorption. The method is based on a reduction-aeration method found by Kimura and Miller (ref. 1). The procedure used is similar to that reported by Omang (ref. 2). The sample and working standard are put through the same procedure. Analyses are done in triplicate. Measurements were made at up to six Hg pressures at each temperature.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Metallic mercury purified by distillation under reduced pressure.
- (2) Water. Redistilled water. Both aerated and deoxygenated water were used with no difference.

ESTIMATED ERROR:

 $\delta T/K = \pm 0.05$ 

- Kimura, Y.; Miller, V. L. Anal. Chim. Acta <u>1962</u>, 27, 325.
- Omang, S. H.
   Anal. Chim. Acta 1971, 53, 415.

# COMPONENTS: (1) Mercury; Hg; [7439-97-6] (2) Water; H<sub>2</sub>O; [7732-18-5] VARIABLES: T/K = 378.15 - 475.15 P<sub>t</sub>/MPa = 1.6 - 102.3 CRIGINAL MEASUREMENTS: Sorokin, V. I.; Alekhin, Yu. V.; Dadze, T. P. Ocherki Fiz.-Khim. Petrol. 1978, 8, 133 - 49. PREPARED BY: H. L. Clever

Temperature Total Pressure		M	ercury Solubilit	у		
t/°C	<i>T</i> /K	<i>P<sub>t</sub></i> /atm	<i>P<sub>t</sub></i> /MPa	Weight 10 <sup>2</sup> w <sub>1</sub> /g kg <sup>-1</sup>	Molality 10 <sup>5</sup> m <sub>1</sub> /mol kg <sup>-1</sup>	Mole Fraction <sup>a</sup>
105	378.15	1000	101.3	0.0460	0.229	0.402
200	473.15	16	1.6	5.17	25.8	46.5
200	473.15	530	53.7	2.44	12.2	22.0
202	475.15	1010	102.3	1.22	6.08	11.0

<sup>&</sup>lt;sup>a</sup>Calculated by compiler.

AUXILIARY	INFORMATION
ÆTHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
These are assumed to be similar to that described in the authors earlier work (ref. 1).	
	ESTIMATED ERROR:
	REFERENCES:  1. Sorokin, V. I.  Dokt. Akad. Nauk SSSR 1973, 213(4), 852 - 5.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6] (2) Water; H <sub>2</sub> O; [7732-18-5]	Kawakara, H.; Nakamura, M.; Ishizaki, N.; Yamada, T.; Kawamoto, T.; Hikari, S.; Sogawa, K.; Maehara, S. Shika Rikogaku Zasshi 1979, 20, 137 - 41.
VARIABLES: T/K = 310.15 pH = 7.2 ± 0.1	PREPARED BY: H. L. Clever

Shaking Time	Mercury <sup>a</sup>								
t/days	ppmb	Concentration	Mole Fraction	Molality					
		10 7 c 1 / mol dm - 3	10 * x <sub>1</sub>	10 7 m 1 / mol kg - 1					
1	0.020 <u>≤</u> 0.045 <u>≤</u> 0.070	2.2 <u>+</u> 1.0							
3	0.025 <u>≤</u> 0.060 <u>≤</u> 0.096	3.0 <u>+</u> 1.4							
5	0.078 ≤ 0.086 ≤ 0.090	4.2 ± 0.2							
5	$0.078 \le 0.087 \le 0.095$	$4.3 \pm 0.3$							
5	$0.070 \le 0.095 \le 0.120$	$4.7 \pm 1.0$							
		4.4 ± 0.7°	8.0	4.4					

 $<sup>^{\</sup>mathbf{a}}$ The compiler assumes that the five day shaking time represents solubility equilibrium.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

Metallic mercury (0.3 g) and 25 ml of water solution were placed in an Erlenmeyer flask. The rubber stoppered flask was rotated 1 to 5 days in a thermostat at 37°C.

The aqueous phase was sampled. Acidified  $(\mathrm{H}_2\mathrm{SO}_4)$  potassium permanganate solution was added. The sample was wet ashed and the mercury reduced by air and vaporized as described in ref. 1.

The mercury was determined by flameless atomic absorption spectro-photometry using a mercury analyzer (JEOL AA-HG 01) and an atomic absorption spectrophotometer (JEOL JAA-7000).

Three determinations were performed on each sample.

The solubility was pH dependent. Much larger solubility values were obtained in the pH 2 - 3 and pH 10 - 11 ranges. All reported solubility values are for solutions at pH 7.2 ± 0.1. There was no mention of exclusion of oxygen from the samples.

### SOURCE AND PURITY OF MATERIALS:

No information was given on the source and purity of materials.

### ESTIMATED ERROR:

 $\delta c_{7}/\text{ppm}$  See ranges in table above.  $\delta T/K$  Not given.

### REFERENCES:

 Kimura, Y.; Miller, V. L. Anal. Chim. Acta <u>1962</u>, 27, 325.

bThe compiler calculated the concentration of mercury assuming that ppm means grams of mercury in 1 x 10 cm of solution.

<sup>&</sup>lt;sup>C</sup>The average is from the five days of shaking time.

COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Mercury; Hg; [7439-97-6] (2) Water; H <sub>2</sub> O; [7732-18-5]	Baltisberger, R. J.; Hildebrand, D. A.; Grieble, D.; Ballintine, T. A.		
	Anal. Chim. Acta <u>1979</u> , 111, 111 - 2.		
VARIABLES:	PREPARED BY:		
T/K = 303.15	H. L. Clever M. Iwamoto		

Tempe	rature	ure Mercury Solubility			
t/°C	T/K	ppb <sup>a</sup>	Concentration <sup>b</sup> 10 <sup>7</sup> c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction <sup>b</sup> 10°x <sub>7</sub>	Molality <sup>b</sup> 10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
30	303.15	63 <u>+</u> 2 <sup>C</sup>	3.1 <sub>4</sub> ± 0.10	5.68	3.15

a ppb = parts per billion

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

The solutions were sparged with nitrogen gas for 45 minutes, a drop of mercury was added, and then the mixture sparged another 30 minutes with nitrogen. Solutions were stirred for 24 hours with a glass-covered stirring bar. Samples of solution were withdrawn by syringe with a maintained nitrogen flow to prevent oxygen diffusion into the solutions.

An aliquot of the saturated solution was transferred to a non-reducing cell. The mercury was collected by nitrogen sparging and analyzed by cold vapor atomic absorption.

The non-reducing cell was a cell that had never contacted reducing agents.

Hg + H<sub>2</sub>O was quite prone to oxidation. The presence of Cl prevented the disproportionation of any Hg(I).

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Prepared by distillation from mercury(II) oxide under a N<sub>2</sub> atmoshpere.
- (2) Water. Triple distilled.

### ESTIMATED ERROR:

See standard deviation of solubility in water above.

 $<sup>^{\</sup>rm b}$  Calculated by the compiler. The concentration was calculated assuming grams of mercury per 1 x 10  $^{\rm s}$  cm  $^{\rm s}$  of solution.

 $<sup>^{\</sup>mathbf{c}}$  Standard deviation of ten analyses.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6] (2) Water; H <sub>2</sub> O; [7732-18-5]	Okouchi, S.; Sasaki, S.  Bull. Chem. Soc. Jpn. 1981, 54, 2513 - 4.  Report of the College of Engineering of Hosei University 1983, (No. 22), 55 - 106.
VARIABLES:	PREPARED BY:
T/K = 278.15 - 313.15	H. L. Clever M. Iwamoto

Temperature		Mercury Solubility				
		Concentration <sup>a</sup> 10'c <sub>1</sub> /mol dm <sup>-3</sup>	Mole Fraction 10°x <sub>1</sub>	Molality <sup>a</sup> 10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>		
5	278.15	2.2	3.9	2.2		
10	283.15	2.3	4.2	2.3		
20	293.15	2.7	4.8	2.7		
25	298.15	3.0	5.4	3.0		
30	303.15	3.2	5.8	3.2		
40	313.15	4.1	7.4	4.1		

aCalculated by compilers.

Dr. S. Okouchi kindly provided the experimental mole fraction solubility values which did not appear in the original papers.

The authors fitted the data to the following equation:

 $\log x_1 = -147.56 + 5581.3/(T/K) + 48.723\log(T/K)$ 

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

Solubility experiments were conducted by shaking the solvent with a drop of mercury for 24 hours in a thermostat. Separate experiments showed the mercury concentration remained constant after 24 hours of shaking.

A 0.5 cm³ sample of the equilibrated solution was analyzed by the cold-vapor atomic absorption method. Steps in the procedure included tin(II) chloride reduction, nitrogen bubbling and passage through magnesium perchlorate to dry the Hg vapor.

The mercury was determined from the area under the atomic absorption peak at 253.7 nm compared to a calibration curve.

In experiments with water, phosphinic acid (0.001 mol) was added to prevent mercury oxidation. Water-hydrocarbon distribution constants of Hg were also directly determined.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Purified as did Glew and Hames (ref. 1).
- (2) Water. Distilled, containing 0.001 mol/dm<sup>-3</sup> of phosphinic acid to prevent mercury oxidation.

### ESTIMATED ERROR:

 $\delta T/K = \pm 0.1$  $\delta x_1/x_1 = \pm (0.03 - 0.05)$  (compilers)

### REFERENCES:

Glew, D. N.; Hames, D. A.
 Can. J. Chem. 1971, 49, 3114.

## COMPONENTS: (1) Mercury; Hg; [7439-97-6] (2) Water; H<sub>2</sub>O; [7732-18-5] Variables: T/K Not given, assumed to be room temperature. ORIGINAL MEASUREMENTS: Gjessing, E. T.; Rogne, A. K. G. Vatten 1982, 38, 406 - 8.

### EXPERIMENTAL VALUES:

Temperature	Mercury Solubility			
	Concentration		Mole Fraction	Molality
	10°c <sub>1</sub> /g dm -3	10 ° c 1 / mol dm - 3	10°x <sub>1</sub>	10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
"Room"	7	0.35	0.63	0.35
	9	0.45	0.81	0.45
	13 <sup>b</sup>	0.65	1.2	0.65

- <sup>a</sup> All mercury solubility values calculated by the compiler except values in the left column. The authors labelled the values in the left column as micrograms per liter.
- b The first two values were measured in distilled water. The third value was measured in an artificial "surface water" without organic material. It contained 5.62 mg dm<sup>-3</sup> NaHCO<sub>3</sub>, 1.18 mg dm<sup>-3</sup> MgCO<sub>3</sub>, 7.17 mg dm<sup>-3</sup> CaSO<sub>4</sub>, and 10.96 mg dm<sup>-3</sup> CaCl<sub>2</sub>. The total ionic strength is 6.3 x 10<sup>-2</sup>.

These measurements appear to give solubility data that are too small. In addition the mercury solubility is greater in the electrolyte solution indicating salting in which is not normal behavior.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

The experiment was performed by adding five drops of mercury from a polarographic analyzer to a 500 cm³ sample of water. The samples were placed on a shaking table for 19 hours. The supernatant liquid was analyzed for mercury atomic absorption spectrophotometry (Perkin Elmer 460).

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Source not given. Stated to be pure mercury.
- (2) Water. Distilled.

ESTIMATED ERROR:

# COMPONENTS: (1) Mercury; Hg; [7439-97-6] Mercury-203; 20 3 Hg; [13982-78-0] (2) Water; H<sub>2</sub>O; [7732-18-5] VARIABLES: T/K = 295, 298 ORIGINAL MEASUREMENTS: Hursh, J. B. JAT, J. Appl. Toxicol. 1985, 5, 327 - 32. PREPARED BY: H. L. Clever

### EXPERIMENTAL VALUES:

1							
	Tempe	erature	Carrier Gas	Ostwald Coefficient <sup>a</sup>	Mercury Solubil Vapor		
l	t/°C	<i>T</i> /K		L	Vapor, 10 <sup>7</sup> c <sub>1</sub> /mol dm <sup>-3b</sup>	10°x <sub>1</sub>	10 <sup>7</sup> m <sub>1</sub> /mol kg <sup>-1</sup>
l	22	295.15	-	(3.05) <sup>C</sup>	2.47	4.49	2.48
	25	298.15	N <sub>2</sub>	2.79 ± 0.03(4)	2.88	5.21	2.89

- <sup>a</sup> The Ostwald coefficient is ((ng Hg/mL fluid)/(ng Hg/mL gas)). Given above is the average  $\pm$  standard error (number of determinations).
- b The concentrations were calculated by the compiler for mercury vapor in equilibrium with pure liquid mercury from the vapor pressure evaluation of Ambrose and Sprake (ref. 1). The mercury vapor pressure and vapor concentration used at each temperature are:

T/K		295	298
p%/Pa		19.90	25.62
c9/(ng	Hg/mL gas)	16.27	20.73

The Ostwald coefficient in () is not an experimental value. It is an extrapolated value from measurements of the mercury solubility in the water + hemoglobin system. See that data sheet for more details. Ostwald coefficients estimated from data in the mercury + water evaluation by the compiler are 3.22 and 2.75 for 295 and 298 K, respectively.

### AUXILIARY INFORMATION

### METHOD/APPARATUS/PROCEDURE:

The equilibrium cell is a 50 mL syringe thermostated in a Dewar flask. A 10 mL liquid sample and a 40 mL carrier gas with Hg vapor sample are drawn into the cell. The cell is turned and rolled on the cylinder axis for 120 to 300 sec. Equilibrium is rapidly attained through the large contact area between liquid and vapor phases. Both the liquid and vapor phases are sampled. The liquid phase is aerated and the Hg adsorbed on Hopcalite. The Hg radioactivity is measured on a liquid scintillation counter. Corrections are applied for the counter efficiency, and for radioactive decay of the Hg.

Nitrogen carrier gas was used to prevent oxidation of mercury during the experiment.

### SOURCE AND PURITY OF MATERIALS:

- (1) Mercury. Prepared by reduction of 202 HgCl<sub>2</sub>. The Hg vapor is swept into a leak-proof Saran bag.
- (2) Water. Deionized and double distilled.

ESTIMATED ERROR:

### REFERENCES:

 Ambrose, D.; Sprake, C. H. S. J. Chem. Thermodynam. <u>1972</u>, 4, 603.