COMPONENTS:	EVALUATOR:
(1) Mercury; Hg; [7439-97-6] (2) Halocarbons	H. Lawrence Clever Chemistry Department Emory University Atlanta, Georgia 30322 USA 1985, August

CRITICAL EVALUATION:

An Evaluation of the Solubility of Mercury in Halocarbons.

The solubility of mercury in four halocarbons is reported in five papers. Three of the papers are from the laboratory of Professor A. F. Voigt of Iowa State University. A fourth paper referenced their data to a solubility value from one of the Voigt papers. Thus, the data are not as independent as one would like for a good evaluation. The halocarbons include one cyclic perfluoronated compound, tetrachloromethane, and two monohalo benzenes. Each system is discussed briefly below.

Mercury + Hexafluorobis(trifluoromethyl)cyclobutane; C_6F_{12}; [28677-00-1]

Kuntz and Mains (ref. 3) report one solubility value at 298.15 K and Spencer and Voigt (ref. 4) report five solubility values between 273.15 and 298.15 K. At 298.15 K the Kuntz and Mains value is 10 percent smaller than the Spencer and Voigt value. Considering the difference in methods, the difficulty of the measurement, and possible differences in the isomer composition, the agreement is considered satisfactory. The tentative values for all of the data were treated by a linear regression in the solubility units of concentration, mole fraction and molality. The regression constants are in Table 1 and the smoothed data and thermodynamic changes are in Table 2. The solvent is a mixture of at least two isomers. The four possible isomers are *cis*- and *trans*-perfluoro-1,2-dimethylcyclobutane and *cis*- and *trans*-perfluoro-1,3-dimethylcyclobutane (ref. 6).

Table 1. Mercury + Hexafluorobis(trifluoromethyl)cyclobutane. Linear regression constants for the equation $\ln(\text{soly}) = A(1) + A(2)/(T/100\ \text{K})$.

Solubility	A(1) ± Error	A(2) ± Error	Std. Error about the Regression Line
c_1/mol dm^{-3}	9.4968 ± 1.2713	-72.3371 ± 3.6912	2.8×10^{-8}
x_1	8.0555 ± 1.2545	-73.1675 ± 3.6422	5.0×10^{-8}
m_1/mol kg^{-1}	11.0061 ± 1.4985	-78.3298 ± 4.3509	2.0×10^{-8}

Table 2. The solubility of mercury in hexafluorobis(trifluoromethyl)-cyclobutane. Tentative values of the solubility in concentration, mole fraction and molality as a function of temperature at 0.1 MPa and thermodynamic changes.

Temperature		Mercury Solubility		
		Concentration	Mole Fraction	Molality
t/°C	T/K	$10^7 c_1$/mol dm^{-3}	$10^8 x_1$	$10^7 m_1$/mol kg^{-1}
0	273.15	0.42	0.73	0.21
5	278.15	0.68	1.2	0.35
10	283.15	1.08	1.9	0.58
15	288.15	1.7	3.0	0.94
20	293.15	2.6	4.6	1.5
25	298.15	3.9	6.9	2.3
ΔH_1[a]		60.1 ± 3.1	60.8 ± 3.0	65.1 ± 3.6
ΔS_1[b]		79.0 ± 10.6	67.0 ± 10.4	91.5 ± 12.5

[a] units kJ mol^{-1}
[b] units J K^{-1} mol^{-1}

Mercury + Tetrachloromethane; CCl_4; [56-23-5]

Three papers report mercury solubility values in tetrachloromethane at 298.15 K. Moser and Voigt (ref. 1) and Klehr and Voigt (ref. 2) both used a radioactive tracer method. Klehr and Voigt also obtained the same value by a distribution method. Vogel and Gjaldbaek (ref. 5) used an atomic absorption spectroscopy method and found a solubility that increased with time.

The results are below.

T/K	Saturation Time, t/days	Concentration $10^6 c_1$/mol dm^{-3}	Mole Fraction $10^7 x_1$	Molality $10^6 m_1$/mol kg^{-1}	ref.
298.15	3+	7.5 ± 0.3	7.3	4.7	1
	up to 10	7.5 ± 0.1	7.3	4.7	2
	2	9	9	6	5
	9	30	29	19	5

Both Moser and Voigt (ref. 1) and Klehr and Voigt (ref. 2) treated the tetrachloromethane with aqueous bisulfite solution to remove any traces of chlorine, then dried and distilled the solvent. Vogel and Gjaldbaek (ref. 5) apparently used no purification procedure. Vogel and Gjaldbaek point out a slow reaction between mercury and tetrachloromethane is known at 670 K; however, the purification of the tetrachloromethane appears important. The possibility of reaction of mercury and tetrachloromethane is important, but until the reaction is better characterized the data from the Voigt laboratory is classed as tentative.

Mercury + Bromobenzene; C_6H_5Br; [108-86-1]

Klehr and Voigt (ref. 2) measured the solubility by a radioactive tracer technique at 298.15 K. The value is classed as tentative and is given below in units of concentration, mole fraction and molality.

Temperature		Mercury Solubility		
		Concentration	Mole Fraction	Molality
t/°C	T/K	$10^6 c_1$/mol dm^{-3}	$10^7 x_1$	$10^6 m_1$/mol kg^{-1}
25	298.15	16.0 ± 0.3	16.9	10.8

COMPONENTS:	EVALUATOR:
(1) Mercury; Hg; [7439-97-6] (2) Halocarbons	H. Lawrence Clever Chemistry Department Emory University Atlanta, Georgia 30322 USA 1985, August

CRITICAL EVALUATION:

Mercury + Chlorobenzene; C_6H_5Cl; [108-90-7]

Klehr and Voigt (ref. 2) measured the solubility of free mercury in chlorobenzene as a function of temperature from 273.15 to 308.15 K. Their data are classed as tentative. The data were treated by a linear regression in each of the solubility units of concentration, mole fraction, and molality. the reqresion constants are in Table 3 and the smooth solubility values at five degree intervals are in Table 4.

Table 3. Mercury + Chlorobenzene. Linear regression constants for the equation ln(soly) = A(1) + A(2)/(*T*/100 K).

Solubility	A(1) ± Error	A(2) ± Error	Std. Error about the Regression Line
c_1/mol dm^{-3}	4.4111 ± 0.5013	-47.0116 ± 1.4539	5.0 x 10^{-7}
x_1	2.3982 ± 0.5378	-47.8134 ± 1.5596	5.3 x 10^{-8}
m_1/mol kg^{-1}	4.5404 ± 0.5160	-47.6801 ± 1.4966	4.7 x 10^{-7}

Table 4. Solubility of mercury in chlorobenzene. Tentative values of the solubility in concentration, mole fraction, and molality as a function of temperature at 0.1 MPa and thermodyanmic changes.

Temperature		Mercury Solubility		
		Concentration	Mole Fraction	Molality
t/°C	*T*/K	10$^6 c_1$/mol dm^{-3}	10$^7 x_1$	10$^6 m_1$/mol kg^{-1}
0	273.15	2.8	2.8	2.5
5	278.15	3.8	3.8	3.4
10	283.15	5.1	5.1	4.6
15	288.15	6.8	6.8	6.1
20	293.15	8.9	9.1	8.1
25	298.15	11.7	11.9	10.6
30	303.15	15.2	15.6	13.8
35	308.15	19.5	20.1	17.9
ΔH_1[a]		39.1 ± 1.2	39.8 ± 1.3	39.6 ± 1.2
ΔS_1[b]		36.7 ± 4.2	19.9 ± 4.5	37.8 ± 4.3

[a] units kJ mol^{-1}
[b] units J K^{-1} mol^{-1}

REFERENCES:

1. Moser, H. C.; Voigt, A. F. *USAEC Report* 1957, *ISC-892*, 65 pp.
2. Klehr, E. H.; Voigt, A. F. *Radioisot. Phys. Sci. Ind., Proc. Conf., Copenhagen* 1960, *1*, 517 (pub. 1962).
3. Kuntz, R. R.; Mains, G. J. *J. Phys. Chem.* 1964, *68*, 408.
4. Spencer, J. N.; Voigt, A. F. *J. Phys. Chem.* 1968, *72*, 464.
5. Vogel, A.; Gjaldbaek, J. C. *Arch. Pharm. Chemi Sci. Ed.* 1974, *2*, 25.
6. Hauptshein, M.; Fainberg, A.; Braid, M. *J. Am. Chem. Soc.* 1958, *80*, 842.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6] (2) Hexafluorobis(trifluoromethyl)-cyclobutane or Perfluorodimethylcyclobutane; C_6F_{12}; [28677-00-1]	Kuntz, R. R.; Mains, G. J. *J. Phys. Chem.* 1964, *68*, 408 - 10.
VARIABLES: T/K = 298.15	PREPARED BY: S. H. Johnson M. Iwamoto H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Mercury Solubility		
t/°C	T/K[a]	Concentration $10^7 c_1$/mol dm^{-3}	Mole Fraction[a] $10^8 x_1$	Molality[a] $10^7 m_1$/mol kg^{-1}
25	298.15	3.4	6.1	2.0

[a]Calculated 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 $\varepsilon_{2560} = 7.35 \times 10^3$ dm^3 mol^{-1} cm^{-1} at 25°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) Perfluorodimethylcyclobutane. Phillips Petroleum Co. Pure Grade hydrocarbon solvent. Purified by passage through silica gel until optically pure, degassed and distilled.

ESTIMATED ERROR:

REFERENCES:

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

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6]; Mercury-203; ^{203}Hg; [13982-78-0] (2) Hexafluorobis(trifluoromethyl)-cyclobutane or Perfluorodimethylcyclobutane; C_6F_{12}; [28677-00-1]	Spencer, J. N.; Voigt, A. F. *J. Phys. Chem.* 1968, *72*, 464 - 470. Spencer, J. N. Dissertation, Iowa State University, 1967.
VARIABLES: T/K = 273.15 - 298.15	PREPARED BY: S. H. Johnson M. Iwamoto H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Mercury Solubility		
t/°C	T/K[a]	Concentration $10^7 c_1$/mol dm^{-3}	Mole Fraction[a] $10^8 x_1$	Molality[a] $10^7 m_1$/mol kg^{-1}
0	273.15	0.4 ± 0.1	0.7	0.2
16.5	289.65	2.1 ± 0.3	3.7	1.2
18	291.15	2.2 ± 0.2	3.9	1.3
21	294.15	3.0 ± 0.1	5.4	1.8
25	298.15	3.8 ± 0.1	6.8	2.3

[a]Calculated by compilers.

The authors smoothed their data according to the equation:

$$\log x_1 = (26.921 \pm .347)\log(T/\mathrm{K}) - 73.746$$

for the 273.15 to 298.15 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 scintillation 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.

The solvent density at 298.15 was taken from Hauptschein *et al.* (ref. 1). For the other temperatures, it was assumed the temperature coefficient of density was the same as that observed for perfluoromethylcyclohexane (ref. 2).

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) Perfluorodimethylcyclobutane. Research grade obtained from Du Pont. Mixture of isomers; used as received.

ESTIMATED ERROR:

δT/K = ±0.1; See random error reported by authors with concentration values above.

REFERENCES:

1. Hauptschein, M.; Fainberg, A. H.; Braid, M. *J. Am. Chem. Soc.* 1958, *80*, 842.

2. Clever, H. L.; Saylor, J. H.; Gross, P. M. *J. Phys. Chem.* 1958, *62*, 89.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6] Mercury-203; ^{203}Hg; [13982-78-0] (2) Tetrachloromethane or Carbon tetrachloride; CCl_4; [56-23-5]	Moser, H. C.; Voigt, A. F. USAEC Report 1957, ISC-892. Chem. Abstr. 1958, *52*, 10691h.
VARIABLES: T/K = 298.15	PREPARED BY: H. L. Clever M. Iwamoto

EXPERIMENTAL VALUES:

Temperature		Mercury Solubility		
t/°C	T/K[a]	Concentration $10^6 c_1$/mol dm^{-3}	Mole Fraction[a] $10^7 x_1$	Molality[a] $10^6 m_1$/mol kg^{-1}
25	298.15	7.5 ± 0.3	7.3	4.7

[a]Calculated by compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A globule of Hg metal prepared from radioactive mercury(II) nitrate by reduction with hypophosphorous acid was equilibrated with 5 - 10 ml of liquid by shaking in a thermostat. Aliquotes of the liquid were withdrawn periodically for up to two weeks and the Hg concentration determined radiochemically.

The aliquot was diluted with acetone and equilibrated with $Hg(NO_3)_2$ carrier to exchange the radioactive mercury. The mercury was precipitated as HgS, mounted on a stainless steel planchet and counted with a Geiger-Mueller tube.

SOURCE AND PURITY OF MATERIALS:

(1) Mercury and Mercury-203. Oak Ridge National Lab; recieved as 0.31 M $Hg(NO_3)_2$ in 1.56 HNO_3 solution. Initial activity 50 millicuries g^{-1}; half-life 48 days. Reduced to Hg by hypophosphorous acid; coagulated to a Hg droplet by addition of concentrated HI.

(2) Carbon tetrachloride. Eastman Co. Spectro-grade; shaken with aqueous Na_2SO_3, passed through a column of dry silica gel and redistilled.

ESTIMATED ERROR:

δT/K = ±0.1

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6]; Mercury-203; ^{203}Hg; [13982-78-0]	Klehr, E. H.; Voigt, A. F.
(2) Tetrachloromethane or Carbon tetrachloride; CCl_4; [56-23-5]	*Radioisot. Phys. Sci. Ind., Proc. Conf., Copenhagen* 1960, *1*, 517 - 29 (Pub. 1962).
VARIABLES:	PREPARED BY:
T/K = 298.15	S. H. Johnson M. Iwamoto H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Mercury Solubility		
t/°C	T/K[a]	Concentration $10^6 c_1$/mol dm^{-3}	Mole Fraction[a] $10^7 x_1$	Molality[a] $10^6 m_1$/mol kg^{-1}
25	298.15	7.5 ± 0.1	7.3	4.7

[a]Calculated by compilers.

The value above is from the direct measurement technique. The indirect measurement result is 7.5 x 10^{-6} mol dm^{-3} at 298.15 K. Obtained by multiplying the mercury solubility in water, 3.0 x 10^{-7} mol dm^{-3}, times the distribution coefficient.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Direct Method. A globule of mercury containing 203-Hg was placed in 50 ml of solvent in a 100 ml flask and agitated in a thermostated bath. Samples were taken until the solution appeared to be at equilibrium. Analyses were made by GM-counting by one of two techniques:

(i) Solid precipitate counting. The Hg in a 0.5 ml aliquot was exchanged and reprecipitated on a stainless steel panchet as the sulfide was dried and counted. Details in Moser and Voigt (ref. 1).

(ii) Liquid aliquot scintillation-counting. A 0.5 ml aliquot of the saturated solution was diluted and transferred to the counting tube with a known volume of benzene.

The 0.28 MeV gamma radiation was counted. Error due to radiation adsorbed by the benzene and water was shown to be less than one percent.

Indirect Method. The distribution coefficient between solvent and water was measured.

SOURCE AND PURITY OF MATERIALS:

(1) Mercury and Mercury-203. Reduced from a mercury nitrate sample. Half-life is 47 days.

(2) Carbon tetrachloride. Shaken with an aqueous solution of sodium sulfate, dried by passing it through a silica gel column, and redistilled.

ESTIMATED ERROR:

See random error reported by authors withthe concentration value above.

REFERENCES:

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

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6]; (2) Tetrachloromethane of Carbon tetrachloride; CCl_4; [56-23-5]	Vogel, A.; Gjaldbaek, J. Chr. *Arch. Pharm. Chem. Sci. Ed.* 1974, *2*, 25 - 9.
VARIABLES: T/K = 298.15	PREPARED BY: H. L. Clever, M. Iwamoto

EXPERIMENTAL VALUES:

Temperature		Mercury Solubility			
t/°C	T/K[a]	Time t/day	Concentration $10^6 c_1$/mol dm^{-3}	Mole Fraction[a] $10^7 x_1$	Molality[a] $10^6 m_1$/mol kg^{-1}
25	298.15	2	9	9	5
		9	30	29	19

[a]Calculated by compilers.

ADDITIONAL COMMENTS:

The authors' suspect a slow reaction between mercury and carbon tetrachloride, but they were unable to characterized the reaction.

The authors took special care to see that the glassware surface of the sampling pipet was equilibrated with the saturated solution of mercury. Special care was taken to see that colloidal mercury did not form in the solution.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mercury was analyzed by cold vapor atomic absorption spectroscopy (ref. 1).

The solvent was saturated with Hg in a special glass container in which a few grams of mercury was kept in a cellulose extraction thimble. The container was shaken at least 48 hours at 25°C.

A 10.00 cm³ sample of the saturated solution was taken. It was treated to convert the Hg to Hg^{2} and extracted into an aqueous phase.

An aliquot of the aqueous phase was diluted, treated with tin(II) chloride to reduce the mercury, and the solution analyzed by cold vapor atomic absorption spectroscopy. The apparatus allowed measurements down to one part per billion of Hg.

Similtaneous measurements were made under the same conditions of samples containing a known amount of mercury.

SOURCE AND PURITY OF MATERIALS:

(1) Mercury. Source not given, purified by distillation.

(2) Carbon tetrachloride. Merck, Uvasol grade spectroscopic quality, used without further purification.

ESTIMATED ERROR:

REFERENCES:

1. Hatch, W. R.; Ott, W. L. *Anal. Chem.* 1968, *10*, 2085.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6]; Mercury-203; ^{203}Hg; [13982-78-0] (2) Chlorobenzene; C_6H_5Cl; [108-90-7]	Klehr, E. H.; Voigt, A. F. *Radioisot. Phys. Sci. Ind., Proc. Conf., Copenhagen* 1960, *1*, 517 - 29 (Pub. 1962).
VARIABLES: T/K = 273.15 - 308.15	PREPARED BY: S. H. Johnson M. Iwamoto H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Mercury Solubility		
t/°C	T/K[a]	Concentration $10^6 c_1$/mol dm^{-3}	Mole Fraction[a] $10^7 x_1$	Molality[a] $10^6 m_1$/mol kg^{-1}
0	273.15	2.8 ± 0.1	2.8	2.5
10	283.15	5.0 ± 0.1	5.0	4.5
15	288.15	6.8 ± 0.1	6.9	6.1
20	293.15	8.4 ± 0.1	8.5	7.6
25	298.15	12.5 ± 0.1	12.8	11.4
35	308.15	19.3 ± 0.1	19.9	17.7

[a]Calculated by compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Direct Method. A globule of mercury containing 203-Hg was placed in 50 ml of solvent in a 100 ml flask and agitated in a thermostated bath. Samples were taken until the solution appeared to be at equilibrium. Analyses were made by GM-counting by one of two techniques:

(i) Solid precipitate counting. The Hg in a 0.5 ml aliquot was exchanged and reprecipitated on a stainless steel panchet as the sulfide was dried and counted. Details in Moser and Voigt (ref. 1).

(ii) Liquid aliquot scintillation-counting. A 0.5 ml aliquot of the saturated solution was diluted and transferred to the counting tube with a known volume of benzene.

The 0.28 MeV gamma radiation was counted. Error due to radiation adsorbed by the benzene and water was shown to be less than one percent.

SOURCE AND PURITY OF MATERIALS:

(1) Mercury and Mercury-203. Reduced from a mercury nitrate sample. Half-life is 47 days.

(2) Chlorobenzene. Used without further purification.

ESTIMATED ERROR:

See random error reported by authors with concentration values above.

REFERENCES:

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

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury; Hg; [7439-97-6]; Mercury-203; ^{203}Hg; [13982-78-0] (2) Bromobenzene; C_6H_5Br; [108-86-1]	Klehr, E. H.; Voigt, A. F. *Radioisot. Phys. Sci. Ind., Proc. Conf., Copenhagen* 1960, *1*, 517 - 29 (Pub. 1962).
VARIABLES: T/K = 298.15	PREPARED BY: S. H. Johnson M. Iwamoto H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Mercury Solubility		
t/°C	T/K[a]	Concentration $10^6 c_1$/mol dm^{-3}	Mole Fraction[a] $10^7 x_1$	Molality[a] $10^6 m_1$/mol kg^{-1}
25	298.15	16.0 ± 0.3	16.9	10.8

[a]Calculated by compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Direct Method. A globule of mercury containing 203-Hg was placed in 50 ml of solvent in a 100 ml flask and agitated in a thermostated bath. Samples were taken until the solution appeared to be at equilibrium. Analyses were made by GM-counting by one of two techniques:

(i) Solid precipitate counting. The Hg in a 0.5 ml aliquot was exchanged and reprecipitated on a stainless steel panchet as the sulfide was dried and counted. Details in Moser and Voigt (ref. 1).

(ii) Liquid aliquot scintillation-counting. A 0.5 ml aliquot of the saturated solution was diluted and transferred to the counting tube with a known volume of benzene.

The 0.28 MeV gamma radiation was counted. Error due to radiation adsorbed by the benzene and water was shown to be less than one percent.

SOURCE AND PURITY OF MATERIALS:

(1) Mercury and Mercury-203. Reduced from a mercury nitrate sample. Half-life is 47 days.

(2) Bromobenzene. Repurified by shaking with stannous chloride and redistilling.

ESTIMATED ERROR:

See random error reported by authors with the concentration value above.

REFERENCES:

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