Compilation and Evaluation of Solubility Data in the Mercury (I) Chloride-Water System

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The more than one dozen papers dealing with the solubility of mercury (I) chloride in water or in aqueous chloride solutions have been compiled in the format set by the IUPAC Solubility Data Project, and have been evaluated. Mercury (I) chloride dissolves in water, forming the following species: $Hg(OH)_2$, $HgCl_2$, $HgOH^+$, $HgCl^+$, Hg_2^{2+} and Hg_2OH^+, in addition to H^+ and Cl^-. In excess chloride solutions it dissolves to give, mainly, $HgCl_3^-$ and $HgCl_4^{2-}$. Thus, many homogeneous equilibria have to be considered beside the two heterogeneous ones: $Hg_2Cl_2(s) = Hg_2^{2+}(aq) + 2Cl^-(aq)$ and $Hg_2^{2+}(aq) = Hg^{2+}(aq) + Hg(\ell)$, of which K°_{s0} and $(K^\circ_r)^{-1}$, respectively, are the equilibrium constants. The papers in which the total solubility (sum of all the mercury containing aqueous species) and the solubility product (derived from e.m.f. data) are reported do not give as accurate and reliable quantities as are obtained from the appropriate standard electrode potentials. The following values are recommended as valid at 298.15 K: $\log (K^\circ_{s0}/\text{mol}^2\text{kg}^{-2}) = -17.844 \pm 0.017$, $d \log (K^\circ_{s0}/\text{mol}^2\text{kg}^{-2})/dT = (0.0622 \pm 0.0002) - (6.0 \pm 0.4) \times 10^{-4}\ (T/\text{K} - 298.15)$, $\Delta G^\circ_{s0} = 101.86 \pm 0.10$ kJ mol^{-1}, $\Delta S^\circ_{s0} = -12.7 \pm 0.9$ JK^{-1} mol^{-1}, $\Delta H^\circ_{s0} = 98.08 \pm 0.18$ kJ mol^{-1}, $\Delta C^\circ_{p,s0} = -0.36 \pm 0.04$ JK^{-1} mol^{-1} (this item, tentatively), and $c_{Hg} = (8.4 \pm 1.6) \times 10^{-6}$ mol dm^{-3} (the total aqueous solubility).

Key words: Compilation of solubility data; disproportionation of mercury (I); electromotive force measurements; mercury (I) chloride; solubility; solubility product; standard electrode potentials; standard thermodynamic functions.

Contents

1. Introduction

The Subcommittee on Solubility Data of Commission V.6, Equilibrium Data, Analytical Chemistry Division, International Union of Pure and Applied Chemistry, (secretariat: Oxford OX4 3YF, UK), is currently undertaking an extensive project of compiling and evaluating solubility data existing in the literature. As a part of this project, systems involving the solubility of solids in liquids are being treated, and it became necessary to provide prospective authors of compilations and evaluations of such systems with a reasonably complicated, well worked out system as a sample. This led to the commissioning of the author with selecting such a system and providing this sample compilation and evaluation.

The mercury (I) chloride-water system appears to fulfill the requirements of being quite well documented in the literature, of providing reasonably complicated side effects which must be, and can be, dealth with, yet being amenable to a sufficiently rigorous treatment, so as to provide final, recommended

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values. It was therefore selected for presentation as a sample compilation and evaluation.

Three groups of papers have to be examined in order to obtain definite values for the solubility of mercury (I) in water. The first, refs. [1]–[7], deal with direct determinations of the solubility. The second, refs. [3], [8]–[14], deal with determination of the solubility product via e.m.f. measurements. The third, refs. [15], [18], [19], [21]–[28], pertains to papers in which the standard potentials of the calomel electrode and of the mercury/mercury (I) electrode are determined separately, without going on to calculate the solubility product. This last group of papers is not included in the compilation on solubilities. It turns out however, that it provides, over a temperature range, the best values of the solubility.

2. Evaluation

2.1. Solubility Measurements

Kohlrausch [1a]–[1c][1] compared the specific conductivity of saturated mercury (I) chloride solutions at 0.5, 18.0, 24.6 and ~43 °C with that of 0.0005 mol dm^{-3} mercury (I) nitrate (stated as 0.001N $HgNO_3$), knowing its temperature coefficient for conductivity. The conductivity of the water used in the saturated solutions was probably [6] overcorrected for, while on the other hand, the contribution of the hydrolysis to the conductivity, which is overwhelming [6], was disregarded. Hence the value found for the solubility, $s = (5.9 \pm 3.0) \times 10^{-6}$ mol dm^{-3} at 24.6 °C, is fortuitously of the right magnitude.

Richards and Archibald [2] measured the total solubility of mercury in saturated solutions of Hg_2Cl_2 in aqueous HCl, NaCl, and $BaCl_2$ at 25 °C, where $HgCl_4^{2-}$ is the main mercury species, by precipitation as HgS. The equilibrium constant for the reaction

$$Hg_2Cl_2(s) + 2Cl^- = HgCl_4^{2-} + Hg(\ell);\ K_e^\circ\ (\equiv K_{s114}^\circ) \qquad (1)$$

(the solubility product for producing the 4-ligand complex of mercury (II), i.e., K_{s114}°) is obtained from

$$\log K_e^\circ = \lim_{c_{Cl}\to 0} [\log c_{Hg}/c_{Cl}^2)$$

$$- \log (1 + \beta_3\beta_4^{-1}c_{Cl}^{-2}) + \log y_{HgCl_4{}^{2-}} y_{Cl^-}^{-2}] \qquad (2)$$

The second term on the rhs is small at the experimental chloride concentrations c_{Cl} employed, hence activity coefficient corrections to the stability constants β_i of $HgCl_i^{2-i}$ can be neglected. The third term on the rhs, however, is of considerable size, and can be approximated as $-2Ac_{Cl}^{1/2}(1 + 1.6c_{Cl}^{1/2})^{-1} + \Delta b c_{Cl}$. The first term of this approximation is known, and any deviations from the modified Debye-Hückel behavior are included in the second term, and is extrapolated out at the limit. The main uncertainty enters here, since as the $\Delta b c_{Cl}$ term decreases on extrapolation, the second term on the rhs of 2 increases. The solubility data themselves *cannot* be extrapolated to zero excess chloride concentration to give the solubility of Hg_2Cl_2 in water. However, the solubility product can be calculated from

$$\log K_{s0}^\circ = \log K_e^\circ + \log K_r^\circ - \log \beta_4$$

$$- \log y_{\text{trace NaCl in NaClO}_4} \qquad (3)$$

where K_r° is the reproportionation constant for the equilibrium

$$Hg^{2+} + Hg(\ell) = Hg_2^{2+};\ K_r^\circ \qquad (4)$$

The values adopted for the constants are $\log K_r^\circ = 1.94 \pm 0.01$ [15] and $\log (\beta_4(HgCl_4^{2-})/\text{mol}^{-4}\ \text{dm}^{12}) = 15.07$ [16], the latter valid for 0.5 mol dm^{-3} $NaClO_4$ medium. The main errors in K_{s0}° arise from those in K_e° (±12 to 15%) and in β_4 (±15%). The final value $K_{s0}^\circ = (1.86 \pm 0.37) \times 10^{-18}$ mol^{2}dm^{-6} at 25 °C will be seen to be consistent with (but on the high side of) the value recommended further on.

Sherrill [3] presented one datum point, for the solubility of Hg_2Cl_2 in 1 mol dm^{-3} NaCl at 25 °C. A value of K_e° (equil. (1)) could be estimated by using the same value of Δb applicable to the NaCl data of Richards and Archibald [2] evaluated above. This led by means of (3) to $K_{s0}^\circ = 1.2 \times 10^{-18}$ mol^2 dm^{-6}, with a large margin of uncertainty, but still consistent with the recommended value.

Eversole and McLachlan [4] determined the solubility of Hg_2Cl_2 in dilute acids, $HClO_4$ and HNO_3 at 25 °C. The only soluble species of importance which needs to be considered is $HgCl_2$, since the excess acid represses the hydrolysis. In aqueous solutions of Hg_2Cl_2, a major species is soluble $Hg(OH)_2$ [6], and its non-formation in the dilute acid solutions decreases the solubility of mercury (I) chloride below what it is in water. The lack of sufficient data prevents the calculation of this solubility, but the solubility product can be calculated, from the total solubilities c_{Hg} in the acids HA:

$$c_{Hg} = [Hg_2^{2+}] + [Hg_2A^+] + [HgCl^+] + [HgCl_2]$$

$$= (K_{s0}^\circ/4)^{1/3}\, y_{\pm Hg_2Cl_2}^{-1} [1 + \beta_{1A} [A^-] + 2 (K_{s0}^\circ/4)^{1/3} \beta_1 K_r^{-1}]$$

$$+ K_{s0}^\circ K_r^{-1} \beta_2^\circ (y_{\pm HgCl_2}/y_{\pm Hg_2Cl_2})^3 \qquad (5)$$

The first term on the rhs of (5) is a relatively small (~20%) correction term, in which unity dominates over the other terms in the square brackets, and for which K_{s0}° is obtained iteratively. Hence, activity coefficient corrections for β_{1A} ($Hg_2ClO_4^+$ or $Hg_2NO_3^+$) and β_1 ($HgCl^+$) are unnecessary, while $\log y_{\pm Hg_2Cl_2} = -2 \times 0.51\ [A^-]^{1/2}/(1 + 1.6[A^-]^{1/2})$. The value of the solubility product is therefore:

$$K_{s0}^\circ = \frac{c_{Hg} - \text{the first term in the rhs of (5)}}{K_r^{-1}\, \beta_2^\circ\, (y_{\pm HgCl_2}/y_{\pm Hg_2Cl_2})^3} \qquad (6)$$

It is a good approximation to equate the activity coefficient ratio of (the ionically dissociated parts of) $Hg^{2+} \cdot 2Cl^-$ and $Hg_2^{2+} \cdot 2Cl^-$ to unity, and in any case no systematic deviation of K_{s0}° calculated from (6) with $[A^-]$ could be seen. The precision of K_{s0}° depends on that of c_{Hg} while its accuracy depends

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[1] Figures in brackets indicate literature references.

mainly on those of K_r and β_2°. The values adopted for these constants, $\log K_r^\circ = 1.94 \pm 0.01$ [15] and $\log(\beta_2^\circ/\text{mol}^{-2}\text{dm}^6) = 14.26 \pm 0.09$ [6] are responsible for the overall accuracy of the constant $\log K_{s0}^\circ = (1.84 \pm 0.37) \times 10^{-18}$ mol^{2}dm^{-6} at 25 °C, again consistent with the recommended value, but a bit high.

The data of Garret et al. [5] can be treated in a manner similar to the one used on the data of Richards and Archibald [2], eq (2) and (3), but since there are much fewer data, no independent extrapolations could be made. Therefore, the Δb values obtained [2] for NaCl and $CaCl_2$ solutions were used for the calculation of K_e°. The final value is $(1.12 \pm 0.23) \times 10^{-18}$ mol^{2}dm^{-6} at 25 °C, which is somewhat on the low side of the recommended value. (The fact that the data are on the mol kg^{-1} scale produces a small complication, which can be overcome by using the known densities of the salt solutions and converting to mol dm^{-3}.)

The work of Dry and Gledhill [6] has been very carefully done, and gives the best value for the solubility determined directly, $s_{Hg_2Cl_2} = (7.5 \pm 0.3) \times 10^{-6}$ mol dm^{-3} at 25 °C. The method used, treating the filtered saturated solution with dilute HCl and a solution of dithizone in CCl_4, should produce dependable data, when compared with photometric readings from known solutions of $HgCl_2$. The value is within the limits of the recommended value below, although on the low side. However, the primary data were not disclosed, and no basis for the estimate [6] of the ±4% error was given by the authors. Therefore there is no good basis for preferring this lower value, in spite of its apparently higher precision.

The conductivity data of Dry and Gledhill [6] serve to establish the correctness of the value $[H^+] = (8.17 \pm 0.08) \times 10^{-6}$ mol dm^{-3}, obtained primarily from the measured pH of the solutions. This concentration of the acid produced by hydrolysis is a highly important quantity for the establishment of the recommended value of the solubility, see below. Since a value of K_{s0}° obtained from the work of previous authors [12] is used in the calculations [6] of the concentrations of the species, this work [6] cannot be used to obtain an independent value of the solubility product.

The work of Herz [7] should give a value of K_{s0}° at 25 °C in conjunction with the use of a value of $K_s^\circ(\text{HgO(s)} + H_2O = Hg^{2+} + 2OH^-)$, provided that solid Hg_2O disproportionates to HgO(s) + Hg(ℓ). The best value of $K_s^\circ(\text{HgO}) = 2.8 \times 10^{-26}$ [17], [18] (at 25 °C) however leads to a $K_{s0}^\circ(Hg_2Cl_2)$ value which is about two orders of magnitude too small, the same value obtained if the existence of Hg_2O(s) is accepted [10b]. This could be due to the sluggish establishment of equilibrium in the presence of two insoluble solids (Hg_2Cl_2(s) and Hg_2O(s) or HgO(s) + Hg(ℓ)). The period during which the phases were equilibrated was not stated (it was only specified as "extended"), and the establishment of equilibrium was not demonstrated [7].

2.2. E.m.f. Measurements

Of the second group of papers dealing with determinations of K_{s0}° by means of e.m.f. measurements, Behrend's work [8] was pioneering, but of low precision. Since only one concentration of mercury (I) in its half cell and of KCl in the calomel half cell were used, an extrapolation procedure is excluded, the liquid junction potential cannot be adequately estimated in spite of Behrend's later attempt, and only rough estimates of the activity coefficients can be made. The value obtained 2×10^{-19} mol^{2}dm^{-6} at 17 °C, is just an estimate of the order of magnitude. Similarly, Sherril's work [3] gives an estimate of $[Hg^{2+}]$ in a saturated Hg_2Cl_2 solution in 1 mol dm^{-3} NaCl, which leads to $K_{s0}^\circ = 0.44 \times 10^{-18}$ which is much too low. The estimate was, however, not supported by definite e.m.f. data on which it was purportedly based.

Ley and Heimbucher [9] provided fuller experimental information, but their data cannot either be used to extrapolate out liquid junction potentials. These were produced by their bridge electrolyte, 0.1 mol dm^{-3} KNO_3, with the half cell solutions 0.05 mol dm^{-3} $Hg_2(ClO_4)_2$ and 0.1 or 1.0 mol dm^{-3} KCl. With the more dilute KCl, the junction potentials could be rather small, estimated at ±0.01 V, leading to a possible error of a factor of two in $K_{s0}^\circ = 1.48 \times 10^{-18}$ mol^2 dm^{-6} at 20 °C. This value is about twice the recommended value at 20 °C. On the other hand, Brodsky's work [10] using the cell

$$\text{Hg/Hg}_2\,(\text{NO}_3)_2, c_\circ,\ \text{HNO}_3\ 0.005\ \text{mol dm}^{-3}/\text{KNO}_3\ \text{satd./KCl}, c$$

$$/\text{Hg}_2\text{Cl}_2, \text{Hg} \tag{7}$$

permitted extrapolation to $c_\circ = 0$ (and less clearly to $c = 0$), thus eliminating the liquid junction potentials, which are probably small in any case, through the use of a saturated KNO_3 bridge. The values obtained at four temperatures are rather close to the recommmended values at these temperatures, the interpolated value for 25 °C being $(1.07 \pm 0.13) \times 10^{-18}$ mol^{2}dm^{-6}, definitely on the low side.

An improved extrapolation method was provided by Law [11], but the ionic strength was not kept constant as $x \to 0$ in the cell

$$\text{Hg,Hg}_2\text{Cl}_2/\text{NaCl}\ (1.5mx)\ \text{mol kg}^{-1},$$

$$\text{HClO}_4\ (m - mx)\ \text{mol kg}^{-1}/\text{HClO}_4\ (m + 0.5mx)\ \text{mol kg}^{-1}/$$

$$\text{Hg}_2\ (\text{ClO}_4)_2\ (0.5mx)\ \text{mol kg}^{-1},$$

$$\text{HClO}_4\ (m - mx)\ \text{mol kg}^{-1}/\text{Hg} \tag{8}$$

the extrapolation, hence, not eliminating sufficiently the liquid junction [14]. Law's data also result in an incorrect value of $E^\circ_{Hg/Hg_2^{2+}}$ (see below), which, in turn, leads to a much too high value of $K_{s0}^\circ = 5.1 \times 10^{-18}$ mol^{2}dm^{-6} at 25 °C. Since Law's values were available only through secondary sources [14], [19], no further comments can be made on the discrepancy.

The work of Jonsson, Qvarfort and Sillen [12] and of Hansen, Izatt and Christensen [13] tried to overcome the liquid junction and activity coefficient problems by using a constant ionic medium of 0.50 mol dm^{-3} $NaClO_4$ (of which 0.01 mol dm^{-3} [12], 0.10 mol dm^{-3} [13], were $HClO_4$ rather than $NaClO_4$). The value obtained at 25 °C in this medium [12], $K_{s0} = (1.32 \pm 0.03) \times 10^{-17}$ mol dm^{-6}, must be multiplied by

$y^3_\pm(\mathrm{Hg}_2^{2+}\cdot 2\mathrm{Cl}^-$ trace in NaClO_4 medium) to obtain K°_{s0}. For this quantity the value 0.09 was suggested, but the evaluator failed to trace its origin through the references provided [12], [16], [20]. Application of this correction leads to $K^\circ_{s0} = (1.19\pm 0.03)\ 10^{-18}\ \mathrm{mol^2dm^{-2}}$ at 25 °C. A somewhat different value of the correction term [6], 0.101 ± 0.001, leads to $K^\circ_{s0} = (1.33\pm 0.03)\times 10^{-18}\ \mathrm{mol^2dm^{-6}}$, which is rather near the recommended value, but a bit low. Again no details of the derivation of this $y^3_\pm$ were provided [6]. The values of K_{s0} for 0.50 mol dm^{-3} NaClO_4 medium at 7 and 40 °C are [13] 6.4×10^{-19} and $6.29\times 10^{-17}\ \mathrm{mol^2dm^{-6}}$, respectively. Conversion to K°_{s0} requires estimates of $y^3_\pm(\mathrm{Hg}_2^{2+}\cdot 2\mathrm{Cl}^-$ trace in NaClO_4 medium) at these temperatures. Acceptance of 0.10 ± 0.02 as valid for the range 7–40 °C, in lieu of any better values, leads to $K^\circ_{s0} = (6.5\ \pm\ 1.3)\times 10^{-20}$ at 7 °C and $(6.9\pm 1.4)\times 10^{-18}$ at 40 °C as the best estimates. These are about 30% lower than the recommended values.

No experimental details are provided in these studies [12], [13] to evaluate the results from the point of view of the purity of the reagents (e.g., contamination with bromide) or of the instrumentation used, although the former [12] contains enough details on the care with which the work was carried out to assure acceptability of the data on this account.

The work of Galloway [14] combined the merits of constant ionic strength media (for extrapolating away the effect of excess chloride concentrations) with the possibility to eliminate the activity coefficients by providing series of data at decreasing ionic strengths. The cell employed

$$\begin{gathered}\mathrm{Hg,Hg_2Cl_2/BaCl_2}\ (xm/2)\ \mathrm{mol\ kg^{-1}},\ \mathrm{HClO_4}\ (m-xm)\ mol\ kg^{-1}\\ \mathrm{/Ba(ClO_4)_2}\ (xm/3)\ \mathrm{mol\ kg^{-1}},\ \mathrm{HClO_4}\ (m-xm)\ \mathrm{mol\ kg^{-1}}\\ \mathrm{/Hg_2\ (CLO_4)_2}\ (xm/3)\ \mathrm{mol\ kg^{-1}},\ \mathrm{HClO_4}\ (m-xm)\ \mathrm{mol\ kg^{-1}}\\ \mathrm{/Hg_2Cl_2,\ Hg}\end{gathered}\tag{9}$$

was measured at 5 K intervals over the range 15 to 40 °C. At first extrapolation at constant m (and T) from $0.1\leqslant x\leqslant 0.6$ to $x=0$ was followed by adding an activity coefficient correction term, which carried the main burden of the second extrapolation from $0.01\leqslant m\leqslant 0.05$ to $m=0$. This device puts relatively small weights on this extrapolation on the one hand, and on inadequacies of the activity coefficient term on the other, leading to results of high validity. The final value of $K^\circ_{s0} = (1.49\pm 0.05)\times 10^{-18}\ \mathrm{mol^2kg^{-2}}$ (practically the same as $\mathrm{mol^2dm^{-6}}$) does not differ significantly from the recommended value $(1.43\pm 0.06)\times 10^{-18}\ \mathrm{mol^2kg^{-2}}$, both at 25 °C. For other temperatures there are increasing differences, but still within the combined uncertainities.

2.3. Standard Electrode Potentials

A third group of papers is now considered, in some of which the standard electrode potentials of the calomel electrode $E^\circ_{\mathrm{Hg/Hg_2Cl_2}}$, and in others, those of the mercury/mercury(I) electrode, $E^\circ_{\mathrm{Hg/Hg_2^{2+}}}$ were determined, for purposes other than the calculation of the solubility product of mercury(I) chloride. These papers will not be reviewed here, since they have been reviewed quite adequately previously, and only the latest or "best" results will be presented here. The solubility constant can, obviously, be calculated from

$$\log K^\circ_{s0} = (E^\circ_{\mathrm{Hg/Hg_2Cl_2}} - E^\circ_{\mathrm{Hg/Hg_2{}^{2+}}})/(RT/2F)\ \ln 10.\tag{10}$$

The most extensive and careful study of the calomel electrode has been made over the years by Ives and his coworkers [21a]–[21d]. Their work is well confirmed by those of Ahluwalia and Cobble [22] and others (see refs. [14], [15]). The value for 25 °C is established at $E^\circ_{\mathrm{Hg/Hg_2Cl_2}} = 0.26818\pm 0.00002$ V [24] and at other temperatures can be obtained from

$$\begin{gathered}E^\circ_{\mathrm{Hg/Hg_2Cl_2}}\ (T)/\mathrm{V} = 0.26818\pm 0.00002\\ -\ (2.99\pm 0.03)\ 10^{-4}\Delta T\ -\ (3.1\pm 0.3)\ 10^{-6}(\Delta T)^2\end{gathered}\tag{11}$$

where $\Delta T - T/\mathrm{K} - 298.15$, with an overall precision of ± 0.00004 V. The corresponding entropy term is $F(dE^\circ_{\mathrm{Hg/Hg_2Cl_2}}/dT) = 151.37 - 0.6044\Delta T\mathrm{JK^{-1}\ mol^{-1}}$. At 298.15 K $\Delta S^\circ = -28.83\ \mathrm{JK^{-1}\ mol^{-1}}$, compared with the value suggested by Ahluwalia and Cobble [22] $-$ 28.49 $\mathrm{JK^{-1}\ mol^{-1}}$.

The standard potential of the mercury/mercury(I) electrode has not been studied as extensively, and is not established to that degree of accuracy obtained for the calomel electrode. The thermodynamic functions of formation of Hg_2^{2+} (aq) were given in the latest NBS compilation [23] as $\Delta G^\circ_f = 153.55$ kJ $\mathrm{mol^{-1}}$ and $\Delta H^\circ_f = 172.4$ kJ $\mathrm{mol^{-1}}$ (the latter with one less significant digit than the former). These values lead to $E^\circ_{\mathrm{Hg/Hg_2{}^{2+}}}$ (298.15 K) $= (0.79574\pm 0.00022)$ V and

$$\begin{gathered}E^\circ_{\mathrm{Hg/Hg_2{}^{2+}}}\ (T/\mathrm{K})/\mathrm{V}\\ = E^\circ_{\mathrm{Hg/Hg_2{}^{2+}}}\ (298.15)/\mathrm{V}\ -\ 3.27\times 10^{-4}\Delta T,\end{gathered}\tag{12}$$

where $\Delta T = T/\mathrm{K} - 298.15$, with a precision of ± 0.00019 V. The apparent precision given here is based merely on the apparent precision (± one unit of the last significant digit) of the values in the compilation [23]. Another set of $E^\circ_{\mathrm{Hg/Hg_2{}^{2+}}}$ (T) data was obtained by Read [24], (quoted in ref. [14]), with 0.7956 V for $T = 298.15$ K, $dE^\circ/dT - -2.97\times 10^{-4}\ \mathrm{VK^{-1}}$ and an overall precision of ± 0.00014 V, in the range 15 to 45 °C. Most other workers used the old data of Linhart [25] corrected in one way or another, except for the more recent data of ElWakkad and Salem [26], of Bonner and Unietis [27], and of Schwarzenbach and Anderegg [28] who gave for $E^\circ_{\mathrm{Hg/Hg_2{}^{2+}}}$ (298.15 K) 0.7960 ± 0.0005 V, and 0.7966 ± 0.0010 V, respectively. The latest review of these data, by Venderzee and Swanson [15] selected the value (0.7960 ± 0.0005)V as the best for 298.15 K. As for the temperature coefficient, $dE^\circ/dT = -(3.25\pm 0.06)\times 10^{-4}\ \mathrm{VK^{-1}}$ represents best both Read's [24] and the NBS [23] data.

The standard thermodynamic functions for the reaction

$$\mathrm{Hg_2Cl_2(s)} = \mathrm{Hg_2^{2+}\ (aq)} + \mathrm{2Cl^-(aq)}\tag{13}$$

are obtained from

$$\Delta G^\circ_{s0} = 2F(E^\circ_{Hg/Hg_2Cl_2} - E^\circ_{Hg/Hg_2^{2+}}) \tag{14}$$

and from $\Delta S^\circ_{s0} = -(d\Delta G^\circ_{s0}/dT) = 2Fd(E^\circ_{Hg/Hg_2^{2+}} - E^\circ_{Hg/Hg_2Cl_2})/dT$. The value at 298.15 K of $\Delta G^\circ_{s0} = 101.86 \pm 0.10$ kJ mol^{-1} is consistent with the other thermodynamic data [23]. However, $\Delta S^\circ_{s0}/\text{JK}^{-1}\ \text{mol}^{-1} = 5.06 \pm 1.25 - (1.21 \pm 0.12) \times 10^{-3}\ \Delta T$ (with $\Delta T = T/\text{K} - 298.15$), a positive entropy change resulting from (11), (12) and (14) leads to $\Delta H^\circ_{s0} = 103.36 \pm 0.38$ kJ mol^{-1} at 298.15 K. This differs considerably from the calorimetric value recently obtained by Vanderzee and Swanson [15], 98.08 ± 0.18 kJ mol^{-1}. Since the latter work is very reliable, the fault must be sought with the temperature dependence of either one of the E° values (or both) employed in (14), most probably in that of $E^\circ_{Hg/Hg_2^{2+}}$, which is less well established.

In fact, the enthalpy of formation of Hg_2^{2+} (aq) given by Vanderzee and Swanson [15], $\Delta H^\circ_f = 166.82 \pm 0.21$ kJ mol^{-1} differs considerably from that in the NBS compilation [23], 172.4 kJ mol^{-1} and should be more reliable. Use of the newer value leads to the relation, obtained from the 25 °C standard potential and the enthalpy of precipitation of calomel

$$E^\circ_{Hg/Hg_2^{2+}}\ (T)/\text{V} = 0.7960 \pm 0.0005$$

$$-(2.30 \pm 0.04)\ 10^{-4}\Delta T \tag{15}$$

as the more reliable value.

2.4. Calculated Solubility

The solubility of mercury(I) chloride in water is not, as was assumed in the very early studies, $(K^\circ_{s0}/4)^{1/3}$, because of the disproportionation of Hg_2^{2+} to give Hg^{2+} and Hg(ℓ), the complexing of Hg^{2+} with chloride, its hydrolysis, and to a lesser extent the hydrolysis of Hg_2^{2+}. The following analysis is based on the work of Dry and Gledhill [6], who showed that the saturated solution contains the following mercury species: $Hg(OH)_2$, $HgCl_2$, $HgOH^+$, $HgCl^+$, Hg_2^{2+} and Hg_2OH^+, in addition to H^+ and Cl^- ions. The total concentration of mercury in the solution can be expressed as

$$c_{Hg} = [Hg_2^{2+}]\left\{K_R^{\circ -1}\left[K_W^2\beta^\circ_{112OH}\ (y_{Hg_2^{2+}}/y_{Hg(OH)_2}\ y^2_{H^+})\ [H^+]^{-2}\right.\right.$$

$$+\ \beta^\circ_{112Cl}(y_{Hg_2^{2+}}\ y^2_{Cl^-}\ y_{HgCl_2})[Cl^-]^2$$

$$+\ K_W\beta^\circ_{111OH}\ (y_{Hg_2^{2+}}/y_{HgOH^+}\ y_{H^+})\ [H^+]^{-1}$$

$$\left.+\ \beta_{111Cl}\ (y_{Hg_2^{2+}}\ y_{Cl^-}/y_{HgCl^+})\ [Cl^-]\right]$$

$$\left.+\ 2 + 2K_W\beta^\circ_{11OH}\ (y_{Hg_2 2+}/y_{Hg_2OH^+}y_{H^+})\ [H^+]^{-1}\right\} \tag{16}$$

In this expression, the activity coefficients will be calculated according to the modified Debye-Hückel equation

$$\log y_i = -0.51z_i^2I^{1/2}/(1 + 1.6I^{1/2}) \tag{17}$$

where I, the ionic strength will be put equal to $[H^+]$, and z_i is the charge of the i-th ion. Since the ionic strength is very low, $I = [H^+] \simeq 8.2 \times 10^{-6}$ mol dm^{-3}, the activity coefficient corrections are quite small, and any deviation of (17) from the true behaviour leads to negligible errors. Other equations which must be considered are

$$[Hg_2^{2+}]\ [Cl^-]^2 = K^\circ_{s0}y^{-1}_{Hg_2^{2+}}\ y^{-2}_{Cl^-} \tag{18}$$

$$[Cl^-] = 2(c_{Hg} - [HgCl_2] - \frac{1}{2}[HgCl^+])$$

$$\simeq 2(c_{Hg} - [HgCl_2]) \tag{19}$$

The approximation in (19) is permissible since, as will be found, $[HgCl_2]/c_{Hg} \simeq 0.37$, but $[HgCl^+]/c_{Hg} \simeq 0.01$. The hydrogen ion concentration, due to hydrolysis, obtained by pH measurements and confirmed by conductivity [6], is taken as $[H^+] = (8.17 \pm 0.08) \times 10^{-6}$ mol dm^{-3} at 25 °C. The following values of the constants appearing in (16) and valid for 25 °C will be used: $K^\circ_R(Hg^{2+} + Hg(\ell) = Hg_2^{2+}) = 10^{1.944 \pm 0.008}$ [15], $K^2_W\beta^\circ_{112OH}\ (Hg^{2+} + 2H_2O = Hg(OH)_2 + 2H^+) = 10^{-5.65 \pm 0.12}$ [6], $\beta^\circ_{112Cl}\ (Hg^{2+} + 2Cl^- = HgCl_2) = 10^{19.26 \pm 0.09}$ [6], $K_W\beta^\circ_{111OH}\ (Hg^{2+} + H_2O = HgOH^+ + H^+) = 10^{-3.09 \pm 0.20}$ [6], $\beta^\circ_{111Cl}\ (Hg^{2+} + Cl^- = HgCl^+) = 10^{7.34 \pm 0.27}$ [6], $K_W\beta^\circ_{11OH}\ (Hg_2^{2+} + H_2O = Hg_2OH^+ + H^+) = 10^{-4.4 \pm 0.4}$ [6] and for $K^\circ_{s0}\ (Hg_2Cl_2\ (s) = Hg_2^{2+} + 2Cl^-) = 10^{-17.844 \pm 0.017}$ will be used.

The values quoted were estimated [6] as valid for the ionic strength of the saturated solution, from corrections applied to published values [16] valid for 0.50 mol dm^{-3} $NaClO_4$ medium. With these values of the constants, the value of $[H^+]$ and eq (16), (18) and (19), the following implicit equation is obtained (valid for 25 °C):

$$c^3_{Hg}\ (1 - (3.09 \pm 0.65)/10^6\ c_{Hg})^2 = (4.25 \pm 0.05)$$

$$\times 10^{-21}\{10^{7.63 \pm 0.27}\ c_{Hg}\ (1 - (3.09 \pm 0.65)/10^6\ c_{Hg})$$

$$+\ 10^{14.85 \pm 0.09}\ c^2_{Hg}\ (1 - (3.09 \pm 0.65)/10^6\ c_{Hg})^2$$

$$+\ (3.43 \pm 1.06) \times 10^4\}. \tag{20}$$

This was solved iteratively to give the value for the solubility

$$c_{Hg} = (8.4 \pm 1.0) \times 10^{-6}\text{mol dm}^{-3} \tag{21}$$

as the solubility of mercury(I) chloride in water at 25 °C. This value is consistent with the solubility measured directly [6], $(7.5 \pm 0.3) \times 10^{-6}$ mol dm^{-3}, as discussed above.

3. Recommended Values

3.1. Solubility Product Constant of Hg_2Cl_2

The above analysis and eq (10), (11) and (15) yield for the

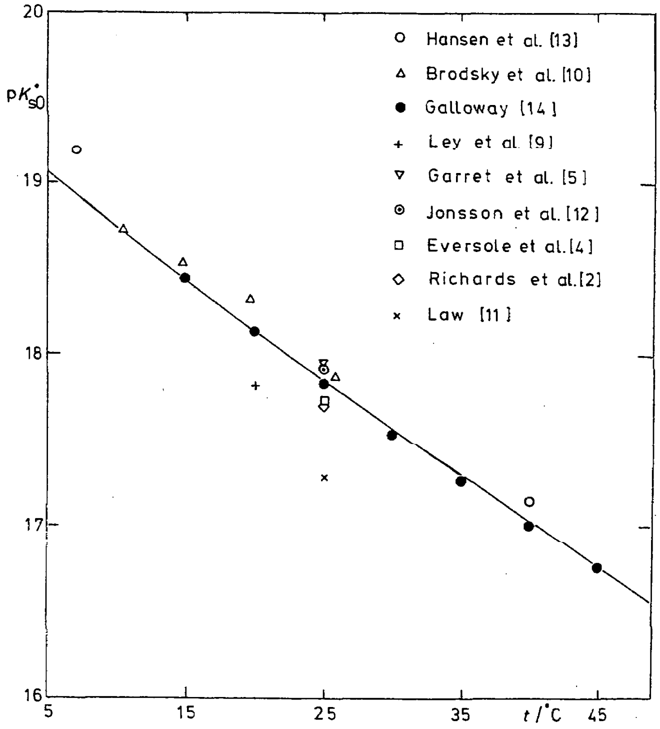

Figure 1. Values of pK°_{s0} (= $-\log K^{\circ}_{s0}$) recalculated from the authors' data compared with the "recommended" values (continuous line).

solubility product of mercury(I) in water in the range 5 to 45 °C

$$\log(K^{\circ}_{s0}/\mathrm{mol^2kg^{-2}}) = -17.844 \pm 0.017 + (0.0622 \pm 0.0002)\Delta T - (3.0 \pm 0.2) \times 10^{-4} (\Delta T)^2 \quad (22)$$

where $\Delta T = T/\mathrm{K} - 298.15$. The first term on the rhs represents the value for 25 °C

$$K^{\circ}_{s0}/\mathrm{mol^2kg^{-2}}(298.15\ \mathrm{K}) = (1.43_3 \pm 0.05_6) \times 10^{-18} \quad (23)$$

the relative error being ±3.9%. The value in $(\mathrm{mol\ dm^{-3}})^2$ units is 0.6% lower, i.e., insignificantly different. The values of $\log K^{\circ}_{s0}$ at different temperatures are plotted in figure 1, and compared there with values obtained by several authors.

3.2. Standard Thermodynamic Functions

There are several fixed quantities, selected above as reliable, to which the thermodynamic functions must conform. These are $E^{\circ}_{\mathrm{Hg/Hg_2Cl_2}}$ (298.15 K) = 0.26818±0.00002 V, $\Delta S^{\circ}_{298.15}$ ($\mathrm{Hg/Hg_2Cl_2}$) = −28.83 $\mathrm{JK^{-1}\ mol^{-1}}$, $E^{\circ}_{\mathrm{Hg/Hg_2{}^{2+}}}$ (298.15 K) = 0.7960±0.0005 V and $\Delta H^{\circ}_{298.15}$ ($\mathrm{Hg_2^{2+}}$ (aq) + $2\mathrm{Cl^-}$ (aq) = $\mathrm{Hg_2Cl_2}$ (s)) = −98.08±0.18 kJ $\mathrm{mol^{-1}}$. These lead to the following functions for reaction (13)

$$\Delta G^{\circ}_{s0}/\mathrm{kJ\ mol^{-1}} = 101.86 \pm 0.10 + (0.0127 \pm 0.0009)\Delta T + (0.60 \pm 0.06) \times 10^{-3} (\Delta T)^2 = -151.4 + 0.345\ T + 0.60 \times 10^{-3} T^2 \quad (24)$$

$$\Delta S^{\circ}_{s0}/\mathrm{JK^{-1}mol^{-1}} = -12.7 \pm 0.9 - (1.20 \pm 0.12)\Delta T = 345 - 1.20\ T \quad (25)$$

$$\Delta H^{\circ}_{s0}/\mathrm{kJ\ mol^{-1}} = 98.08 \pm 0.18 - (0.358 \pm 0.036)\Delta T - (0.60 \pm 0.06) \times 10^{-3} (\Delta T)^2 = 151.4 - 0.60 \times 10^{-3} T^2 \quad (26)$$

$$\Delta C^{\circ}_{p,s0}/\mathrm{JK^{-1}mol^{-1}} = -(0.358 \pm 0.036) - (1.20 \pm 0.12) \times 10^{-3}\Delta T = -1.20 \times 10^{-3} T \quad \text{(tentative value)} \quad (27)$$

These functions have the following values at 25 °C:

$$\begin{aligned}\Delta G^\circ_{s0}(298.15) &= 101.86 \pm 0.10 \text{ kJ mol}^{-1},\\ \Delta S^\circ_{s0}(298.15) &= -12.70 \pm 0.9 \text{ JK}^{-1}\text{ mol}^{-1},\\ \Delta H^\circ_{s0}(298.15) &= 98.08 \pm 0.18 \text{ kJ mol}^{-1}\\ \Delta C^\circ_{p,s0}(298.15) &= 0.36 \pm 0.04 \text{ JK}^{-1}\text{mol}^{-1}\\ &\quad \text{(tentative value)}\end{aligned} \tag{28}$$

The uncertainty about $\Delta C^\circ_{p,s0}$ is due to the ignorance of $\Delta C^\circ_{p,f}$ (Hg_2^{2+} (aq)), so that it is based solely on the second derivative of E°_{Hg/Hg_2Cl_2}. The standard entropy change vanishes at 14.4 °C (according to Galloway at 19.0 °C [14]).

3.3. The Aqueous Solubility of Hg_2Cl_2

The aqueous solubility of mercury(I) chloride at 25 °C is given by eq (16) to (20) as

$$c_{Hg} = (8.4 \pm 1.0) \times 10^{-6} \text{ mol dm}^{-3} \tag{21}$$

The values at other temperatures cannot be calculated, since the temperature coefficients of the various constants and of the pH of the saturated solutions are unknown.

Acknowledgements

Acknowledgements. The help of Prof. H.L. Clever, in providing copies of hard to obtain literatuure sources, is gratefully acknowledged. Useful remarks and encouragement have been obtained from Profs. L.G. Hepler, D.N. Hume, A.S. Kertes, and G.H. Nancollas and Dr. M. Salomon.

4. References

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5. Compilation

5.1. Data of Behrend (1893, 1894)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Potassium chloride, KCl (7447-40-7)
3. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Behrend, R., Z. Phys. Chem. (1893) 11, 466; (1894) 15, 498.

VARIABLES:

One temperature
One KCl concentration

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

E.m.f. *E* at room temperature (17°C) of cell:

$Hg/Hg_2(NO_3)_2$ 0.05M, HNO_3 (?M)/0.1M $KNO_3/Hg_2Cl_2(s)$, 0.1M KCl/Hg

found to be 0.356V and 0.360V in two experiments. Final value adopted is 0.358V. This value has to be multiplied by 1.092 to give 0.391V, as stated by the author in the correction published by him in the second source quoted (see below). From this is derived (Y.M.)

$$\log K^\circ_{s0}(Hg_2Cl_2,\ 17^\circ C) = -17.10 - (E_j/V)/0.02879$$

A realistic estimate for E_j is 0.05±0.03V, hence $\log K^\circ_{s0} = -17.1 - (1.7\pm1.0) \approx -18.8\pm1.0$ at 290K.

AUXILIARY INFORMATION

METHOD:

$$\log K^\circ_{s0}(Hg_2Cl_2,\ 17^\circ C) = -(2/0.05757)[(E/V) - (E_j/V)] - \log(c_{Hg_2(NO_3)_2}\cdot c_{KCl}^2) - \log(y_{Hg_2(NO_3)_2}\cdot y_{KCl}^2\cdot y_{KNO_3}^{-2}) =$$

$$= -2(0.391 - E_j/V)/0.05757 - \log(0.05\cdot 0.1^2) - \log(0.55\cdot 0.77^2/0.74^2)$$

$$= -13.58 - (E_j/V)/0.02879 - 3.30 - 0.22$$

$$= -17.10 - (E_j/V)/0.02879$$

$y_{Hg_2(NO_3)_2}$ estimated from value for $Ca(NO_3)_2$[1], value for that, KCl and KNO_3 from ref. 2.

Unthermostated cell, using an electrometer, a resistance box and a Leclanché standard cell, constant to ca. ±3 mV over two months.

SOURCE AND PURITY OF MATERIALS:

Not stated

ESTIMATED ERROR: From range of *E* (±0.002V), uncertainty of temperature (±2°C) and activity coefficient product (±10%), error of $\log K_s$ is ±0.22.

REFERENCES:

1. Bonner, O.D., Unietis, F., J. Am. Chem. Soc. (1953) 75, 5111.
2. Robinson, R.A., Stokes, R.H., Electrolyte Solutions, Butterworth, London, 2nd Ed., 1959.

5.2. Data of Richards and Archibald (1902)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Hydrochloric Acid, HCl (7647-01-0)
3. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Richards, T.W., Archibald, E.H., Z. phys. Chem. (1902) 40, 385.

VARIABLES:

HCl concentration
One temperature

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

Solubility of Hg_2Cl_2 in aqueous HCl at 25°C. Composition of the solutions:

$c_{HCl}/\text{mol dm}^{-3}$	$c'_{Hg,total}/\text{g dm}^{-3}$	$10^4 c_{Hg,total}/\text{mol dm}^{-3}$
0.83	0.034	1.69
0.83	0.034	1.69
1.00	0.048	2.39
1.00	0.048	2.39
2.50	0.206	10.27
2.50	0.208	10.37
4.15	0.400	19.94
4.15	0.398	19.84
5.48	0.548	27.32
5.48	0.548	27.32

(Remarks: $c_{Hg,total}$ calculated by compiler. Data were also presented for 7.00, 7.30, 8.31 and 10.00 mol dm^{-3} HCl, but not used for calculations below.)

$\log K_e^\circ(Hg_2Cl_2(s) + 2Cl^- = Hg(\ell) + HgCl_4^{2-}) = -3.93 \pm 0.01$ (calculated by YM)

$\log K_{s0}^\circ(Hg_2Cl_2(s) = Hg_2^{2+} + 2Cl^-) = -17.72 \pm 0.08$ (calculated by YM with additional data$^{1-3}$).

AUXILIARY INFORMATION

METHOD:

$$\log K_e^\circ = \log(c_{Hg,total}/c_{HCl}^2) - \log(1+\beta_3\beta_4^{-1}c_{HCl}^{-1} + \beta_2\beta_4^{-1}c_{HCl}^{-2})^{\text{ref. 2}} - 2AI^{1/2}/(1+BI^{1/2}) + \Delta bI;$$

$A = 0.51$, $B = 1.6$, $I = c_{HCl}$.

Least squares calc. gave $\log K_e^\circ = -3.93$ and $\Delta b = -0.146$.

$$\log K_{s0}^\circ = \log K_e^\circ + \log K_r(Hg^{2+} + Hg(\ell) = Hg_2^{2+})^{\text{ref. 1}} - \log \beta_4\,(Hg^{2+} + 4Cl^- = HgCl_4^{2-})^{\text{ref. 2}} - 4 \log y(\text{trace NaCl in 0.5M NaClO}_4)^{\text{ref. 3}} =$$

$$= -3.93+1.94-15.07-0.66 = -17.72.$$

Excess $HgCl_2$ shaken for >7 hr with 0.1 g Hg(ℓ) and 50 ml HCl solution in glass vessel provided with purified rubber stopper in a thermostated bath at 25.00±0.05°C. Total Hg in equilibrium solutions determined gravimetrically as HgS precipitated by H_2S, washed and dried at 100°C.

SOURCE AND PURITY OF MATERIALS:

Hg_2Cl_2 sublimed at low temperature, the source shown to be immaterial. HCl was redistilled c.p. acid.

ESTIMATED ERROR:

$\log K_e^\circ$: ±0.05 from least squares fitting

$\log K_{s0}^\circ$: ±0.06 on $\log \beta_4$, ±0.01 on $\log y_{NaCl}$ and ±0.02 on $\log K_r$ yield total ±0.08

REFERENCES:

1. Hietanen, S., Sillèn, L.G., Ark. Kemi (1956) 10, 103.
2. Sillèn, L.G., Acta Chem. Scand. (1949) 3 539.
3. Estimated by YM from Robinson, R.A., Stokes, R.H., Electrolyte Solutions, Butterworth, London, 2nd ed., 1959, and Lanier, R.D., J. Phys. Chem. (1965) 69, 3992

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2a. Sodium chloride, NaCl (7647-14-5)
2b. Calcium chloride, $CaCl_2$ (10043-52-4)
2c. Barium chloride, $BaCl_2$ (10361-56-3)
3. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Richards, T.W., Archibald, E.H.,
Z. phys. Chem. (1902), 385.

VARIABLES:

NaCl, $CaCl_2$ or $BaCl_2$ concentrations
One temperature

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

Solubility of Hg_2Cl_2 in aqueous chlorides at 25°C. Composition of the solutions:

c_{NaCl} mol dm^{-3}	$10^4 c_{Hg,total}$ mol dm^{-3}	c_{CaCl_2} mol dm^{-3}	$10^4 c_{Hg,total}$ mol dm^{-3}	c_{BaCl_2} mol dm^{-3}	$10^4 c_{Hg,total}$ mol dm^{-3}
1.00	2.04	0.36	1.10	0.50	2.19
2.00	6.43	0.50	1.64	0.75	4.39
2.50	9.67	1.00	4.04	1.00	5.33
3.80	18.9	1.25	5.88	1.50	11.5
5.00	32.1	1.76	11.5		

Remarks: $c_{Hg,total}$ calculated by compiler from $c_{Hg,total}/g\ dm^{-3}$ data, which are averages of two experiments at each concentration. Data also presented for 2.32 and 2.93 mol dm^{-3} $CaCl_2$, but not used for calculations below. Salt concentrations presented as equivalents dm^{-3}, recalculated here.

$$\log K_e^\circ(Hg_2Cl_2(s) + 2Cl^- = Hg(\ell) + HgCl_4^{2-}) \begin{array}{l} = -3.98 \text{ for NaCl solutions} \\ = -3.94 \text{ for } CaCl_2 \text{ solutions} \\ = -3.93 \text{ for } BaCl_2 \text{ solutions} \end{array} \Bigg]\ \text{av.} = -3.95 \pm 0.06$$

$\log K_{s0}^\circ(Hg_2Cl_2(s) = Hg_2^{2+} + 2Cl^-) = -17.74 \pm 0.09$ on the average for the three series.

AUXILIARY INFORMATION

METHOD:

$\log K_e^\circ = \log(c_{Hg,total}/c_{MCl}^2) - \log(1 + \beta_3\beta_4^{-1}c_{MCl}^{-1} + \beta_2\beta_4^{-1}c_{MCl}^{-2})^{ref.2} - 2AI^{1/2}/(1+BI^{1/2}) + \Delta bI$; $A=0.51$, $B=1.6$, M=Na, $\frac{1}{2}$Ca or $\frac{1}{2}$Ba. Least squares calc. gave $\log K_e^\circ$ values given and $\Delta b=0.160$ for NaCl, 0.198 for $CaCl_2$ and 0.136 for $BaCl_2$.

$\log K_{S0}^\circ = \log K_e^\circ + \log K_r(Hg^{2+} + Hg(\ell) = Hg_2^{2+})^{ref.1} - \log \beta_4(Hg^{2+} + 4Cl^- = HgCl_4^{2-})^{ref.2} - 4 \log y(\text{trace NaCl in 0.5M } NaClO_4)^{ref.3} = 3.95+1.94-15.07-0.66 = = -17.74 \pm 0.008.$

Excess Hg_2Cl_2 shaken for >7 hr with 0.1 g $Hg(\ell)$ and 50 ml aqueous NaCl, $CaCl_2$ or $BaCl_2$ in glass vessel provided with purified rubber stopper in thermostated bath at 25.00±0.05°C. Total Hg in equilibrium solutions determined gravimetrically as HgS precipitated by H_2S, washed and dried at 100°C.

SOURCE AND PURITY OF MATERIALS:

Hg_2Cl_2 sublimed at low temperature, the source shown to be immaterial. NaCl precipitated from solution by HCl, then recrystallized, $CaCl_2$ prepared from pure $Ca(NO_3)_2$, converted to $CaCO_3$ and to $CaCl_2$ and then recrystallized.

ESTIMATED ERROR: $\log K_e^\circ$: ±0.06 from least squares fitting. $\log K_{s0}^\circ$: ±0.06 on $\log \beta_4$, ±0.01 on $\log y_{NaCl}$ and ±0.02 on $\log K_r$ yiel yield ±0.09.

REFERENCES:

1. Hietanen, S., Sillèn, L.G., Ark. Kemi (1956) 10, 103.
2. Sillèn, L.G., Acta Chem. Scand. (1949) 3, 539.
3. Estimated by Y.M. from Robinson, R.A., Stokes, R.H., Electrolyte Solutions, Butterworth, London, 2nd Ed., 1959.

5.3. Data of Sherrill (1903)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Sodium chloride, NaCl (7647-14-5)
3. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Sherrill, M.S., Z. physik. Chem. (1903) 43, 705.

VARIABLES:

One NaCl concentration
One temperature

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

(a) Total solubility of $Hg_2Cl_2(s)$ in aqueous NaCl, 1 mol dm^{-3}, at 25°C is 1.51×10^{-4} mol dm^{-3}.

(b) Concentration of species $[Hg^{2+}]$ in aqueous NaCl, 1 mol dm^{-3}, at equilibrium with $Hg_2Cl_2(s)$ at 25°C is 5.3×10^{-20} mol dm^{-3}.

From datum (b), $K_r(Hg^{2+} + Hg(\ell) = Hg_2{}^{2+}) = 120$[1] and the assumed degree of dissociation of the NaCl of 0.75,[1] the author obtained

$$\log K_s(Hg_2Cl_2(s) = Hg_2{}^{2+} + 2Cl^-) = \log 5.3\times10^{-20} + \log 120 + 2\log(1\times0.75) = -17.45$$

Calculated (Y.M.) from datum (b), $K_r(Hg^{2+}+Hg(\ell) = Hg_2{}^{2+}) = 88\pm4$[2] and the activity coefficient of calcium chloride[3] in 1 mol dm^{-3} sodium chloride[4]

$$\log K_s^\circ(Hg_2Cl_2(s) = Hg_2{}^{2+} + 2Cl^-) = \log 5.3\times10^{-20} + \log 88 + 2\log 1 + 3(-0.344) = -18.36$$

Calculated (Y.M.) from datum (a): $\log K_e(Hg_2Cl_2(s) + 2Cl^- = Hg(\ell) + HgCl_4{}^{2-}) = -4.1$

$$\log K_s^\circ = \log K_e + \log K_r^{\text{ref.}2} - \log \beta_4(Hg^{2+} + 4Cl^- = HgCl_4{}^{2-})^{\text{ref.}5} - 4\log y_{NaCl} = -4.1+1.94-15.07-0.66 = -17.9$$

AUXILIARY INFORMATION

METHOD:

(a) This datum appears in Table 18 of the paper; the accompanying text does not make it clear that it is the author's own determination, rather than Richards and Archibald's[6], but the value does not appear in these authors' paper.

(b) This datum apparently obtained from E.m.f. measurements, but these have not been specified.

E.m.f. measured by compensation method using capillary electrometer as null instrument. Cells, not described, kept in thermostated bath at 25°. Total mercury in solution determined by precipitation as HgS gravimetrically with no details given.

SOURCE AND PURITY OF MATERIALS:

Pure commercial salts (Kahlbaum), not further purified.

ESTIMATED ERROR:

Large, since experimental details are not given.

REFERENCES: 1. Abel, E., Z. anorg. Chem. (1901) 26, 361. 2. Hietanen, S., Sillèn, L.G., Ark. Kemi (1956) 10, 103. 3. Bonner, O.D., Unietis, F., J. Am. Chem. Soc. (1953) 75, 5111. 4. Lanier, R.D., J. Phys. Chem. (1965) 69, 3992. 5. Sillèn, L.G., Acta. Chem. Scand. (1949) 3, 539. 6. Richards, T.W., Archibald, E.H., Z. physik. Chem. (1902) 40, 385.

5.4. Data of Ley and Heimbucher (1904)

COMPONENTS:

1. Mercury (I) chloride, Hg_2Cl_2 (10112-91-1)
2. Potassium chloride, KCl (7447-40-7)
3. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Ley, H., Heimbucher, C., Z. Elektrochem. (1904) 10, 301.

VARIABLES:

Two KCl concentrations
One temperature

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

The e.m.f. E of the following cell determined at 20°C

$$Hg/Hg_2(ClO_4)_2\ 0.05M/0.1M\ KNO_3/Hg_2Cl_2(s),\ cM\ KCl/Hg\ (M = mol\ dm^{-3}).$$

Found

c = 0.1M	E/V = 0.4193	0.4197	0.4200	0.4199
c = 1.0M	E/V = 0.4721	0.4717		

Authors took $[Hg_2^{2+}]$ = 0.047M in 0.05M $Hg_2(ClO_4)_2$ (the rest being hydrolyzed species), 0.73 as its degree of dissociation. For 0.1M and 1.0M KCl the degrees of dissociation used were 0.86 and 0.75 respectively. For $(RT/2F)\ln 10$ the authors took 0.0295V. For the two KCl concentrations they calculated

$$\log K_{s0}^{\circ}(Hg_2Cl_2(s) = Hg_2^{2+} + 2Cl^-) = -17.83\ (c = 0.1M)\ \text{and}\ -17.95\ (c = 1.0M).$$

Calculated from the data (YM), avoiding rounding-off errors, using the accepted value of $(RT/2F)\ln 10$ at 20°C (0.02908V), and the authors' estimate of "degree of dissociation" and hydrolysis

$$\log K_{s0}^{\circ} = -18.03 (c = 0.1M)\ \text{and}\ -17.95\ (c = 1.0M).$$

No correction for any liquid junction potentials can, however, be applied.

AUXILIARY INFORMATION

METHOD:

E.m.f. measured by compensation method. Degree of hydrolysis by comparing rate of inversion of sucrose by 0.05M $Hg_2(ClO_4)_2$ with that by (1/250)M $HClO_4$. Degree of dissociation by comparing conductivity of 0.05M $Hg_2(ClO_4)_2$ with that of 0.05M $Ba(ClO_4)_2$ in an unspecified manner.

Capillary electrometer used as null detector in e.m.f. measurements.

SOURCE AND PURITY OF MATERIALS:

$Hg_2(ClO_4)_2$ obtained by dissolving Hg_2O (prepared by precipitating purest (Merck) $Hg_2(NO_3)_2$ with NaOH) in 2M $HClO_4$, and recrystallizing from water. This was then dissolved in conductivity water. Excess acid remaining <0.08%. No sources for other materials given.

ESTIMATED ERROR: Main error in assumed activity coefficients (authors' "degree of dissociation"), ±0.06 units in log K_s (after rounding off errors corrected).

REFERENCES:

5.5. Data of Kohlrausch (1908)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 [10112-91-1]
2. Water, H_2O [7732-18-5]

ORIGINAL MEASUREMENTS:

Kohlrausch, F., Z. physik. Chem. (1908) 64, 129.

VARIABLES:

Four temperatures

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

Solubilities s_{Hg} given in mg mercury(I) chloride per dm^{-2} of saturated solution:

$t/°C$	0.5	18.0	24.6	(43)
$s_{Hg}/mg\ dm^{-3}$	1.4	2.1*	2.8	7
$10^6 s_{Hg}/mol\ dm^{-3}$**	3.0	4.4	5.9	15

*In the earliest study[1], the estimated solubility at this temperature was 3.1 mg dm^{-3}.

**Calculated by YM.

AUXILIARY INFORMATION

METHOD:

The conductivity of saturated solutions of Hg_2Cl_2 compared with that of 5×10^{-4} mol dm^{-3} $Hg_2(NO_3)_2$, taking into account its temperature coefficient and the expansibility of the solutions. Hydrolysis recognized as contributing to the conductivity, but not corrected for.

The apparatus and procedure were described in earlier work[1,2].

Material as finely divided powder suspended in conductivity water as often as needed until constant conductivity achieved. Daylight was excluded. Conductivity of the water employed subtracted from that of the saturated solution.

SOURCE AND PURITY OF MATERIALS:

Described in earlier work[1,2]. Hg_2Cl_2 precipitated from aqueous solution of $Hg_2(NO_3)_2 \cdot xH_2O$ with excess HCl. Some reexamined after 2.5 years' storage.

ESTIMATED ERROR:

Author's estimate: data could be 50% wrong.

REFERENCES:

1. Kohlrausch, F., Rose, F., Z. physik. Chem. (1893) 12, 234.
2. Kohlrausch, F., Rose, F., Z. physik. Chem. (1903) 44, 197.

5.6. Data of Herz (1911)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Potassium hydroxide, KOH (1310-58-3)
3. Potassium chloride, KCl (7447-40-7)
4. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Herz, W., Z. Anorg. Chem. (1911) 70, 170.

VARIABLES:

One temperature, varying KOH and KCl concentrations.

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

The composition of the aqueous salts in equilibrium with a mixture of solid Hg_2Cl_2 and Hg_2O (= Hg(ℓ) + HgO ?)[1] determined at 25°C:

$c_{KOH}/\text{mol dm}^{-3}$	0.038	0.018	0.009
$c_{KCl}/\text{mol dm}^{-3}$	2.177	1.087	0.543

Calculated (YM): $\log K_s(Hg_2Cl_2(s) = Hg_2^{2+} + 2Cl^-) = \log (c_{KCl}/c_{KOH})^2 + \log K(HgO(s) = Hg^{2+} + 2OH^-) + \log K(Hg^{2+} + Hg(\ell) = Hg_2^{2+}) + \log(y_{\pm KCl}/y_{\pm KOH})^2 = 3.61 \pm 0.04 - 25.4$ (ref. 2) $+ 1.94$ (ref. 3) $- 0.03$ (ref. 4) $= -19.9 \pm 0.1$.

Alternatively, if existence of solid Hg_2O is accepted, with the solubility product $K_s(Hg_2O(s) = Hg_2^{2+} + 2OH^-) = 1.8 \times 10^{-24}$ (ref. 5), then

$$\log K_s(Hg_2Cl_2(s)) = \log K_s(Hg_2O(s)) + \log(c_{KCl}/c_{KOH})^2 + \log(y_{\pm KCl}/y_{\pm KOH})^2 =$$
$$= -23.74 + 3.61 \pm 0.04 - 0.03 = -20.16 \pm 0.05.$$

AUXILIARY INFORMATION

METHOD:

Excess solid Hg_2Cl_2 shaken at 25°C for an extended period (unspecified) with aqueous KOH. The remaining base titrated with standardized acid to the phenolphthalein endpoint. The KCl content of the equilibrium solution obtained by difference. Solids assumed to be Hg_2Cl_2 and Hg_2O, but latter probably[1] disproportionates.

SOURCE AND PURITY OF MATERIALS:

Not given

ESTIMATED ERROR: Main error arises from ignorance of the nature of the solid "Hg_2O," hence from K_s of HgO[2]. The concentrations of KOH are imprecise, contributing to the error.

REFERENCES: .. Sillèn. L.G.., Martell. A.E.., Stability Constants, Chem. Soc. Spec. Publ.1 17, London, 1964, p. 64. 2. Feitknecht, W., Schindler, P., Pure Appl. Chem. (1963) 6, 130. 3. Hietanen, S., Sillèn, L.G., Arkiv Kemi (1956) 10. 103. 4. Harned. H.S.. Hamer, W.J., J. Am. Chem. Soc. (1937) 59, 1890. 5. Brodsky, A.E., Z. Electrochem. (1929) 35, 833.

5.7. Data of Brodsky and Scherschewer (1926)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Potassium chloride, KCl (7447-40-7)
3. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Brodsky, A.E., Scherschewer, J.M., Z. Elektrochem. (1926) <u>32</u>, 1.

VARIABLES:

Temperature
KCl concentration
$Hg_2(NO_3)_2$ concentration

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

The e.m.f. of the following cell determined (M = mol dm^{-3})

$Hg/Hg_2(NO_3)_2 c_0 M$, HNO_3 0.005M^1/KNO_3 satd./Hg_2Cl_2(s), KClcM/Hg

c_0/mol dm^{-3} t/°C	10.8		14.9				19.2		26.5
c/mol dm^{-3}	0.01	0.1	0.01	0.1	0.5	1.0	0.1	1.0	0.1
	10^4E/V (Int. volts corrected to volts)								
0.0466	3756	4133	3754	4124	4475	4664	4103		4089
0.0233	3524	4080	3514	4067	4424	4608	4054	4609	4032
0.01165	3463	4023	3465	4002	4366	4555	4000		3977
0.00583	3399	3959	3397	3949	4307	4491	3934	4488	3914
0.00291	3275	3866	3324	3879	4233	4426	3881		3833
0.00146	3256	3825	3256	3807	4164	4350	3813	4435	3749
0.000728	3185	3751	3146	3700	4055	4243	3781	4360	3667
0.000364	3077	3627	3062	3611	3958	4158		4328	
log K^{*}_{s0}(Hg_2Cl_2(s) = Hg_2^{2+}+2Cl^-)	-18.72±0.09		-18.54±0.05				-18.33±0.05		-17.88±0.05

*Calculated by Y.M.

AUXILIARY INFORMATION

METHOD:

$$\log K^{\circ}_{s0} = \lim_{c_0 \to 0} [(-2FE/RT \ln 10) + \log c_0 c^2 y^2_{\pm KCl}]$$

where $y_{\pm KCl}$ is activity coefficient of KCl at temp. T and molar concentration c. Authors' values of F and $y^1_{\pm KCl}$ replaced by modern values. Extrapolation to c_0=0 intended to eliminate $y_{K^+}/y_{Hg_2^{2+}} y_{Cl^-}$.

E.m.f. measured by compensation method with calibrated Weston cell standard, a mirror galvanometer as null instrument, and half-cells which were intercompared for consistency. No thermostat was used, but e.m.f.'s and temperatures steady for 4 hrs at least.

SOURCE AND PURITY OF MATERIALS:

$Hg_2(NO_3)_2$ freshly prepared from salt of undisclosed source.

ESTIMATED ERROR: Errors given for log K°_{s0} are the nonsystematic errors from the relationship of the measured E, c_0, c and T, and the extrapolation. The systematic error inherent in the latter is less than ±0.1.

REFERENCES:

1. Brodsky, A.E., Z. Elektrochem. (1929) <u>35</u>, 833.

5.8. Data of Eversole (1932)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Perchloric acid, $HClO_4$ (7601-90-3)
3. Nitric acid, HNO_3 (7697-37-2)
4. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Eversole, W.G., McLachlan, R.W., J. Am. Chem. Soc. (1932) 52, 864.

VARIABLES:

One temperature, several concentrations of $HClO_4$ or HNO_3.

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

Concentration of soluble mercury species in equilibrium with solid Hg_2Cl_2 at 25.0°C in solutions of the acids

$c_{HClO_4}/\mathrm{mol\ dm^{-3}}$:	0.0005	0.005	0.01	0.1	0.2
$10^6 c_{Hg(total)}/\mathrm{mol\ dm^{-3}}$:	4.7	4.8	5.0	5.5	6.3

$c_{HNO_3}/\mathrm{mol\ dm^{-3}}$:	0.005	0.01	0.1
$10^6 c_{Hg(total)}/\mathrm{mol\ dm^{-3}}$:	5.2	5.6	5.8

Calculated (Y.M.): The contributions of the species $HgNO_3^+$, $HgOH^+$, $Hg(OH)_2$ are negligible, those of $Hg_2ClO_4^+$, $Hg_2NO_3^+$ and $HgCl^+$ are small$^{1-3}$, so that Hg_2^{2+} and $HgCl_2$ are the main species. Thus to a good approximation

$$c_{Hg} = (K^\circ_{sO}/4)^{1/3} y_{\pm Hg_2Cl_2}^{-1} \{1+\beta_{1(A)}[A^-] + 2(K^\circ_{sO}/4)^{1/3}\beta_1 K_r^{-1}\} + K^\circ_{sO} K_r^{-1} \beta_2 (y_{\pm HgCl_2}/y_{\pm Hg_2Cl_2})^3$$

Following estimates were used: $y_{\pm Hg_2Cl_2} \approx y_{\pm HgCl_2} = 10^{-3\sqrt{I}/(1+1.6\sqrt{I})}$; $I = c_{acid}$; $\beta_{1(ClO_4^-)} = 0.9\ \mathrm{mol\ dm^{-3}}$; $\beta_{1(NO_3^-)} = 2.25\ \mathrm{mol\ dm^{-3}}$; $\beta_1(HgCl^+) = 10^{7.34}$; $\beta_2(HgCl_2) = 10^{14.26}$; $K_r = 10^{1.94}$. These gave for all acid concentrations by a short iteration the consistent value $\log K^\circ_{sO} = -17.74 \pm 0.02$.

AUXILIARY INFORMATION

METHOD:

Increasing volumes of very dilute (10^{-4} mol dm^{-3}) aqueous $Hg_2(ClO_4)_2$ and KCl added together with excess water, until incipient precipitation could be observed by Tyndall effect. Equilibrium tested by cooling 0.2°C, then reheating to 25.0°C, with no change in results. Solubility given as that solution which is just short of showing Tyndall effect. Solutions agitated for >4 hrs at 25°C regulated to ±0.02°C and carefully guarded against dust.

Sealed pyrex glass vessels used. A home-made Tyndallometer was employed, in conjunction with a Zeiss Pulfrich gradation photometer.

SOURCE AND PURITY OF MATERIALS:

H_2O redistilled from $KMnO_4$; KCl, c.p. twice recryst. from redist. H_2O; $Hg_2(ClO_4)_2$ prepared by authors^4; HNO_3, c.p., twice redistilled and nitrous gases expelled; $HClO_4$ distilled in vacuum.

ESTIMATED ERROR: Error in solubility data ca. 2%, to which error in K°_{sO} is proportional. Main uncertainties are in $\log K_r$ (±0.02) and $\log \beta_2$ (±0.09), contributing ±0.10 systematic error in $\log K^\circ_{sO}$.

REFERENCES:

1. Hietanen, S., Sillèn, L.G., Arkiv Kemi (1956), 10, 103.
2. Hietanen, S., Sillèn, L.G., Acta Chem. Scand. (1952) 6, 747.
3. Sillèn, L.G., Acta Chem. Scand. (1949) 3, 539.
4. Popoff, S., J. Am. Chem. Soc. (1931) 53, 1195.

5.9. Data of Garrett, Noble and Miller (1942)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2a. Sodium chloride, NaCl (7647-14-5)
2b. Calcium chloride, $CaCl_2$ (10043-52-4)
3. Water (7732-18-5)

ORIGINAL MEASUREMENTS:

Garrett, A.B., Noble, M.V., Miller, S., J. Chem. Educ. (1942) 19, 485.

VARIABLES:

One temperature, several NaCl or $CaCl_2$ concentrations

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

1. The solubility of Hg_2Cl_2 in water at 25°C is 5.9×10^{-6} mol (kg $H_2O)^{-1}$.
2. The solubility of Hg_2Cl_2 in aqueous salt solution at 25°C is

	m/mol kg^{-1}	c*/mol dm^{-3}	$10^6 m_{\mathrm{Hg,total}}$/mol kg^{-1}	$10^6 c^*_{\mathrm{Hg,total}}$/mol dm^{-3}
NaCl	0.101	0.100	8.7	8.6
	1.02	1.00	88.4	86.7
	2.12	2.03_4	185.	177.
$CaCl_2$	0.374	0.370	48.5	48.0
	0.528	0.522	74.2	73.4
	1.05	1.02	170.	165.

*Calculated (Y.M.). Calculated also

$$\log K^{\circ}_{s0} = \lim_{m_{\mathrm{Cl^-}}\to 0} [\log(c_{\mathrm{Hg,total}}/c^2_{\mathrm{Cl^-}}) - \log(1 + \beta_3\beta_4^{-1}c^{-1}_{\mathrm{Cl^-}} + \beta_2\beta_4^{-1}c^{-2}_{\mathrm{Cl^-}}) - 2AI^{1/2}/(1 + BI^{1/2})] + \log K_r(\mathrm{Hg^{2+} + Hg(\ell)) = Hg_2^{2+}}) - \log \beta_4 - 4 \log y_{\pm}(\text{trace NaCl in 0.5M NaClO}_4)^{\text{ref.3}} = -17.95\pm0.08.$$

AUXILIARY INFORMATION

METHOD:

$\beta_i(\mathrm{Hg^{2+} + \mathit{i}Cl^- = HgCl_{\mathit{i}}^{2-\mathit{i}}}) = 10^{13.22}$ for $i=2$, $10^{14.07}$ for $i=3$, $10^{15.07}$ for $i=4$, valid for 0.5M (mol dm^{-3}) $NaClO_4$.[1] A = 0.51 and B = 1.6, I = ionic strength, is arbitrary form of activity coefficient term, the rest of which is taken into account by the extrapolation. $K(\mathrm{Hg^{2+} + Hg(\ell) = Hg_2^{2+}}) = 88$ (ref. 2).

No details are given of the apparatus and procedure.

SOURCE AND PURITY OF MATERIALS:

No details given.

ESTIMATED ERROR: Mainly from activity coefficient terms, necessitating the extrapolation, and uncertainties in the constants.

REFERENCES:

1. Sillèn, L.G., Acta Chem. Scand. (1949) 3. 539.
2. Hietanen, S., Sillèn, L.G., Arkiv Kemi (1956) 10, 103.
3. Estimated (YM) from Robinson, R.A., Stokes, R.H., Electrolyte Solutions, Butterworth, London, 2nd Ed., 1959.

5.10. Data of Law (1946)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Sodium chloride, NaCl (7647-14-5)
3. Perchloric acid, $HClO_4$ (7601-90-3)
4. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Law, J.T., M.S. Thesis, University of New Zealand, 1946.

VARIABLES:

Temperatures, between 15 and 45°C; concentrations of NaCl and $HClO_4$.

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

E.m.f.'s of the cell

$Hg/Hg_2Cl_2(s)$, NaCl $(1.5mx)$m, $HClO_4$ $(m-mx)$m/$HClO_4$ $(m+0.5mx)$m/$Hg_2(ClO_4)_2$ $(0.5mx)$m,

$HClO_4$ $(m-mx)$m/Hg

measured at 5K intervals between $288.15 \le T/K \le 318.15$ for various concentrations in the ranges $0.02 \le m \le 0.05$ and $0.2 \le x \le 0.6$. The results were summarized as follows:

1. $\lim_{m\to 0}[\lim_{x\to 0, m \text{ const.}}(E + (RT/2F)\ln(4.5mx)] = 0.5108 V_{\text{int}} = 0.5110 V$ for T/K=298.15 (ref. 1)
2. $\Delta G°(Hg_2Cl_2(s) = Hg_2^{2+} + 2Cl^-)/\text{kJ mol}^{-1} = 42.947 + 0.3243T - 4.588T^2$ (ref. 2)

   $\Delta H°/\text{kJ mol}^{-1} = 42.947 + 4.588T^2$ (ref. 2)

   $\Delta S°/\text{JK}^{-1}\text{mol}^{-1} = -324.3 + 0.9177T$ (ref. 2)
3. $E°(Hg/Hg_2^{2+}) = 0.7789V$ for T/K = 298.15 (ref. 2)

Calculated (Y.M.) from 1. $\log K°_{s0}(Hg_2Cl_2(s)) = -0.5110/(RT\ln 10/2F) = -17.275$;

from 2. $\log K°_{s0} = -\Delta G°/RT\ln 10 = -98849.5/5708 = -17.318$;

from 3. $\log K°_{s0} = (-0.7789 + E°(Hg/Hg_2Cl_2))/(RT\ln 10/2F) = (-0.7789 + 0.2680)/0.02958 =$

$= -17.272$, all at 298.15K

AUXILIARY INFORMATION

METHOD:

Information as to apparatus/procedure is not available to evaluator, who saw only quotations of the work in refs. 1 and 2.

SOURCE AND PURITY OF MATERIALS:

Information is not available to evaluator, who saw only quotations of the work in refs. 1 and 2.

ESTIMATED ERROR:

REFERENCES:

1. Berecki, C., Biedermann, G., Sillèn, L.G. Report to Commission V.6 of IUPAC (rather, its precursor), 1953.
2. Galloway, W.J., M.S. Thesis, University of New Zealand, 1961.

5.11. Data of Jonsson, Qvarfort and Sillèn (1947)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Sodium chloride, NaCl (7647-14-5)
3. Sodium perchlorate, $NaClO_4$ (7601-89-0)
4. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Jonsson, A., Qvarfort, I., Sillèn, L.G.,

Acta Chem. Scand. (1947) 1, 461.

VARIABLES:

One temperature, constant ionic strength, variable NaCl concentration.

PREPARED BY:

Y. Marcus, January 1978.

EXPERIMENTAL VALUES:

Measured at 25°C:

1) E.m.f. $E/V = E_1^\circ/V + (RT/2F)\ln(b/\mathrm{mol\ dm}^{-3})$ of cell
Hg, $Hg_2Cl_2(s)$, NaCl 4M/$NaClO_4$ 0.5M/$Hg_2(ClO_4)_2$ bM, $HClO_4$ 0.010M, $NaClO_4$ 0.490-3b M/Hg
(E_1° = authors' "millimolar potential" E_{10} + $(6RT/F)\ln 10$; M ≡ mol dm^{-3}).

2) Em.f. $E/V = E_2^\circ/V - (RT/F)\ \ln(c/\mathrm{mol\ dm}^{-3})$ of cell
Hg, $Hg_2Cl_2(s)$, NaCl 4M/$NaClO_4$ 0.5M/$Hg_2Cl_2(s)$, NaCl cM, $HClO_4$ 0.010M, $NaClO_4$ 0.490-cM/Hg
(E_2° = authors' "millimolar potential" E_{1X}+ $(3RT/F)\ln 10$)

For one experiment, b was specified as $4.83\ \mathrm{x}10^{-3}/(1+0.01v/\mathrm{cm}^3)$M, and $c = 0.05(v/\mathrm{cm}^3)/(100 + v/\mathrm{cm}^3)$M. For v see under Method.

Six values of $\Delta E^\circ = E_2^\circ - E_1^\circ$ obtained over a period of a year are reported:
$\Delta E^\circ/V$ = -0.4990, -0.4994, -0.4995, -0.4995, -0.4993, -0.4995
average: -0.4993 ± 0.0003. Hence $\log K'_{s0} = \Delta E^\circ/(RT/2F)\ln 10 = -16.88 \pm 0.01$ for 0.5M $NaClO_4$ medium. Correction for activity coefficients[2] is -1.05, hence $\log K_s = -17.93$.

AUXILIARY INFORMATION

METHOD:

$100\mathrm{cm}^3$ of a solution containing bM $Hg_2(ClO_4)_2$ + 0.008b M $Hg(ClO_4)_2$ + 0.010M $HClO_4$ + 0.490 - 3b M $NaClO_4$, connected via a 0.5 M $NaClO_4$ bridge to the Hg, $Hg_2Cl_2(s)$, 4M NaCl reference electrode, were titrated with $v\mathrm{cm}^3$ of a solution containing cM NaCl + 0.010 M $HClO_4$ + 0.490 - cM $NaClO_4$.
Care was taken to exclude O_2 from the solutions by bubbling purified and water vapor presaturated nitrogen. Salt bridge designed to minimize diffusion of contaminating ions. E.m.f. measured to ± 0.1 mV by Radiometer potentiometer, calibrated with Weston cell, or with Raps or Jensen compensators and Multiflex galvanometer to ± 0.05 mV. Temperature kept at 25.0 ± 0.1°C of all parts of cell and buret.

SOURCE AND PURITY OF MATERIALS:

$NaClO_4$ thrice recrystallized from 70% ethanol and dried. NaCl freed from bromide[3]. Hg twice distilled. $Hg_2(ClO_4)_2$ prepared[4] from Hg, HgO (Merck) and $HClO_4$ (Schering) analytical reagents. Hg_2Cl_2 was formed during titrations, but no description given of that salt in the (left hand) reference electrode.

ESTIMATED ERROR:

Error in $\log K'_{s0}$ is ± 0.01, from ± 0.3mV error in ΔE°.

REFERENCES:

1. Sillèn, L.G., Svensk Kem. Tidskr. (1946) 58, 52.
2. Sillèn, L.G., Acta Chem. Scand. (1949) 3, 539; Qvarfort, I., Sillèn, L.G., Acta Chem. Scand. (1949) 3, 517.
3. Güntelberg, E., Dissertation, Univ. Copenhagen (1938).
4. Pugh, W., J. Chem. Soc. (1937), 1824.

5.12. Data of Dry and Gledhill (1955)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Dry, M.E., Gledhill, J.A., Trans. Faraday Soc. (1955) 51, 1119.

VARIABLES:

One temperature

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

1. Conductivity of a saturated aqueous Hg_2Cl_2 solution at 25°C is 350.8 ± 1.0 μSm^{-1}.
2. The pH of a saturated aqueous Hg_2Cl_2 solution at 25°C is 5.085 ± 0.010.
3. The total concentration of soluble mercury species in a saturated aqueous Hg_2Cl_2 solution at 25°C is $(7.5 \pm 0.3) \times 10^{-6}$ mol dm^{-3}.

In an iterative procedure, utilizing equilibrium constants[1-3] and estimates of activity coefficient terms, authors estimated following concentrations, in 10^{-6} mol dm^{-3} to be present in the saturated solution:

H^+ 8.17 ± 0.08; Cl^- 8.40 ± 0.14; $Hg(OH)_2$ 4.03 ± 0.10; $HgCl_2$ 3.3 ± 0.4; Hg_2OH^+ 0.10; $HgCl^+$ 0.027; Hg_2^{2+} 0.0190 ± 0.0001; $HgOH^+$ 0.014.

These values sum up to the total concentration and are consistent with the pH and the conductivity (which is 99.5% due to H^+ and Cl^-). The ionic strength is 8.4×10^{-5} mol dm^{-3}, hence:

$$\log K^\circ_{s0}\ (Hg_2Cl_2(s) = Hg_2^{2+} + 2Cl^-) = \log(1.9\times10^{-8}) + 2\log(8.4\times10^{-6}) + 3\log y_{\pm Hg_2Cl_2} =$$
$$= -17.873 - 0.009 = -17.882.$$

AUXILIARY INFORMATION

METHOD:

Conductivity data extrapolated to zero time to correct for ion exchange with vessel walls, and to zero bubbling rate of nitrogen. Total mercury determined with dithizone[4] at 490 nm in supernatant solutions filtered through a sintered glass filter, made 0.06 mol dm^{-3} in HCl. Treatment with Cl_2 and boiling gave same results as without treatment. Dithizone applied in equal volume of CCl_4, and spectrophotometric readings compared with those from known amounts of $HgCl_2$, similarly treated. The pH measured with a glass electrode pH-meter, N_2 bubbled to remove dissolved CO_2, instrument standardized at pH=4.005 for 0.05 mol dm^{-3} potassium hydrogen phthalate. A Cenco-Sheard "photelometer" used for the mercury-dithizone spectrophotometric determinations. Results were independent from addition of liquid Hg to the samples for all measurements.

SOURCE AND PURITY OF MATERIALS:

Hg_2Cl_2 was precipitated in the cold from pure $Hg_2(NO_3)_2$ or $Hg_2(ClO_4)_2$ with KCl solutions at equivalent concentrations, digested and washed 50 times with conductivity water. Latter had conductivities between 1.1 and 2.4 μSm^{-1}.

ESTIMATED ERROR: No data provided to evaluate the reported random error of 4% of the total solubility, but procedure reported should eliminate systematic errors.

REFERENCES: 1. Sillèn, L.G., Acta Chem. Scand. (1949) 3, 539. 2. Hietanen, S., Sillèn, L.G., Acta Chem. Scand. (1952) 6, 747. 3. Forsling, W., Hietanen, S., Sillèn, L.G., Acta Chem. Scand. (1952) 6, 901. 4. Fischer, H., Leopoldi, G., Z. anal. Chem. (1935) 103, 241.

5.13. Data of Galloway (1961)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Barium chloride, $BaCl_2$ (10361-37-2)
3. Perchloric acid, $HClO_4$ (7601-90-3)
4. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Galloway, W.J., M.S. Thesis, Univ. of New Zealand, 1961.

VARIABLES:

Seven temperatures, five ionic strengths

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

Measured and reported e.m.f. *E* of the cell

$Hg,Hg_2Cl_2/BaCl_2$ $(1/2)xmm$, $HClO_4$ $(1-x)mm/Ba(ClO_4)_2$ $(1/3)xmm$, $HClO_4$ $(1-x)mm/$
$Hg_2(ClO_4)_2$ $(1/3)xmm$, $HClO_4$ $(1-x)mm/Hg_2Cl_2$, Hg

at seven temperatures at intervals of 5°C from 15 to 45°C, varying the concentrations in the range $0.005 \leq m$ (five values) ≤ 0.05 and $0.1 \leq x$ (four values) ≤ 0.6. Calculated and reported the double limit

$$\lim_{m\to 0}[\lim_{x\to 0(m=\text{const.})} (E-(3RT/2F)\ln(xm/3)-(RT/F)\ln 2)+3RTAm^{1/2}/(1+m^{1/2})] = -(RT/2F)\ln K^\circ_{s0}$$

$t/°C$	15	20	25	30	35	40	45
$-(RT/2F)\ln K^\circ_{s0}/V$	0.5273	0.5272	0.5273	0.5277	0.5280	0.5284	0.5291

Expressed this as the polynomial $-(RT/2F)\ln K^\circ_{s0}/V = 1.3587-7.59\times10^{-3}T + 2.273\times10^{-5}T^2 - 2.222\times10^{-8}T^3$ from least squares fitting. Hence obtained expressions for the standard thermodynamic functions for the process $Hg_2Cl_2(s) = Hg_2^{2+}(aq)+2Cl^-(aq)$ as a function of T, and specifically for $T = 298.15K$:

$\log K^\circ_{s0} = -17.827$, $\Delta G^\circ_s = 101.77$ kJ mol^{-1}, $\Delta H^\circ_s = 99.65$ kJ mol^{-1} and $\Delta S^\circ_s = -7.10$ JK^{-1} mol^{-1}

AUXILIARY INFORMATION

METHOD:

Extrapolation procedure for E° of the cell removes first the effect of the chloride concentration at a constant ionic strength, *m*, and then extrapolates to zero ionic strength a function partly corrected for activity coefficients. The points at m=0.005m were disregarded in this extrapolation (to avoid hydrolysis effects). Other activity coefficient expressions, within reason, lead to similar results.

A Cambridge Instrument potentiometer, with calibrated Weston std. cell (1.01861V), Galvanometer readable to 0.2 mA, permitting precision of ±0.1mV (at 45°C ±0.2mV). Temperature regulated to ±0.02°C. Electrodes prepared according to Hilles and Ives[1]. Deoxygenated N_2 bubbled through solutions or kept above them for removal of O_2.

SOURCE AND PURITY OF MATERIALS: Analytical reagent $HClO_4$, $BaCl_2$, HCl, $Ba(OH)_2$; prepared solutions of $Hg_2(ClO_4)_2$ by dissolving HgO in $HClO_4$, recrystallizing twice from dilute $HClO_4$, and reducing with Hg under CO_2 atmosphere, and keeping it with CO_2 and Hg. Prepared Hg_2Cl_2 by anodic dissolution of Hg in dilute HCl, washing with HCl and H_2O and drying. $Ba(ClO_4)_2$ prepared by dissolving $Ba(OH)_2$ in $HClO_4$.

ESTIMATED ERROR:

The precision of $\log K^\circ_{s0}$ is ±0.003, while the accuracy is within ±0.014.

REFERENCES:

1. Hills, G.J., Ives, D.J.G., J. Chem. Soc. (1951) 154, 311.

5.14. Data of Hansen, Izatt and Christensen (1963)

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Sodium chloride, NaCl (7647-14-5)
3. Sodium perchlorate, $NaClO_4$ (7601-89-0)
4. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Hansen, L.D., Izatt, R.M., Christensen, J.J.
Inorg. Chem. (1963) 2, 1243.

VARIABLES:

Two temperatures, constant ionic strength, variable NaCl concentration.

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

Measured e.m.f. of cells (M ≡ mol dm^{-3})

$Hg,Hg_2Cl_2(s)/NaClO_4$ 0.40M, $HClO_4$ 0.1M/$Hg_2(ClO_4)_2$ *b*M, $NaClO_4$ (0.40-3*b*)M, $HClO_4$ 0.10M/Hg

$Hg,Hg_2Cl_2(s)/NaClO_4$ 0.40M, $HClO_4$ 0.1M/$Hg_2Cl_2(s)$, NaCl *c*M, $NaClO_4$ (0.40-*c*)M, $HClO_4$ 0.10M/Hg

No primary data reported, only final results of calculations:

log K'_{s0}= -18.19 at 7°C log K'_{s0}= -16.16 at 40°C

valid for 0.40M $NaClO_4$+ 0.10M $HClO_4$ medium. Measurements and calculations followed closely those of Jonsson, Qvarfort and Sillèn[1]. If estimate of -1.05 for activity coefficient term for 0.49M $NaClO_4$+0.01M $HClO_4$ at 25°C is taken to be valid also for 0.40M $NaClO_4$+0.10M $HClO_4$ medium at 7 and 40°C, then

log K°_{s0}= -19.24 at 7°C log K°_{s0}= -17.21 at 40°C

AUXILIARY INFORMATION

METHOD:

Procedure of measurement similar to that in ref. 1, except that E° for Hg/Hg_2^{2+} obtained from the appropriate concentration cell, rather than from titration, while E° for Hg/Hg_2Cl_2-$2Cl^-$ obtained from titration of freshly precipitated Hg_2Cl_2 with excess NaCl solution.

SOURCE AND PURITY OF MATERIALS:

Solutions of $HClO_4$, $NaClO_4$ and NaCl prepared from commercial reagents of highest purity. $Hg_2(ClO_4)_2$ solutions prepared by equilibrating Hg, HgO and $HClO_4$ and filtration.

ESTIMATED ERROR: Precision given by authors on log K'_{s0} is ±0.007. Precision for log K°_{s0}, due to uncertainty in activity coefficient term is ±0.08.

REFERENCES:

1. Jonsson, A., Qvarfort, I., Sillèn, L.G., Acta Chem. Scand. (1947) 1, 461.

5.15. Other data

COMPONENTS:

1. Mercury(I) chloride, Hg_2Cl_2 (10112-91-1)
2. Water, H_2O (7732-18-5)

ORIGINAL MEASUREMENTS:

Unknown[1]

VARIABLES:

Three temperatures

PREPARED BY:

Y. Marcus, January 1978

EXPERIMENTAL VALUES:

The solubility of Hg_2Cl_2 in water given as

t/°C	0	20	40
$10^6 s_{Hg}$/mol kg^{-1}	3.0	4.9	12.7

The solubility product is reported as 2×10^{-18} mol^{2}kg^{-2} at 25°C

AUXILIARY INFORMATION

METHOD:

The report appears in a compilation[1] which does not give its sources.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

1. Freier, R.K., Aqueous Solutions, de Gruyter, Berlin (1976), p. 68.