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# Thermodynamic Properties of Import to Environmental Processes and Remediation. I. Previous Thermodynamic Property Values for Cadmium and Some of Its Compounds

Donald G. Archer<sup>a)</sup>

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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The sources of previous thermodynamic property values are detailed for cadmium and some compounds of cadmium that might be expected as derivative from anthropogenic introduction of cadmium into the environment or are required for calculation of thermodynamic properties of cadmium-containing systems. Included are descriptions of the sources of information and methodology used to obtain the values for these compounds reported in the NBS series of publications loosely and collectively referred to as the NBS Thermodynamics Tables. © 1998 American Institute of Physics and American Chemical Society. [S0047-2689(98)00105-6]

Key words: aqueous solutions; thermodynamic properties.

## Contents

1. Introduction.....	915
1.1. Considerations Concerning Cadmium Compounds.....	916
1.2. Acknowledgments.....	917
1.3. References for the Introduction.....	917
2. Cd(cr).....	917
3. Cd <sup>2+</sup> (aq).....	918
4. CdCl <sub>2</sub> (cr).....	926
5. CdCl <sub>2</sub> ·H <sub>2</sub> O(cr).....	926
6. CdCl <sub>2</sub> ·2.5H <sub>2</sub> O(cr).....	928
7. CdCl <sup>+</sup> (aq).....	928
8. CdCl <sub>2</sub> <sup>0</sup> (aq).....	930
9. CdCl <sub>3</sub> <sup>-</sup> (aq).....	930
10. CdO(cr).....	931
11. Cd(OH) <sub>2</sub> (cr).....	933
12. Cd(OH) <sub>2</sub> <sup>0</sup> (aq).....	934
13. CdOH <sup>+</sup> (aq).....	935
14. Cd(OH) <sub>3</sub> <sup>-</sup> (aq).....	936
15. Cd(OH) <sub>4</sub> <sup>2-</sup> (aq).....	936
16. HCdO <sub>2</sub> <sup>-</sup> (aq).....	937
17. CdO <sub>2</sub> <sup>2-</sup> (aq).....	937
18. CdSO <sub>4</sub> <sup>0</sup> (aq).....	937
19. CdSO <sub>4</sub> (cr).....	938
20. CdSO <sub>4</sub> ·H <sub>2</sub> O(cr).....	939
21. CdSO <sub>4</sub> ·(H <sub>2</sub> O) <sub>8/3</sub> (cr).....	940
22. (CdO) <sub>2</sub> ·CdSO <sub>4</sub> (cr).....	942
23. CdCO <sub>3</sub> (cr).....	942
24. CdCO <sub>3</sub> <sup>0</sup> (aq).....	944
25. Appendix.....	944

## 1. Introduction

This is the first in a series of documents that describe some of the sources of values of thermodynamic properties of materials and systems that are essential in the calculation and prediction of environmental fates of particular materials and environmental remediation technologies. Also essential in the environmental arena is the determination of “risk” (93CAR). A risk analysis incorporates validation of the data being used in calculations and in decision-making processes. The present series of documents contain information required to assess the reliability of values calculated from some environmental simulations.

Many believe these thermodynamic properties are well enough known that such calculations, for example calculation of the aqueous concentration of cadmium in an aquifer, are primarily an exercise in numerical analysis. This belief has been fostered, perhaps, by the large number of “data evaluations” and/or compendia that list thermodynamic properties of these substances and the observation that these values are almost always nearly identical. However, many of these sources of thermodynamic information merely repeat “evaluated” thermodynamic information gleaned from other literature sources rather than having examined the measurements that might have led to the thermodynamic properties. As an example, both 78ROB/HEM and 84PAN cite the NBS Tables (68WAG/EVA) as a source for some of the thermodynamic properties they gave for compounds and minerals containing cadmium. Indeed, the number of “thermodynamic property evaluations” for many individual cadmium compounds far outnumber the thermodynamic measurements upon which they are based. This was recently and ably demonstrated for cadmium carbonate (otavite) by 93STI/PAR. They showed, in their Fig. 1, the existence of a large number (28) of “data evaluations,” most of which were directly or indirectly traceable to only a very small number (4) of actual thermodynamic measurements for crystalline cadmium carbonate (counting the CdCO<sub>3</sub> decomposition studies as one

<sup>a)</sup>Electronic mail: donald.archer@nist.gov

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study). Furthermore, the few direct examinations of the thermodynamic measurements often did not describe the measurements examined and/or how the "evaluated" thermodynamic properties were obtained from those measurements. For example, all of the  $\Delta_f H$  values for  $\text{CdCO}_3(\text{cr})$  arose from a measurement reported in 1883, but one is not told this in the thermodynamic property compendia.

The existence of a large number of compendia reporting similar values, combined with the absence of critical examinations of the foundations of these compendia, have led to a widespread, but mistaken, impression that sufficient knowledge exists of the thermodynamic properties of toxic metals released or redistributed in the environment.

A heavily mentioned source of thermodynamic property values, the NBS Tables, was cited above (68WAG/EVA, 82WAG/EVA). These values were not documented as to source and methodology. The present series of articles describe, as best as can be discerned, how those values were determined. The present series of articles include not just the measurements and pathways used, but also itemize the measurements considered, but not used, by Wagman *et al.* The present document should not be cited as a source for thermodynamic property values from either 68WAG/EVA or from 82WAG/EVA; values from those sources should be cited as being from those sources, even if the individual doing the citing has corrected an arithmetic error contained in those values based on information contained in this document. Finally, the articles detail relevant measurements that have appeared in the literature since the time the NBS Tables values were prepared.

The documentation and investigation of the methods used by Wagman *et al.* have been prompted, in large part, by creation of a new investigation of some of these properties at NIST and, in lesser part, by difficulties encountered by current NIST staff in response to requests for information from the technical community. Our examinations have identified arithmetic errors affecting the tabulated values, as well as errors in the processing of the measured values.

The organization of the current series of articles is as follows. Under each substance described will be six sections. The first section, A, will describe the methodology and the measurements that led to the value given in the NBS Tables. This information was kept on loose papers, "worksheets," that have been kept in file cabinets at NIST. Not all of the "worksheets" were equally understandable. As such, we have not been able to discern sources for all values; sometimes the worksheets have been too cryptic to be understood. This also applies to some of the auxiliary values; many of these were not listed on the worksheets. Tracing all auxiliary values (osmotic coefficients, saturation molalities, etc.) and in many cases making assumptions from where they may have come did not seem a wise investiture of resources. Therefore, the sources of these values were not guessed if they were not identified on a worksheet. The second section, B, contains comments by the author of the article regarding the methodology used in generation of the NBS Tables values. In section B, such things as arithmetic errors, erroneous

auxiliary values that might have been used, etc., will be identified. Section C details the auxiliary substances required to obtain the NBS Tables thermodynamic property values for the title substance. The measurements examined by the NBS Tables staff, but not used in their final assessment, are described in section D. Section E describes more recent measurements that could lead to thermodynamic property values. Other evaluations or compendia of thermodynamic properties of the substances are not listed in this section, regardless of quality. This is due to the large number of such evaluations (*vide supra*). Finally, references are given within section F for each title substance.

It is not always clear-cut for which substance one might place some of the new measurements in a document such as this. Thus, one reader might consider inclusion of, say, osmotic coefficient measurements for aqueous cadmium chloride underneath  $\text{Cd}^{2+}(\text{aq})$  as correct, whereas another might consider entry under  $\text{CdCl}^+(\text{aq})$  to be more correct. We choose not to involve ourselves with that level of minutiae.

### 1.1. Considerations Concerning Cadmium Compounds

Cadmium poses health concerns at very low levels of ingestion or inhalation. Ongoing federal regulations concern anthropogenically caused cadmium concentrations in the workplace and in the environment. Large natural deposits of cadmium minerals are primarily limited to forms of cadmium sulfide ( $\text{CdS}$ ), e.g., greenockite, Hawleyite, and xanthochroite, and one significant-sized deposit of otavite,  $\text{CdCO}_3$ , located in Africa. Other mineral forms of cadmium are generally found in deposits of other metals. Cadmium is recovered commercially from ore processing and is found in the tailings from zinc, copper, and lead mineral deposits. Runoff from tailings-piles can potentially contaminate ground water and surface water. Commercially, cadmium is found in batteries and solders, is used in electroplating and fission control, and is also used as a pigment and in phosphors. Thus, cadmium might be found at low levels in solid-waste streams intended for incineration, either as simple waste elimination or as fuel in waste-to-energy facilities.

Cadmium ions dissolved in water are strongly precipitated by hydroxide and by carbonate ions. However, these precipitation mechanisms are significantly dependent on imposed or natural conditions. For example, the solubility of cadmium hydroxide in water changes by two orders of magnitude for every unit change in pH. Otavite solubility depends on pH and on  $\text{CO}_2$  partial pressure. Further complicating the impact of cadmium on the environment is the ready ability of cadmium to substitute for calcium in crystal lattices, thus resulting in such substitution in calcite-containing formations.

Some of the values given in the NBS Tables for the cadmium compounds, discussed below, were found to have been miscalculated. This is unfortunate as some of these values have been used in calculation of thermodynamic properties of other, more complex cadmium-containing compounds.

It is also worth noting that heavy use of  $\text{Cd}(\text{Hg})$  amalgam electrodes was made in determining the thermodynamic

properties of  $\text{Cd}^{2+}(\text{aq})$  and some of the other species. Hence, most of the tabulated Gibbs energies of formation of cadmium-containing compounds ultimately contain within their pedigree the Gibbs energy of the reaction,  $\text{Cd}(\text{cr}) + \text{Hg}(\text{l}) = \text{Cd}(\text{Hg, two-phase})$ . Yet, there are very few measurements, most old, of this reaction in the literature. The problem of validating reliability has been exacerbated by not describing this weak link. As an example, the CODATA Key Values for Thermodynamics (89COX/WAG) does not mention the thermodynamic properties of cadmium amalgam, but includes the aqueous cadmium ion as a key species. In their description of the source of their properties for aqueous cadmium ion, they stated “ $\Delta_f G^\circ$  was calculated from the electromotive forces (emfs) of the following types of cells containing Cd/Cd<sup>2+</sup> electrodes.” But this was not really true, almost all of the cell measurements involved amalgam cells, not cadmium metal cells. 89COX/WAG had to use some value for the generation of the amalgam reaction and they did not inform the reader of the value or its basis. One can easily argue that because the thermodynamic properties of  $\text{Cd}^{2+}(\text{aq})$  were determined primarily from the thermodynamic properties of cadmium amalgams, the cadmium amalgams are more “key” than  $\text{Cd}^{2+}(\text{aq})$  and should have been included in the Key Values.

There is no doubt that cadmium forms complexes in solution. However, the only evidence of some of the complexes that have been reported in the literature was their inclusion in the representation of a set of thermodynamic measurements. The author invokes the principle that a set of thermodynamic measurements can be supportive of more than one set of complexation assumptions, particularly when one can tinker with nonideality models in the process. It is possible that some of the aqueous species described below are fictitious and are nothing more than a fitting parameter. They have nonetheless been included because they were included in 82WAG/EVA and the reader can judge for himself. The author makes no claim in this article regarding the usefulness of the reported aqueous species.

The present document is relevant to the origin of values from both 68WAG/EVA and 82WAG/EVA. The 82WAG/EVA values are slightly different than the 68WAG/EVA values because the former chose to tabulate values relative to 1 bar standard pressure, whereas the latter chose 1 atm. The effect of this small pressure difference on the tabulated values is described in 82WAG/EVA. The specific calculations in the following pages should give the numerical values in 68WAG/EVA, rather than those in 82WAG/EVA. This is because the worksheets correspond to the 1 atm standard pressure.

## 1.2. Acknowledgments

The author wishes to recognize the efforts of Rhoda Levin and of Tamar Thorne in the collection of literature articles and especially thanks Rhoda Levin for a very careful proof-reading of the article.

## 1.3. References for the Introduction

- 68WAG/EVA Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., Selected Values of Chemical Thermodynamic Properties. Tables for the first Thirty-Four Elements in the Standard Order of Arrangement. (NBS Tech. Note 270-3, 1968).
- 78ROB/HEM Robie, R. A., Hemingway, B. S., Fisher, J. R., Thermodynamic Properties of Minerals and Related Substance at 298.15 K and 1 Bar ( $10^5$  Pascals) Pressure and at Higher Temperatures. (USGS Bull. 1452, 1978).
- 82WAG/EVA Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L., J. Phys. Chem. Ref. Data **11**, Suppl. 2 (1982).
- 84PAN Pankratz, L. B., Thermodynamic Properties of Halides. (USBM Bull. 674, 1984).
- 89COX/WAG Cox, J. D., Wagman, D. D., Medvedev, V. A., CODATA Key Values for Thermodynamics (Hemisphere, New York, 1989).
- 93CAR Carnegie Commission on Science, Technology, and Government, Risk and the Environment, Improving Regulatory Decision Making (Carnegie Commission, NY, 1993).
- 93STI/PAR Stipp, S. L. S., Parks, G. A., Nordstrom, D. K., Leckie, J. O. Geochim. Cosmochim. Acta **57**, 2699 (1993).

## 2. Cd(cr)

### A. Selected Values, NBS Tables

The NBS Tables list two forms of crystalline cadmium,  $\alpha$  and  $\gamma$ . The NBS Tables values for  $\text{Cd}(\gamma, \text{cr})$  were taken from 63HUL/ORR as  $H^\circ(T=298.15 \text{ K}) - H^\circ(T=0 \text{ K}) = 6.238 \text{ kJ}\cdot\text{mol}^{-1}$  ( $1.491 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $S^\circ = 51.76 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $12.37 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and  $C_p^\circ = 25.98 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $6.21 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

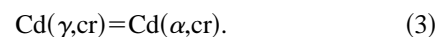
The Gibbs energy of formation of the  $\alpha$  form of cadmium from the  $\gamma$  form was calculated from the emf for the cell reaction:



The 298.15 K emf value was listed as 0.04742 V (17GET) with a temperature coefficient of  $-0.000200 \text{ V/K}$ . The compilers combined this emf with an emf value for the electrochemical cell:



of 0.05047 V  $-0.0002437 \text{ V/K}$  ( $T=298.15 \text{ K}$ ). The appropriate difference gave  $E^\circ = 0.00305 \text{ V} - 0.0000437 \text{ V/K}$  ( $T=298.15 \text{ K}$ ) as the emf for reaction



Conversion to joules gave the Gibbs energy of formation of the  $\alpha$  phase from the  $\gamma$  phase as  $-0.59 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.141 \text{ kcal}\cdot\text{mol}^{-1}$ ). The temperature dependence of the two cell's emfs was used to give  $\Delta_f S^\circ$  of  $-8.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-2.0 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and  $\Delta_f H^\circ$  of  $-3.08 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.737 \text{ kcal}\cdot\text{mol}^{-1}$ ). However, these two latter values do not match the NBS Tables entries that are consistent only with  $\Delta_f S^\circ$  of  $0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Other calculations under the heading Cd(Hg) gave  $\Delta_f S^\circ$  of  $0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for Cd( $\alpha$ , cr). This value was consistent with measurements from 34PAR/LAM.

## B. Comments

No examination of the thermal property measurements for the  $\gamma$  phase appeared to have been made. No explanation was found for the differences between the tabulated values and the values on the worksheets for the entropy and the heat of formation of the  $\alpha$  phase.

## C. Auxiliary Values Required for Data Pathway

$$\Delta_f G^\circ[\text{Cd}(\text{Hg})]$$

## D. Other Thermodynamic Measurements Considered

The emf for the Cd(Hg)=Cd( $\gamma$ ,cr) cell was supported by the measurements from 34PAR/LAM on a similar cell.

## E. More Recent Determinations of the Thermodynamic Properties of Cd(cr)

69CET/HOL reported measurements of heat capacity from 1 to 30 K.

## F. Bibliography

- 17GET Getman, F. H., *J. Am. Chem. Soc.* **39**, 1806 (1917).
- 34PAR/LAM Parks, W. G., La Mer, V. K., *J. Am. Chem. Soc.* **56**, 90, 2797 (1934).
- 63HUL/ORR Hultgren, R. R., Orr, R. L., Anderson, P. D., Kelley, K. K., *Selected Values of Thermodynamic Properties of Metals and Alloys* (Wiley, New York, 1963).
- 69CET/HOL Cetas, C. T., Holste, J. C., Swenson, C. A., *Phys. Rev.* **182**, 679 (1969).

## 3. Cd<sup>2+</sup>(aq)

### A. Selected Values, NBS Tables

The entropy of Cd<sup>2+</sup>(aq) was obtained as the average of three values. The first was obtained from the combination of a heat of solution measurement of CdSO<sub>4</sub>(cr) and an entropy determination for the same, both from 55PAP/GIA, and values of the solubility and activity coefficient at saturation. The worksheets indicated these values (some unspecified) gave an entropy of Cd<sup>2+</sup>(aq) of  $-73.39 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-17.54$

$\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). Another value,  $-75.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-18.0 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) was obtained from the entropy of CdCl<sub>2</sub>(cr) from 59ITS/STR, the enthalpy of the solution of CdCl<sub>2</sub>(cr) from 1887PIC, the enthalpy of dilution measurements from 42ROB/WAL, vapor pressure measurements, an aqueous solubility and an activity coefficient of saturated CdCl<sub>2</sub>(aq). The source of the latter three was not given, but probably corresponds to values described under CdCl<sub>2</sub>(cr); refer to Sec. 4. A third value,  $-71.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-17.0 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), was listed as having been determined from decomposition pressure, heat of solution (30ISH/UED, item 9 in section D below), an aqueous solubility value, a saturated solution activity coefficient and an entropy for CdBr<sub>2</sub>(cr). Sources and values for these were not present on the worksheets. The unweighted average of the three values was  $-73.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-17.5 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

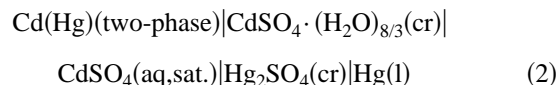
The  $\Delta_f G^\circ$  of Cd<sup>2+</sup>(aq) appears to have been taken from an average of 18 different values obtained from measurements on the sulfate, chloride and bromide, and 10 of the 18 were counted twice for the average. The 18 values were:

1. The 31LAM/PAR measurements for the electrochemical cell:



were indicated as one source of the aqueous ion's  $\Delta_f G^\circ$ . The emf of this cell, 0.04641 abs. V, was converted to a  $\Delta_f G^\circ = -8.956 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.1405 \text{ kcal}\cdot\text{mol}^{-1}$ ). This was combined with  $\Delta_f G^\circ$  values for Pb(Hg), Cd(Hg), and PbSO<sub>4</sub>(cr) of  $-1.13 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.27 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-9.740 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.328 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-813.20 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-194.36 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively, to obtain  $\Delta_f G^\circ[\text{CdSO}_4\cdot(\text{H}_2\text{O})_{8/3}] = -1464.02 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-349.909 \text{ kcal}\cdot\text{mol}^{-1}$ ). On the worksheets for Cd<sup>2+</sup>(aq), it was indicated that these measurements gave a value of  $\Delta_f G^\circ$  for Cd<sup>2+</sup>(aq) of  $-77.442 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.509 \text{ kcal}\cdot\text{mol}^{-1}$ ); the worksheets for CdSO<sub>4</sub> indicate they gave a value of  $-76.199 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.212 \text{ kcal}\cdot\text{mol}^{-1}$ ).

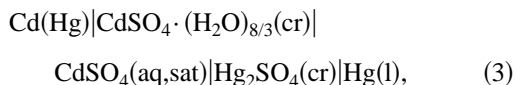
2. 41VIN/BRI measured the emf of the electrochemical cell:



from 293.15 to 323.15 K. The worksheets indicated the Gibbs energy change for Eq. (2) at 298.15 K to be  $-196.447 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-46.952 \text{ kcal}\cdot\text{mol}^{-1}$ ) calculated from the emf of 1.01844 abs. V. This quantity was combined with  $\Delta_f G^\circ$  values for Cd(Hg), Hg<sub>2</sub>SO<sub>4</sub>(cr), and H<sub>2</sub>O(l) of  $-9.740 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.328 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-625.880 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-149.589 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-237.183 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-56.688 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively, and a contribution from the nonideality of 8/3 mol of water in the saturated solution,  $-0.761 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.182 \text{ kcal}\cdot\text{mol}^{-1}$ ). The  $\Delta_f G^\circ[\text{CdSO}_4(\text{H}_2\text{O})_{8/3}(\text{cr})]$  was calculated to be  $-1465.316 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-350.219 \text{ kcal}\cdot\text{mol}^{-1}$ ). Removal of the  $\Delta_f G^\circ$  for 8/3 mol of water and the nonideality contribution for water, followed by inclusion of the nonideality con-

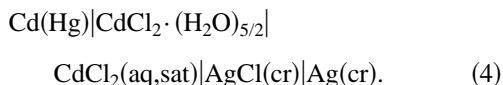
tribution for  $\text{CdSO}_4(\text{aq})$  in saturated solution gave  $\Delta_f G^\circ[\text{CdSO}_4(\text{aq})] = -822.127 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-196.493 \text{ kcal}\cdot\text{mol}^{-1}$ ).  $\Delta_f G^\circ[\text{Cd}^{2+}(\text{aq})] = -77.500 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.523 \text{ kcal}\cdot\text{mol}^{-1}$ ).

3. 31ISH/MUR measured the emf of the electrochemical cell:



obtaining 1.01845 int. V for 298.15 K. This value was used to obtain a Gibbs energy of formation of  $-1465.404 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-350.240 \text{ kcal}\cdot\text{mol}^{-1}$ ). See  $\text{CdSO}_4\cdot(\text{H}_2\text{O})_{8/3}(\text{cr})$ , section 22. From this value, the  $\Delta_f G$  for 8/3 mol of  $\text{H}_2\text{O(l)}$  and the nonideality contribution for the solvent were removed and then to it was added a nonideality contribution for the solute, taken to be  $9.941 \text{ kJ}\cdot\text{mol}^{-1}$  ( $2.376 \text{ kcal}\cdot\text{mol}^{-1}$ ). The resulting  $\Delta_f G^\circ$  for  $\text{CdSO}_4(\text{aq})$  was  $-822.215 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-196.514 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $\Delta_f G^\circ$  for  $\text{Cd}^{2+}(\text{aq})$  was  $-77.588 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.544 \text{ kcal}\cdot\text{mol}^{-1}$ ). However,  $-18.544$  was transcribed as  $-18.514$  for the calculation of the average.

4. 21TAY/PER measured the electrochemical potential of the cell:



The 298.15 K emf yielded a value of  $\Delta_r G = -120.608 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-28.826 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value was combined with  $\Delta_f G^\circ$  values for  $\text{AgCl}(\text{cr})$ ,  $\text{H}_2\text{O(l)}$ , and  $\text{Cd(Hg)}$ , of  $-109.805 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-26.244 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-237.183 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-56.688 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-9.740 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.328 \text{ kcal}\cdot\text{mol}^{-1}$ ) and a nonideality correction for the water in saturated solution  $-0.473 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.113 \text{ kcal}\cdot\text{mol}^{-1}$ ) per mole of water. These values yielded  $\Delta_f G^\circ[\text{CdCl}_2\cdot(\text{H}_2\text{O})_{5/2}(\text{cr})] = -944.094 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-225.644 \text{ kcal}\cdot\text{mol}^{-1}$ ).

5. 36HAR/FIT measured the emf of the electrochemical cell:



from 0.0005 to 1 M and from 273.15 to 313.15 K. The Gibbs energy calculated from the 298.15 K  $E^\circ$  was  $-110.784 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-26.478 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this with  $\Delta_f G^\circ$  values for  $\text{AgCl}(\text{cr})$ , and  $\text{Cd(Hg)}$ , given in the preceding paragraph, gave  $\Delta_f G^\circ[\text{CdCl}_2(\text{aq})]$  of  $-340.134 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-81.294 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $\Delta_f G^\circ[\text{Cd}^{2+}(\text{aq})] = -77.613 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.550 \text{ kcal}\cdot\text{mol}^{-1}$ ).

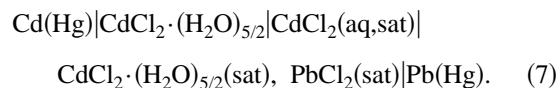
6. 58TRE/FER measured the emf of the electrochemical cell:



at 298.15 K and for values of  $m$  from  $\sim 0.0011$  to  $\sim 0.022 \text{ mol}\cdot\text{kg}^{-1}$ . Their value of  $E^\circ = 0.5745$  abs. V was used to determine  $\Delta_r G = -110.863 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-26.497 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with  $\Delta_f G^\circ$  values for  $\text{AgCl}(\text{cr})$ , and  $\text{Cd(Hg)}$ , given in item 4, gave

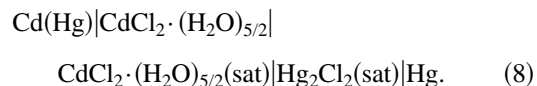
$\Delta_f G^\circ[\text{CdCl}_2(\text{aq})]$  of  $-340.214 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-81.313 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $\Delta_f G^\circ[\text{Cd}^{2+}(\text{aq})] = -77.693 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.569 \text{ kcal}\cdot\text{mol}^{-1}$ ).

7. 30PRI/VOS measured the emf of the electrochemical cell:



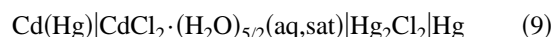
The 298.15 K emf of the cell, 0.14072 int. V, was used to calculate  $\Delta_r G = -27.167 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-6.493 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this with  $\Delta_f G^\circ$  for  $\text{H}_2\text{O(l)}$ ,  $\text{Cd(Hg)}$ ,  $\text{Pb(Hg)}$ , and  $\text{PbCl}_2(\text{cr})$  of  $-237.183 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-56.688 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-9.740 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.328 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-1.13 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.27 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-314.14 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-75.08 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively, and a nonideality correction for the water in saturated solution, was used to calculate  $\Delta_f G^\circ[\text{CdCl}_2\cdot(\text{H}_2\text{O})_{5/2}(\text{cr})] = -944.053 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-225.634 \text{ kcal}\cdot\text{mol}^{-1}$ ).

8. 30PRI/VOS measured the emf of the electrochemical cell:



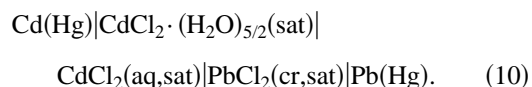
The 298.15 K emf, 0.6706 int. V, was used to calculate  $\Delta_r G = -129.449 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-30.939 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value was combined with  $\Delta_f G^\circ$  for  $\text{H}_2\text{O(l)}$ ,  $\text{Cd(Hg)}$ , and  $\text{Hg}_2\text{Cl}_2(\text{cr})$  of  $-237.183 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-56.688 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-9.740 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.328 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $-210.777 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-50.377 \text{ kcal}\cdot\text{mol}^{-1}$ ), and a nonideality correction for the water in saturated solution of  $-0.473 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.113 \text{ kcal}\cdot\text{mol}^{-1}$ ). These values yielded  $\Delta_f G^\circ[\text{CdCl}_2\cdot(\text{H}_2\text{O})_{5/2}(\text{cr})] = -944.107 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-225.647 \text{ kcal}\cdot\text{mol}^{-1}$ ).

9. 16LIP/HUL determined the emf of the electrochemical cell:



from 288.15 to 303.15 K. The 298.15 K emf, 0.67102 abs. V was used to calculate  $\Delta_r G = -129.491 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-30.949 \text{ kcal}\cdot\text{mol}^{-1}$ ). No other auxiliary values were given on the worksheets. Checking their worksheet value of  $\Delta_f G^\circ[\text{CdCl}_2\cdot(\text{H}_2\text{O})_{5/2}(\text{cr})] = -944.144 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-225.656 \text{ kcal}\cdot\text{mol}^{-1}$ ) with other values on those sheets and  $\Delta_f G^\circ[\text{Hg}_2\text{Cl}_2(\text{cr})]$  from the NBS Tables gave  $\Delta_f G^\circ[\text{CdCl}_2\cdot(\text{H}_2\text{O})_{5/2}(\text{cr})] = -944.115 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-225.649 \text{ kcal}\cdot\text{mol}^{-1}$ ).

10. The worksheets used information that 32ISH/KIM indicated was from OBA (year unknown). Purportedly, OBA measured the emf of the cell:

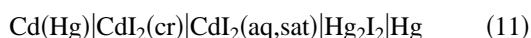


The emf was taken to be 0.14074 abs. V at 298.15 K which was then used to obtain  $\Delta_r G = -27.158 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-6.491 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value was

combined with  $\Delta_f G^\circ$  values for  $\text{PbCl}_2(\text{cr})$ ,  $\text{Cd}(\text{Hg})$ ,  $\text{H}_2\text{O}(\text{l})$ ,  $\text{Pb}(\text{Hg})$  ("0.72% by weight"), of  $-314.135 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-75.08 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-9.740 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.328 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-237.183 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-56.688 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-2.109 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.504 \text{ kcal}\cdot\text{mol}^{-1}$ ) and also a non-ideality correction for the water in saturated solution of  $-0.473 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.113 \text{ kcal}\cdot\text{mol}^{-1}$ ) per mole of water. The lead amalgam was taken as saturated and its  $\Delta_f G^\circ$  was taken to be  $-1.130 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.27 \text{ kcal}\cdot\text{mol}^{-1}$ ). These values yielded  $\Delta_f G^\circ[\text{CdCl}_2\cdot(\text{H}_2\text{O})_{5/2}(\text{cr})] = -944.044 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-225.632 \text{ kcal}\cdot\text{mol}^{-1}$ ).

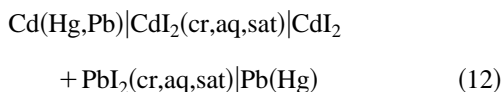
Each of the  $\Delta_f G^\circ$  values for  $\text{CdCl}_2\cdot(\text{H}_2\text{O})_{5/2}(\text{cr})$  was converted into a value for  $\text{CdCl}_2(\text{aq, std})$  by removing  $\Delta_f G^\circ$  for 2.5 mol  $\text{H}_2\text{O}$ , removing the nonideality contribution for water and adding a nonideality contribution for the solute  $\{-RT \ln[4(m\gamma)^3]\}$ . The values taken for the saturation molality and activity coefficient were  $6.566 \text{ mol}\cdot\text{kg}^{-1}$  and 0.02564. The Gibbs energy of formation of the aqueous chloride ion was taken to be  $-131.260 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-31.372 \text{ kcal}\cdot\text{mol}^{-1}$ ). This resulted in calculated values for  $\Delta_f G^\circ[\text{Cd}^{2+}(\text{aq})]$  of  $-77.617 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.551 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-77.576 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.541 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-77.630 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.554 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-77.672 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.564 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-77.571 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.540 \text{ kcal}\cdot\text{mol}^{-1}$ ), for items 4, 7, 8, 9, and 10, respectively.

11. 28YOS measured the emf of the cell:

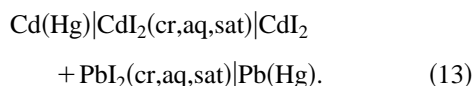


from 298.15 to 308.15 K. The 298.15 K emf of 0.41735 abs. V was used to obtain  $\Delta_r G = -80.538 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-19.249 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with  $\Delta_f G^\circ$ 's of  $\text{Cd}(\text{Hg})$  and  $\text{Hg}_2\text{I}_2(\text{cr})$ ,  $-9.740 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.328 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-111.00 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-26.53 \text{ kcal}\cdot\text{mol}^{-1}$ ), gave  $\Delta_f G^\circ[\text{CdI}_2(\text{cr})] = -201.280 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-48.107 \text{ kcal}\cdot\text{mol}^{-1}$ ).

12. 27VOS measured the emf of the cell:



from 288.15 to 313.15 K. The emf of the cell:  $\text{Cd}(\text{Pb, Hg})|\text{Cd}^{2+}(\text{aq})|\text{Cd}(\text{Hg})$  was also measured and used to obtain the emf of:



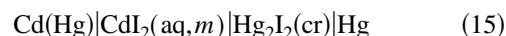
The 298.15 K emf, 0.0996 int. V, was used to calculate  $\Delta_r G = -19.20 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-4.59 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with  $\Delta_f G^\circ$  of  $\text{Cd}(\text{Hg})$ ,  $\text{Pb}(\text{Hg})$  and  $\text{PbI}_2(\text{cr})$ , the former two given in previous items, and the latter,  $-173.64 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-41.50 \text{ kcal}\cdot\text{mol}^{-1}$ ); gave  $\Delta_f G^\circ[\text{CdI}_2(\text{cr})] = -201.46 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-48.15 \text{ kcal}\cdot\text{mol}^{-1}$ ). 27VOS reported a persistent hysteresis of the observed cells corresponding to Eq. (12).

13. 41BAT measured the emf of the cell:



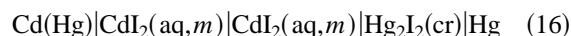
from 278.15 to 313.15 K and from 0.001 224 to 2.0742  $\text{mol}\cdot\text{kg}^{-1}$ . Only the 298.15 K measurements were considered, and of these, only those for  $m = (0.095 42 \text{ to } 2.0742) \text{ mol}\cdot\text{kg}^{-1}$  (six values) were considered. For each of these concentrations a  $\Delta_f G^\circ$  of  $\text{CdI}_2(\text{aq, std})$  was calculated using 41BAT's values for the activity coefficient and  $\Delta_f G^\circ[\text{AgI}(\text{cr})] = -66.19 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-15.82 \text{ kcal}\cdot\text{mol}^{-1}$ ) and then these six values were averaged to obtain  $\Delta_f G^\circ[\text{CdI}_2(\text{aq, std})] = -180.786 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-43.209 \text{ kcal}\cdot\text{mol}^{-1}$ ). (41BAT's value of  $E^\circ$  can be used to obtain  $-180.845 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\Delta_f G^\circ[\text{CdI}_2(\text{aq, std})]$ .)

14. 37ISH/TAK measured the emf of the cell:



for molalities from 0.099 36 to 2.2190  $\text{mol}\cdot\text{kg}^{-1}$  at 298.15 K. The same procedure was used as in item 13, however the activity coefficients were indicated as being from Robinson and Stokes, with no other reference details. Their average of values obtained from the seven molality values gave  $\Delta_f G^\circ[\text{CdI}_2(\text{aq, std})] = -180.845 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-43.223 \text{ kcal}\cdot\text{mol}^{-1}$ ).

15. 37BAT/VOS measured the emf of the electrochemical cell:



from 298.15 to 318.15 K and for molalities from 0.001 025 to 2.366  $\text{mol}\cdot\text{kg}^{-1}$ ; the last of these values being that for the saturated solution. Only the value for the 298.15 K saturated solution was considered. The emf of the cell containing saturated solution, 0.417 16 abs. V, was used to calculate  $\Delta_r G = -80.500 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-19.240 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with  $\Delta_f G^\circ$  for  $\text{Hg}_2\text{I}_2(\text{cr})$  and  $\text{Cd}(\text{Hg})$ , both given above, gave  $\Delta_f G^\circ[\text{CdI}_2(\text{aq})] = -180.845 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-43.223 \text{ kcal}\cdot\text{mol}^{-1}$ ). In this case,  $\Delta_f G^\circ[\text{CdI}_2(\text{aq})] = -180.786 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-43.209 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated using  $m_{\text{sat}} = 2.366 \text{ mol}\cdot\text{kg}^{-1}$  and  $\gamma_{\text{sat}} = 0.0171$ . These values are different from those used for this calculation in other items, the net difference being about  $20 \text{ J}\cdot\text{mol}^{-1}$ .

16. 21TAY/PER measured the emf of the electrochemical cell:



from 273.15 to 313.15 K. The 298.15 K emf, 0.3036 abs. V, was used to calculate  $\Delta_r G = -58.584 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-14.002 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with  $\Delta_f G^\circ$  of  $\text{Cd}(\text{Hg})$  and  $\text{AgI}(\text{cr})$ , given in previous items, gave  $\Delta_f G^\circ[\text{CdI}_2(\text{cr})] = -200.706 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-47.970 \text{ kcal}\cdot\text{mol}^{-1}$ ).

Each of the  $\Delta_f G^\circ$  values for  $\text{CdI}_2(\text{cr})$ , with the exception of item 15, was converted into a value for  $\text{CdI}_2(\text{aq, std})$  by adding a nonideality contribution for the solute  $\{-RT \ln[4(m\gamma)^3]\}$ . The values taken for the saturation molality and activity coefficient were  $2.377 \text{ mol}\cdot\text{kg}^{-1}$  and 0.01698. (Item 15 used different values for solubility and activity coefficient.) The Gibbs energy of formation of the aqueous iodide ion was taken to be  $-51.59 \text{ kJ}\cdot\text{mol}^{-1}$

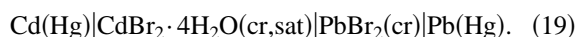
( $-12.33 \text{ kcal}\cdot\text{mol}^{-1}$ ). The resultant values from items 11–16 for  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]$  were  $-77.65$ ,  $-77.84$ ,  $-77.61$ ,  $-77.67$ ,  $-77.61$ , and  $-77.10 \text{ kJ}\cdot\text{mol}^{-1}$ .

17. 37ISH/TAK measured the emf of the electrochemical cell:



for seven molalities from  $m=0.2393$  to  $m_{\text{sat}}=4.120 \text{ mol}\cdot\text{kg}^{-1}$  at  $298.15 \text{ K}$ . The same procedure was used as in item 13; the activity coefficients were indicated as being from Robinson and Stokes with no other reference details. The worksheet indicated the average of six values (the saturation molality was not included) which gave  $\Delta_f G^\circ [\text{CdBr}_2(\text{aq})]=-285.478 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-68.231 \text{ kcal}\cdot\text{mol}^{-1}$ ). (The standard deviation of the sample of the six values was  $\sim 280 \text{ J}\cdot\text{mol}^{-1}$ .)

18. 21OBA measured the emf of the electrochemical cell:



The  $298.15 \text{ K}$  emf of this cell, taken to be  $0.14312 \text{ abs. V}$ , gave  $\Delta_f G = -27.619 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-6.601 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with  $\Delta_f G^\circ$  of  $\text{Cd}(\text{Hg})$ ,  $\text{H}_2\text{O}(\text{l})$ ,  $\text{Pb}(\text{Hg})$ , all given in previous items,  $\text{PbBr}_2(\text{cr})$ ,  $-261.92 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-62.60 \text{ kcal}\cdot\text{mol}^{-1}$ ), and a nonideality correction for the solvent of  $-1.151 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.275 \text{ kcal}\cdot\text{mol}^{-1}$ ), gave  $\Delta_f G^\circ [\text{CdBr}_2\cdot 4\text{H}_2\text{O}(\text{cr})]=-1248.029 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-298.286 \text{ kcal}\cdot\text{mol}^{-1}$ ). Removal of the nonideality term for the solvent and the  $\Delta_f G$  for four moles of water and introduction of a nonideality term for the solute,  $-12.749 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-3.047 \text{ kcal}\cdot\text{mol}^{-1}$ ) gave  $\Delta_f G^\circ [\text{CdBr}_2(\text{aq})]=-285.399 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-68.212 \text{ kcal}\cdot\text{mol}^{-1}$ ).

For items 17 and 18,  $\Delta_f G^\circ [\text{Br}^-(\text{aq})]$  was taken to be  $-103.972 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-24.85 \text{ kcal}\cdot\text{mol}^{-1}$ ). This gave values of  $\text{Cd}^{2+}(\text{aq})$  of  $-77.53$  and  $-77.45 \text{ kJ}\cdot\text{mol}^{-1}$ .

The average of the 18 values given above was taken, with the values from items 1, 2, 4, 5, 6, 7, 8, 12, 13, and 15 counted as occurring twice in the average. The result was  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]=-77.57 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.54 \text{ kcal}\cdot\text{mol}^{-1}$ ).

The enthalpy of formation was calculated through the usual manipulation of the Gibbs energy and entropy of formation.

## B. Comments

The items listed above were chosen from a larger list of values. Why these particular items were chosen was not detailed. The three values averaged for the entropy of  $\text{Cd}^{2+}(\text{aq})$  were ( $-73.4$ ,  $-75.3$ , and  $-71.1$ )  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $\sigma = 2.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). The  $-75.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  value was calculated from measurements for  $\text{CdCl}_2(\text{aq})$  which included an enthalpy of solution value,  $-19.22 \text{ kJ}\cdot\text{mol}^{-1}$ ; this value was indicated as being obtained from 1887PIC (item 12 section D). The two measured values from 1887PIC were significantly different from the values determined by 1882THO and 17COH/BRU. The latter two values were in good agreement with each other, particularly if a reasonable value of the heat capacity of the reaction is used (see items 12–15 in

section D). If the same pathway for calculation of the entropy of  $\text{CdCl}_2(\text{aq})$  is used, with the exception of the substitution of the 1882THO and 17COH/BRU values for the apparently less accurate 1887PIC value, and using the better value of  $\Delta_f C_p$ , then the entropy for  $\text{Cd}^{2+}(\text{aq})$  is calculated to be  $-73.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . An explanation for neither the value  $-19.22 \text{ kJ}\cdot\text{mol}^{-1}$  nor the choice of values from 1887PIC over the others was found. The words of 1887PIC regarding his own measured values for cadmium chloride samples, both fused and dried at  $473 \text{ K}$ , may have some value:

(The values) can only be regarded as approximations; for, on the one hand, it was found impossible to dehydrate the salt completely without fusion, while, on the other, fusion was impossible without a certain amount of decomposition [the specimen No. 2 (fused salt) contained 0.5% of oxide].

However, the agreement of the enthalpy of solution measurements of 1882THO and 17COH/BRU for  $\text{CdCl}_2(\text{cr})$  would suggest that either the salt does become anhydrous at some temperature, or that it reaches some very reproducible value of water content.

A second source of error also exists in the entropy of  $\text{Cd}^{2+}(\text{aq})$  calculated from the cadmium chloride system. This effect is an apparent arithmetic error in the calculation of the Gibbs energy of solution of  $\text{CdCl}_2(\text{cr})$  and is explained in the description of values for  $\text{CdCl}_2(\text{cr})$ . Calculating the entropy of  $\text{Cd}^{2+}(\text{aq})$  from the same pathway but correcting that error then gives  $S^\circ [\text{Cd}^{2+}(\text{aq})]=-71.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The three selected values then become ( $-73.4$ ,  $-71.0$ , and  $-71.1$ )  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  with an average value of  $-71.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $\sigma = 1.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The difference of this average value from that tabulated ( $1.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) corresponds to approximately  $400 \text{ J}\cdot\text{mol}^{-1}$  in the enthalpy of formation of  $\text{Cd}^{2+}(\text{aq})$ .

## C. Auxiliary Values Required for Data Pathway

$$m_{\text{sat}}[\text{CdSO}_4(\text{aq})]; \quad \gamma_{\text{sat}}[\text{CdSO}_4(\text{aq})]$$

$$m_{\text{sat}}[\text{CdCl}_2(\text{aq})]; \quad \gamma_{\text{sat}}[\text{CdCl}_2(\text{aq})]$$

$$m_{\text{sat}}[\text{CdBr}_2(\text{aq})]; \quad \gamma_{\text{sat}}[\text{CdBr}_2(\text{aq})]$$

$$m_{\text{sat}}[\text{CdI}_2(\text{aq})]; \quad \gamma_{\text{sat}}[\text{CdI}_2(\text{aq})]$$

$$S^\circ [\text{CdSO}_4(\text{cr})]; \quad S^\circ [\text{SO}_4^{2-}(\text{aq})]; \quad S^\circ [\text{CdCl}_2(\text{cr})]$$

$$S^\circ [\text{Cl}^-(\text{aq})]; \quad S^\circ [\text{CdBr}_2(\text{cr})]; \quad S^\circ [\text{Br}^-(\text{aq})]$$

$$\Delta_f G^\circ [\text{Pb}(\text{Hg})]; \quad \Delta_f G^\circ [\text{Cd}(\text{Hg})]; \quad \Delta_f G^\circ [\text{H}_2\text{O}(\text{l})];$$

$$\Delta_f G^\circ [\text{PbCl}_2(\text{cr})]$$

$$\Delta_f G^\circ [\text{AgCl}(\text{cr})]; \quad \Delta_f G^\circ [\text{Hg}_2\text{Cl}_2(\text{cr})]; \quad \Delta_f G^\circ [\text{PbSO}_4(\text{cr})];$$

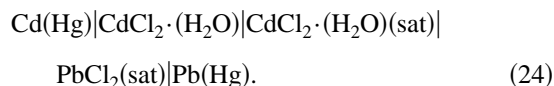
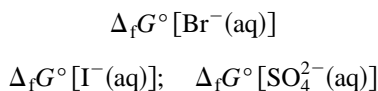
$$\Delta_f G^\circ [\text{Hg}_2\text{SO}_4(\text{cr})]$$

$$\Delta_f G^\circ [\text{PbCl}_2(\text{cr})]; \quad \Delta_f G^\circ [\text{Hg}_2\text{I}_2(\text{cr})]; \quad \Delta_f G^\circ [\text{PbI}_2(\text{cr})];$$

$$\Delta_f G^\circ [\text{AgI}(\text{cr})]$$

$$\Delta_f G^\circ [\text{Hg}_2\text{Br}_2(\text{cr})]; \quad \Delta_f G^\circ [\text{PbBr}_2(\text{cr})]; \quad \Delta_f G^\circ [\text{Cl}^-(\text{aq})];$$

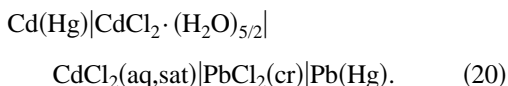




#### D. Other Thermodynamic Measurements Considered

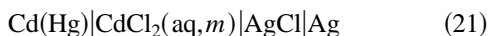
Many other measurements were used in calculations found on the worksheets.

1. 21TAY/PER measured the electrochemical potential of the cell:



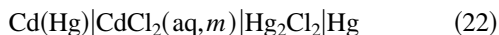
The 298.15 K emf yielded a value of  $\Delta_r G = -28.647 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-6.8468 \text{ kcal} \cdot \text{mol}^{-1}$ ). This value was combined with  $\Delta_f G^\circ$  values for  $\text{PbCl}_2(\text{cr})$ ,  $\text{Cd}(\text{Hg})$ ,  $\text{H}_2\text{O}(\text{l})$ ,  $\text{Pb}(\text{Hg})$  ("0.72% by weight"), of  $-314.135 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-75.08 \text{ kcal} \cdot \text{mol}^{-1}$ ),  $-9.74 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-2.328 \text{ kcal} \cdot \text{mol}^{-1}$ ),  $-237.183 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-56.688 \text{ kcal} \cdot \text{mol}^{-1}$ ),  $-2.109 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-0.504 \text{ kcal} \cdot \text{mol}^{-1}$ ) and a nonideality correction for the water in a saturated solution of  $-0.473 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-0.113 \text{ kcal} \cdot \text{mol}^{-1}$ ). These values yielded  $\Delta_f G^\circ [\text{CdCl}_2 \cdot (\text{H}_2\text{O})_{5/2}(\text{cr})] = -944.555 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-225.754 \text{ kcal} \cdot \text{mol}^{-1}$ ) and  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})] = -78.078 \text{ kJ} \cdot \text{mol}^{-1}$ .

2. 19HOR measured the emf of the electrochemical cell:



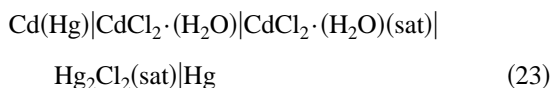
for 298.15 K. The emf of the cell with saturated solution ( $6.62 \text{ mol} \cdot \text{kg}^{-1}$ ),  $0.62203 \text{ int. V}$ , and 19HOR's measured potential for the  $\text{Cd}(\text{Hg})|\text{Cd}$  cell,  $0.0534 \text{ int. V}$ , were used to calculate  $\Delta_r G = -130.378 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-31.161 \text{ kcal} \cdot \text{mol}^{-1}$ ). This was used to calculate  $\Delta_f G^\circ [\text{CdCl}_2 \cdot (\text{H}_2\text{O})_{5/2}(\text{cr})] = -944.128 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-225.652 \text{ kcal} \cdot \text{mol}^{-1}$ ) and  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})] = -77.651 \text{ kJ} \cdot \text{mol}^{-1}$ .

3. 37ISH/TAK measured the 298.15 K emf of the cell:



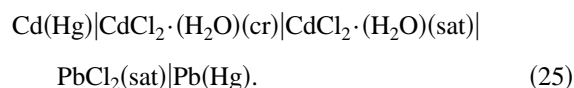
for values of  $m$  from 0.1616 to 5.8696. The emf of the cell for  $0.5302 \text{ mol} \cdot \text{kg}^{-1}$ ,  $0.71764 \text{ abs. V}$ , was used to obtain  $\Delta_r G = -138.486 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-33.099 \text{ kcal} \cdot \text{mol}^{-1}$ ). To this value, a nonideality term of  $-18.309 \text{ kJ} \cdot \text{mol}^{-1}$  ( $4.376 \text{ kcal} \cdot \text{mol}^{-1}$ ) was added, as was the  $\Delta_f G^\circ$  for  $\text{Hg}_2\text{Cl}_2$  and  $\text{Cd}(\text{Hg})$ , yielding  $\Delta_f G^\circ [\text{CdCl}_2(\text{aq})]$  of  $-340.695 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-81.428 \text{ kcal} \cdot \text{mol}^{-1}$ ). This was the value used in subsequent calculations. If one repeats their calculation with the measured emf for a  $1.0325 \text{ mol} \cdot \text{kg}^{-1}$  solution then a different value of  $\Delta_f G^\circ [\text{CdCl}_2(\text{aq})] = -340.247 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-81.321 \text{ kcal} \cdot \text{mol}^{-1}$ ) is obtained. This value is  $400 \text{ J} \cdot \text{mol}^{-1}$  different for the same cell with the exception of a different concentration.

4. 30PRI/VOS measured the emf of the two electrochemical cells:



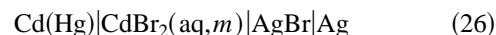
The monohydrate is not thermodynamically stable at 298.15 K, but readily forms at slightly higher temperatures. The monohydrate cells were formed by warming the 2.5 hydrate and then cooling back to 298.15 K. The emf of the first cell,  $0.6671 \text{ int. V}$ , was used to calculate  $\Delta_r G = -128.767 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-30.939 \text{ kcal} \cdot \text{mol}^{-1}$ ). The emf of the second cell,  $0.13759 \text{ int. V}$ , was used to calculate  $\Delta_r G = -26.476 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-6.328 \text{ kcal} \cdot \text{mol}^{-1}$ ). Using the auxiliary values described above, these results gave two values for  $\Delta_f G^\circ [\text{CdCl}_2 \cdot \text{H}_2\text{O}(\text{cr})]$ ,  $-587.074 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-140.314 \text{ kcal} \cdot \text{mol}^{-1}$ ) and  $-587.011 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-140.299 \text{ kcal} \cdot \text{mol}^{-1}$ ). The 298.15 K solubility of the monohydrate and the activity coefficient of that supersaturated solution were taken to be:  $7.565 \text{ mol} \cdot \text{kg}^{-1}$ , and  $0.0222$ , respectively. The resulting values of  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]$  were  $-76.944$  and  $-76.881 \text{ kJ} \cdot \text{mol}^{-1}$ .

5. 27VOS measured the emf of the metastable monohydrate cell:



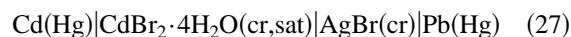
The values were treated as in item 4 of this section to obtain  $\Delta_f G^\circ [\text{CdCl}_2 \cdot \text{H}_2\text{O}(\text{cr})]$ ,  $-587.095 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-140.319 \text{ kcal} \cdot \text{mol}^{-1}$ ) and  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})] = -76.965 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-18.395 \text{ kcal} \cdot \text{mol}^{-1}$ ).

6. 39BAT measured the emf of the electrochemical cell:



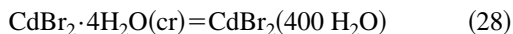
from 278.15 to 313.15 K and from  $0.000324$  to  $1.897 \text{ mol} \cdot \text{kg}^{-1}$ . An extrapolation was used to obtain a 298.15 K value for  $E^\circ$ ,  $0.42281 \text{ abs. V}$ , which was used to calculate  $\Delta_r G = -81.592 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-19.501 \text{ kcal} \cdot \text{mol}^{-1}$ ). Combination with  $\Delta_f G^\circ$  for  $\text{Cd}(\text{Hg})$ , given above, and  $\text{AgBr}(\text{cr})$ ,  $-96.90 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-23.16 \text{ kcal} \cdot \text{mol}^{-1}$ ), gave  $\Delta_f G^\circ$  of  $\text{CdBr}_2(\text{aq}, \text{std})$  as  $-285.14 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-68.15 \text{ kcal} \cdot \text{mol}^{-1}$ ). This value gave a  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})] = -77.20 \text{ kJ} \cdot \text{mol}^{-1}$ .

7. 32SPE/SEL measured the electromotive force of the cell:



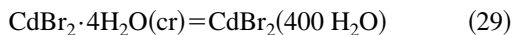
from 298.15 to 308.15 K. The 298.15 K emf,  $0.48845 \text{ abs. V}$ , was used to obtain  $\Delta_r G = -94.257 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-22.528 \text{ kcal} \cdot \text{mol}^{-1}$ ). Using the values of  $\Delta_f G^\circ$  for  $\text{Cd}(\text{Hg})$ ,  $\text{Pb}(\text{Hg})$ , and  $\text{AgBr}(\text{cr})$ , all given above, gave  $\Delta_f G^\circ [\text{CdBr}_2 \cdot 4\text{H}_2\text{O}(\text{cr})] = -1247.681 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-298.203 \text{ kcal} \cdot \text{mol}^{-1}$ ). Removal of the nonideality term for the solvent and the  $\Delta_f G^\circ$  for four moles of water and then introduction of the nonideality term for the solute,  $-12.749 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-3.047 \text{ kcal} \cdot \text{mol}^{-1}$ ), gave  $\Delta_f G^\circ [\text{CdBr}_2(\text{aq})] = -285.399 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-68.212 \text{ kcal} \cdot \text{mol}^{-1}$ ).  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})] = -77.107 \text{ kJ} \cdot \text{mol}^{-1}$ .

8. 1882THO measured the enthalpy of solution of the tetrahydrate of  $\text{CdBr}_2(\text{cr})$  in sufficient water to yield  $\text{CdBr}_2(400 \text{ H}_2\text{O})$ :



at 291.15 K as  $30.510 \text{ kJ} \cdot \text{mol}^{-1}$  ( $7.292 \text{ kcal} \cdot \text{mol}^{-1}$ ). The heat capacity of the reaction was assumed to be  $21 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  ( $5 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ), giving the 298.15 K enthalpy of solution as  $30.656 \text{ kJ} \cdot \text{mol}^{-1}$  ( $7.327 \text{ kcal} \cdot \text{mol}^{-1}$ ). Combination of this value with  $\Delta_f H^\circ$  for 4 mol  $\text{H}_2\text{O}(\text{l})$  and  $\text{CdBr}_2(400 \text{ H}_2\text{O})$ ,  $-319.373 \text{ J} \cdot \text{mol}^{-1}$  ( $-76.332 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ), gave  $\Delta_f H^\circ [\text{CdBr}_2 \cdot 4\text{H}_2\text{O}(\text{cr})] = -1493.35 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  ( $-356.92 \text{ cal} \cdot \text{mol}^{-1}$ ). Note: The heat capacity value for the reaction may be inaccurate. Using  $C_{p,\phi}^\circ$  values for  $\text{Cd}^{2+}(\text{aq})$ ,  $\text{Br}^-(\text{aq})$ , and an estimate of  $C_{p,\phi} - C_{p,\phi}^\circ$  obtained from the apparent molar enthalpy values given by 42ROB/WAL for 288.15 and 298.15 K gives  $\sim -117 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for the contribution from the aqueous species, a DuLong–Petit estimate for  $\text{CdBr}_2(\text{cr})$  is  $\sim 70 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  and the transfer of 4 moles of water from hydrate to liquid contributes  $\sim 4 \cdot (75-43) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , giving a heat capacity of the reaction of approximately  $-59 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , rather than  $+21 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . Using this value of the heat capacity of the reaction,  $\Delta_{\text{sol}} H(T=298.15 \text{ K}) = 30.10 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_f H^\circ [\text{CdBr}_2 \cdot 4\text{H}_2\text{O}(\text{cr})] = -1492.79 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

9. 30ISH/UED measured the enthalpy of solution of the tetrahydrate of  $\text{CdBr}_2(\text{cr})$  in sufficient water to yield  $\text{CdBr}_2(400 \text{ H}_2\text{O})$ :



at 298.15 K as  $29.87 \text{ kJ} \cdot \text{mol}^{-1}$  ( $7.139 \text{ kcal} \cdot \text{mol}^{-1}$ ) (average of three values,  $\sigma = 130 \text{ J} \cdot \text{mol}^{-1}$ ). The same method as in the previous item gave  $\Delta_f H^\circ [\text{CdBr}_2 \cdot 4\text{H}_2\text{O}(\text{cr})] = -1492.56 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-356.73 \text{ kcal} \cdot \text{mol}^{-1}$ ). This value falls within  $2\sigma$  of the 1882THO value, provided the better value of the heat capacity of the reaction is used (see item 8, this section).

10. 30ISH/UED measured the enthalpy of solution of  $\text{CdBr}_2(\text{cr})$  in sufficient water to yield  $\text{CdBr}_2(400 \text{ H}_2\text{O})$ :



at 298.15 K as  $-3.187 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-0.762 \text{ kcal} \cdot \text{mol}^{-1}$ ) (average of three values,  $\sigma = 12 \text{ J} \cdot \text{mol}^{-1}$ ). No further comparison of this value was made on the worksheets. This value gives  $\Delta_{\text{sol}} H^\circ [\text{CdBr}_2(\text{aq})] = -2.804 \text{ kJ} \cdot \text{mol}^{-1}$ .

11. 1882THO measured the enthalpy of solution of  $\text{CdBr}_2(\text{cr})$  in sufficient water to yield  $\text{CdBr}_2(400 \text{ H}_2\text{O})$ :



at 291.15 K as  $-1.82 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-0.436 \text{ kcal} \cdot \text{mol}^{-1}$ ). For this calculation the worksheets indicated the heat capacity of the reaction was  $-125 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  ( $-30 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) giving the heat of solution for 298.15 K as  $-2.70 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-0.646 \text{ kcal} \cdot \text{mol}^{-1}$ ) with an indication that this value was low. Using a more appropriate value of  $\Delta_r C_p$  of  $-190 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , calculated from information given in item 8 of this section, the 298.15 K heat of solution would be

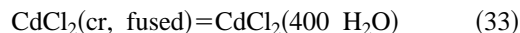
$-3.157 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_{\text{sol}} H^\circ = -2.772 \text{ kJ} \cdot \text{mol}^{-1}$ . The enthalpy of solution value from 1882THO is in very good agreement with the later value from 30ISH/UED, the difference  $= 30 \text{ J} \cdot \text{mol}^{-1}$ , and is not ‘‘low.’’

12. 1887PIC measured the enthalpy of solution of  $\text{CdCl}_2(\text{cr})$  in sufficient water to yield  $\text{CdCl}_2(400 \text{ H}_2\text{O})$ :



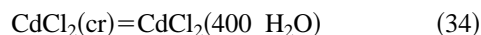
at 291.15 K as  $-14.150 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-3.382 \text{ kcal} \cdot \text{mol}^{-1}$ ). For this calculation the worksheets indicated the heat capacity of the reaction was  $-117 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  ( $-28 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) giving the heat of solution for 298.15 K as  $-14.970 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-3.578 \text{ kcal} \cdot \text{mol}^{-1}$ ). The enthalpy of dilution used for conversion to standard state,  $-4.251 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-1.016 \text{ kcal} \cdot \text{mol}^{-1}$ ), gives the standard-state enthalpy of solution  $\Delta_{\text{sol}} H^\circ = -19.221 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-4.594 \text{ kcal} \cdot \text{mol}^{-1}$ ). A more accurate value of the heat capacity of reaction,  $-215 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , can be obtained as follows.  $C_{p,\phi}^\circ$  values for  $\text{Cd}^{2+}(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  can be combined with an estimate of  $C_{p,\phi} - C_{p,\phi}^\circ$  obtained from the apparent molar enthalpy values given by 42ROB/WAL for 288.15 and 298.15 K to obtain  $\sim -140 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for the heat capacity contribution from the aqueous species. The heat capacity of  $\text{CdCl}_2(\text{cr})$  is  $\sim 75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  and hence the heat capacity of the reaction is approximately  $-215 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . Use of this better value of  $\Delta_r C_p$  gives  $\Delta_{\text{sol}} H^\circ = -19.906 \text{ kJ} \cdot \text{mol}^{-1}$ .

13. 1887PIC measured the enthalpy of solution of fused  $\text{CdCl}_2(\text{cr})$  in sufficient water to yield  $\text{CdCl}_2(400 \text{ H}_2\text{O})$ :



at 291.15 K as  $-13.435 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-3.211 \text{ kcal} \cdot \text{mol}^{-1}$ ). If one assumes  $-215 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for  $\Delta_r C_p$ , (see item 12, this section) then the heat of solution for 298.15 K is  $-14.940 \text{ kJ} \cdot \text{mol}^{-1}$ . The enthalpy of dilution for conversion to standard state,  $-4.251 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-1.016 \text{ kcal} \cdot \text{mol}^{-1}$ ), gives the standard-state enthalpy of solution  $\Delta_{\text{sol}} H^\circ = -19.191 \text{ kJ} \cdot \text{mol}^{-1}$ . 1887PIC indicated that fusing the sample introduced a 0.5% oxide impurity.

14. 1882THO measured the enthalpy of solution of  $\text{CdCl}_2(\text{cr})$  in sufficient water to yield  $\text{CdCl}_2(400 \text{ H}_2\text{O})$ :



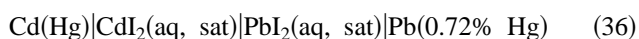
at 290.15 K as  $-12.678 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-3.03 \text{ kcal} \cdot \text{mol}^{-1}$ ). For this calculation the worksheets indicated  $C_{p,\phi}^\circ = -230 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  ( $-55 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) and that the heat capacity of the reaction was thus  $-117 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  ( $-28 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) giving the heat of solution for 298.15 K as  $-13.61 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-3.254 \text{ kcal} \cdot \text{mol}^{-1}$ ). The enthalpy of dilution used for conversion to standard state,  $-4.251 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-1.016 \text{ kcal} \cdot \text{mol}^{-1}$ ), converts this value to the standard-state enthalpy of solution  $\Delta_{\text{sol}} H^\circ = -17.865 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-4.270 \text{ kcal} \cdot \text{mol}^{-1}$ ). Use of the better value of  $\Delta_r C_p$  (see item 12, this section) gives  $\Delta_{\text{sol}} H^\circ = -18.649 \text{ kJ} \cdot \text{mol}^{-1}$ .

15. 17COH/BRU measured the enthalpy of solution of  $\text{CdCl}_2(\text{cr})$  in sufficient water to yield  $\text{CdCl}_2(400 \text{ H}_2\text{O})$ :

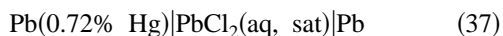


at 291.15 K as  $-12.933 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-3.091 \text{ kcal}\cdot\text{mol}^{-1}$ ). For this calculation the worksheets indicated the heat capacity of the reaction was  $-117 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-28 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) giving the heat of solution for 298.15 K as  $-14.171 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-3.387 \text{ kcal}\cdot\text{mol}^{-1}$ ). The enthalpy of dilution used for conversion to standard state,  $-4.251 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-1.016 \text{ kcal}\cdot\text{mol}^{-1}$ ), converts to the standard-state enthalpy of solution  $\Delta_{\text{sol}}H^\circ = -18.138 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-4.335 \text{ kcal}\cdot\text{mol}^{-1}$ ). Use of the better value of  $\Delta_r C_p$  (see item 12, this section) gives  $\Delta_{\text{sol}}H^\circ = -18.689 \text{ kJ}\cdot\text{mol}^{-1}$ ; the values from 17COH/BRU and 1882THO are in excellent agreement.

16. 21TAY/PER measured the emf of the electrochemical cell:



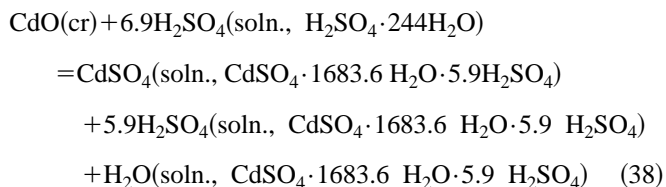
from 273.15 to 313.15 K. The 298.15 K emf, 0.10728 abs. V, was combined with the emf for the cell:



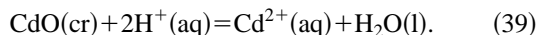
to calculate  $\Delta_r G = -18.593 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-4.444 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with  $\Delta_r G^\circ$  of  $\text{Cd}(\text{Hg})$  and  $\text{PbI}_2(\text{cr})$ , given in previous items above, gave  $\Delta_r G^\circ [\text{CdI}_2(\text{cr})] = -201.97 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-48.272 \text{ kcal}\cdot\text{mol}^{-1}$ ).

### E. More Recent Determinations of the Thermodynamic Properties of $\text{Cd}^{2+}(\text{aq})$

71VOR/BRO measured the enthalpy change for the reaction

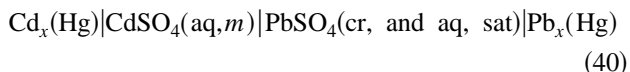


as  $-113.4 \pm 0.2 \text{ kJ}\cdot\text{mol}^{-1}$ . After adjustment for concentration effects and association effects with unspecified values, 71VOR/BRO gave a standard-state enthalpy of reaction of  $-101.67 \text{ kJ}\cdot\text{mol}^{-1}$  for the reaction

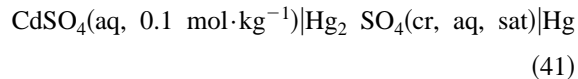
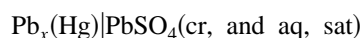


Combination of that value with an unreferenced value for the enthalpy of formation of  $\text{CdO}(\text{cr})$  of  $-259.8 \pm 0.6 \text{ kJ}\cdot\text{mol}^{-1}$ , they gave a standard-state enthalpy of formation of  $\text{Cd}^{2+}(\text{aq})$  of  $-75.7 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$ .

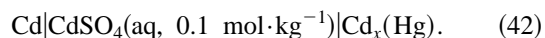
90STA/LAR gave emf values for the following cell reactions



for values of  $m$  from 0.00375 to 0.12344  $\text{mol}\cdot\text{kg}^{-1}$ ,



and



For cell (41) they gave an emf value of 0.0509 V.

71EGU/YAZ measured solubilities of cadmium sulfate in water for temperatures from 373 to 573 K.

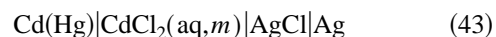
92LAP/AKH and 87MAK/FED each measured the solubility of cadmium sulfate in water for 323.15 K.

72HAM did not give any new measurements for any substance. This is different from what might be inferred from reading page 49 of 89COX/WAG, "From data obtained by Hamer (1972), using a  $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{SO}_4^{2-}(\text{aq})$  electrode, a value for  $\Delta_r G^\circ(\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O})$  equal to  $-(1465.38 \pm 0.50) \text{ kJ}\cdot\text{mol}^{-1}$  was calculated." In 72HAM, Hamer made a small adjustment of earlier emf measurements made by Wolff (reported from 1904 to 1910) for conversion from the international volt to the absolute volt and for small changes in temperature scale. 72HAM then compared those adjusted cell results determined by Wolff with other thermochemical information. The Wolff emf measurements were not found in the NBS Tables notes despite apparently having been performed at the Bureau of Standards. The author is unaware of reasons for either the absence of Wolff's measurements on 137 cadmium sulfate cells from the NBS Tables notes or the apparent attribution of Wolff's measurements to 72HAM in 89COX/WAG.

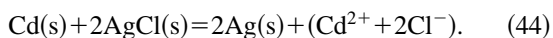
92BAR/BAR measured the enthalpy of solution of a "99 mass %" sample of  $\text{CdCl}_2(\text{cr})$  into water at 298.15 K in the molality range of 0.002–0.035  $\text{mol}\cdot\text{kg}^{-1}$ . The measured values were not reported. A value of  $\Delta_{\text{sol}}H^\circ$ , "calculated by extrapolation," was reported as  $-18.20 \text{ kJ}\cdot\text{mol}^{-1}$ . This value is somewhat smaller in magnitude than the other values for  $\Delta_{\text{sol}}H^\circ$  obtained earlier ( $-18.404$ ,  $-18.364$ ,  $-18.906$ ,  $-19.621$ )  $\text{kJ}\cdot\text{mol}^{-1}$ , when calculated using the  $\Delta_r C_p$  of  $-215 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . We note previous enthalpy of solution measurements for  $\text{NaCl}(\text{aq})$  were discordant from others by about 5% (92ARC).

79LON/MUS reported potential measurements for cadmium amalgam cells against silver chloride cells for varying compositions of cadmium in the amalgam. After combination of these values with measurements by others, they arrived at " $\Delta G^\circ$ " =  $-77.580 \pm 0.050 \text{ kJ}\cdot\text{mol}^{-1}$ , " $\Delta H^\circ$ " =  $-73.580 \pm 0.050 \text{ kJ}\cdot\text{mol}^{-1}$  and " $\Delta S^\circ$ " =  $-65.40 \pm 0.17 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $\text{Cd}^{2+}(\text{aq})$ . The author believes the first two to be formation properties and the latter was not for a change in entropy for a reaction but was actually  $S^\circ$  referred to  $S^\circ[\text{H}^+(\text{aq})] = 0$ . Thermodynamic property values were also given for  $\text{Cd}(\text{Hg})$ .

89VIS/MEK reported measurements of the potential of the cell



and claimed such measurements can result in  $E^\circ$  for



They made heavy use of literature complexation constants for Cd-Cl complexes and also the measurements from 36HAR/FIT. 89VIS/MEK seemed unaware of the widely reported systematic biases present in 36HAR/FIT's activity coefficients, see for example 70REI/STO or 40ROB.

77VAS/BUR measured the heat capacity of CdCl<sub>2</sub>(aq) at 298.15 K and for compositions from ~0.05 to ~3 mol·kg<sup>-1</sup>.

78LIL/CHE measured enthalpies of dilution of CdCl<sub>2</sub>(aq) at 273.15 and 323.15 K. Tables of apparently smoothed values were given for the composition ranges of 7.4–0.4 mol·kg<sup>-1</sup> (323.15 K) and 4.9–0.2 mol·kg<sup>-1</sup> (273.15 K).

84KUD measured the solubility of CdCl<sub>2</sub>(aq) at 308.15 K as 54.35% and the precipitated phase was the monohydrate.

67KRE/ABR measured the enthalpy of solution of CdCl<sub>2</sub>(aq) for low concentrations (~0.01–0.03 mol·kg<sup>-1</sup>) and for unspecified temperatures above and below 298.15 K. Measured values were not reported. Extrapolation to low concentrations appears to have been accomplished with a nonideality model that ignored speciation in the solution.

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- 19HOR Horsch, W. G., J. Am. Chem. Soc. **41**, 1787 (1919).
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- 40ROB Robinson, R. A., Trans. Faraday Soc. **36**, 1135 (1940).
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- 41VIN/BRI Vinal, G. W., Brickwedde, L. H., J. Res. Natl. Bur. Std. **26**, 455 (1941).
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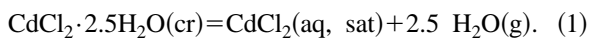
- 92BAR/BAR Barczynska, J., Bartel, L., Mokrzan, J., Taniewska-Osinska, S., *J. Chem. Thermodynam.* **24**, 297 (1992).
- 92LAP/AKH Laptev, V. M., Akhmarov, F. I., Dmitrevskii, B. A., Kamalov, O. K., *Zh. Prikl. Khim.* (St. Petersburg) **65**, 2363 (1992).

#### 4. CdCl<sub>2</sub>(cr)

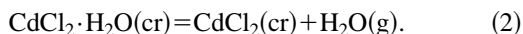
##### A. Selected Values, NBS Tables

The 298.15 K entropy, 115.27 J·K<sup>-1</sup>·mol<sup>-1</sup> (27.55 cal·K<sup>-1</sup>·mol<sup>-1</sup>), the difference of enthalpy between 0 and 298.15 K, 15.863 kJ·mol<sup>-1</sup> (3.7913 kcal·mol<sup>-1</sup>), and the 298.15 K heat capacity, 74.68 J·K<sup>-1</sup>·mol<sup>-1</sup> (17.85 cal·K<sup>-1</sup>·mol<sup>-1</sup>), were all taken from 59ITS/STR.

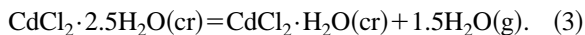
32ISH/KIM measured the pressure of water over CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr) in contact with saturated solution with a mercury manometer. Their measured pressure, 2.618 kPa (19.64 mm Hg), was used to calculate Δ<sub>r</sub>G° = 22.655 kJ·mol<sup>-1</sup> (5.415 kcal·mol<sup>-1</sup>) (per mol Cd) for the reaction:



32ISH/KIM also measured the pressure of water over CdCl<sub>2</sub>·H<sub>2</sub>O(cr). Their measured pressure, 0.23 kPa (1.7 mm Hg), (average of 3, σ = 0.012 kPa, corresponding to ±130 J·mol<sup>-1</sup>) was used to calculate Δ<sub>r</sub>G° = 15.13 kJ·mol<sup>-1</sup> (3.616 kcal·mol<sup>-1</sup>) (per mol Cd) for the reaction:



Finally, 32ISH/KIM measured the pressure of water over CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr). Their measured pressure, 2.258 kPa (16.94 mm Hg), (average of 3, σ = 0.004 kPa corresponding to ±2 J·mol<sup>-1</sup>) was used to calculate Δ<sub>r</sub>G° = 13.460 kJ·mol<sup>-1</sup> (3.217 kcal·mol<sup>-1</sup>) (per mol Cd) for the reaction:



The Gibbs energy of solution, Δ<sub>sol</sub>G°, was then calculated as Δ<sub>r</sub>G° [Eq. (1)] - Δ<sub>r</sub>G° [Eq. (2)] - Δ<sub>r</sub>G° [Eq. (3)] - RT ln[4(m<sub>sat</sub>γ<sub>sat</sub>)<sup>3</sup>], where the latter term is the nonideal-ity contribution, -9.811 kJ·mol<sup>-1</sup> (-2.345 kcal·mol<sup>-1</sup>). Their value of Δ<sub>sol</sub>G° was 3.878 kJ·mol<sup>-1</sup> (0.927 kcal·mol<sup>-1</sup>). They then combined this value with their values of Δ<sub>r</sub>G° [Cd<sup>2+</sup>(aq)] and Δ<sub>r</sub>G° [Cl<sup>-</sup>(aq)] to obtain Δ<sub>r</sub>G<sub>m</sub>°[CdCl<sub>2</sub>(cr)] = -343.97 kJ·mol<sup>-1</sup> (-82.21 kcal·mol<sup>-1</sup>).

A value of the enthalpy of solution, Δ<sub>sol</sub>H°, -18.64 kJ·mol<sup>-1</sup> (-4.455 kcal·mol<sup>-1</sup>) was calculated from the difference of the Δ<sub>sol</sub>G° and an entropy of solution calculated from S° [Cd<sup>2+</sup>(aq)] + 2S° [Cl<sup>-</sup>(aq)] - S° [CdCl<sub>2</sub>(cr)]. This enthalpy of solution was then combined with Δ<sub>r</sub>H° [Cd<sup>2+</sup>(aq)] and Δ<sub>r</sub>H° [Cl<sup>-</sup>(aq)] to obtain Δ<sub>r</sub>H° [CdCl<sub>2</sub>(cr)] = -391.50 kJ·mol<sup>-1</sup> (-93.57 kcal·mol<sup>-1</sup>).

##### B. Comments

Using the values on the worksheet page for Eq. (3), an arithmetic error may have been made; Δ<sub>r</sub>G° [Eq. (3)] should have been calculated to be: 14.143 kJ·mol<sup>-1</sup> (3.380 kcal·mol<sup>-1</sup>) or 680 J·mol<sup>-1</sup> different. This changes Δ<sub>sol</sub>G° to 3.197 kJ·mol<sup>-1</sup> and changes Δ<sub>r</sub>G° [CdCl<sub>2</sub>(cr)] to -343.298 kJ·mol<sup>-1</sup>. The minimum uncertainty in this value should be about 200 J·mol<sup>-1</sup>. Similarly, Δ<sub>sol</sub>H° and Δ<sub>r</sub>H° [CdCl<sub>2</sub>(cr)] will be affected by this error; the actual values should have been -19.32 and -390.88 kJ·mol<sup>-1</sup>, respectively. This standard-state enthalpy of solution is larger in absolute value, than those that were calculated from heat of solution measurements for CdCl<sub>2</sub>(aq).

##### C. Auxiliary Values Required for Data Pathway

$$\Delta_r G^\circ [\text{Cd}^{2+}(\text{aq})]; \Delta_r G^\circ [\text{Cl}^-(\text{aq})]$$

$$S^\circ [\text{Cl}_2(\text{g})]; S^\circ [\text{Cd}(\text{cr})].$$

##### D. Other Thermodynamic Measurements Considered

Other thermodynamic measurements considered but not used for this substance can be found in section D for the species Cd<sup>2+</sup>(aq); refer to section 3.

##### E. More Recent Determinations of the Thermodynamic Properties of CdCl<sub>2</sub>(cr)

92UVA/TIM apparently measured (but not clear from the article to the author) the coexistence pressures of CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr) and CdCl<sub>2</sub>·H<sub>2</sub>O(cr). They gave values of 0.287 kPa for Eq. (2) and 2.261 kPa for Eq. (3). However, these may be only calculated values.

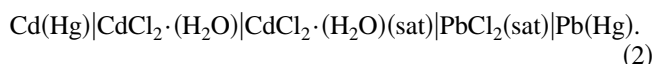
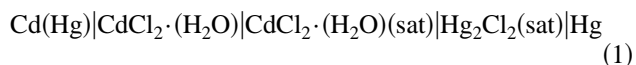
##### F. Bibliography

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#### 5. CdCl<sub>2</sub>·H<sub>2</sub>O(cr)

##### A. Selected Values, NBS Tables

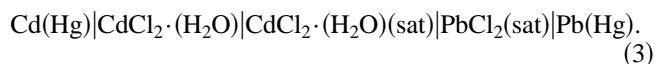
30PRI/VOS measured the emf of the two electrochemical cells:



The monohydrate is not thermodynamically stable at 298.15 K, but readily forms at slightly higher temperatures. The

monohydrate cells were formed by warming the 2.5 hydrates and then cooling back to 298.15 K. The emf of the first cell, 0.6671 int. V, was used to calculate  $\Delta_f G^\circ = -128.767 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-30.939 \text{ kcal}\cdot\text{mol}^{-1}$ ). The emf of the second cell, 0.13759 int. V, was used to calculate  $\Delta_f G^\circ = -26.476 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-6.328 \text{ kcal}\cdot\text{mol}^{-1}$ ). Using the auxiliary values described under the entry  $\text{Cd}^{2+}(\text{aq})$ , these results gave two values for  $\Delta_f G^\circ [\text{CdCl}_2\cdot\text{H}_2\text{O}(\text{cr})]$ , namely,  $-587.074 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-140.314 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $-587.011 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-140.299 \text{ kcal}\cdot\text{mol}^{-1}$ ).

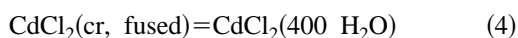
27VOS measured the emf of the metastable monohydrate cell:



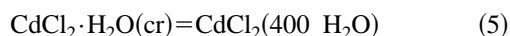
The values were treated as in the preceding paragraph to obtain  $\Delta_f G^\circ [\text{CdCl}_2\cdot\text{H}_2\text{O}(\text{cr})]$ ,  $-587.095 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-140.319 \text{ kcal}\cdot\text{mol}^{-1}$ ).

The average of these three values was taken to be  $\Delta_f G^\circ [\text{CdCl}_2\cdot\text{H}_2\text{O}(\text{cr})] = -587.057 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-140.310 \text{ kcal}\cdot\text{mol}^{-1}$ ).

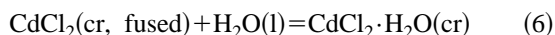
1887PIC measured the enthalpy change for:



and



both for 291.15 K. The measured enthalpy changes were  $-13.435 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-3.211 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-2.615 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.625 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively. Combination gives the enthalpy change for the reaction:



as  $-10.820 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.586 \text{ kcal}\cdot\text{mol}^{-1}$ ) for 291.15 K. The heat capacity of the reaction was assumed to be  $-38 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-9 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), giving the 298.15 K  $\Delta_f H^\circ = -11.09 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.65 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with  $2.5\Delta_f H^\circ [\text{H}_2\text{O}(\text{l})]$  and  $\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$ , where  $\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$  was taken to be  $-391.497 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-93.57 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $40 \text{ J}\cdot\text{mol}^{-1}$  different than the value obtained under the  $\text{CdCl}_2(\text{cr})$  entry. Their final value was  $-688.44 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-164.54 \text{ kcal}\cdot\text{mol}^{-1}$ ).

The entropy of  $\text{CdCl}_2\cdot\text{H}_2\text{O}(\text{cr})$  was obtained from  $-(\Delta_f G^\circ - \Delta_f H^\circ)/(298.15) + S^\circ(\text{Cd}) + S^\circ[\text{Cl}_2(\text{g})] + S^\circ[\text{H}_2(\text{g})] + 0.5S^\circ[\text{O}_2(\text{g})] = 167.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $40.1 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

## B. Comments

In the enthalpy of formation calculation,  $\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$  was used. This value contained an arithmetic error [see Comments for  $\text{CdCl}_2(\text{cr})$ , Sec. 4]. Using  $\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$  without the arithmetic error,  $-390.88 \text{ kJ}\cdot\text{mol}^{-1}$ , rather than  $-391.497 \text{ kJ}\cdot\text{mol}^{-1}$ , the values for  $\Delta_f H^\circ$  and  $S^\circ$  would be:  $-687.80 \text{ kJ}\cdot\text{mol}^{-1}$  and  $169.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively; differences of approximately  $640 \text{ J}\cdot\text{mol}^{-1}$  and  $2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , using the same measurements and calcula-

tional pathway. Additionally, 1887PIC said his enthalpy of solution values for  $\text{CdCl}_2$  "can only be regarded as approximations; for, on the one hand, it was found impossible to dehydrate the salt completely without fusion, while, on the other, fusion was impossible without a certain amount of decomposition (the specimen No. 2 contained 0.5% of oxide)." Specimen No. 2 from 1887PIC is the fused salt of Eq. (4). Finally, Eqs. (4)–(6) introduce a question of thermodynamic consistency. This is because the value of  $\Delta_{\text{sol}} H^\circ$  obtained from 1887PIC and used in the calculation, after consideration of temperature differences, does not correspond to that obtained as  $\Delta_f H^\circ [\text{Cd}^{2+}(\text{aq})] + 2\Delta_f H^\circ [\text{Cl}^-(\text{aq})] - 2\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$ , where the  $\Delta_f H^\circ$  values would be those tabulated.

The  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]$  values obtained from Eqs. (1)–(3) were different from the final NBS Tables values by  $\sim 700 \text{ J}\cdot\text{mol}^{-1}$ . This may indicate a systematic bias in the emf of the cell by this amount, if one accepts the  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]$  value and the auxiliary values described in the appropriate items under  $\text{Cd}^{2+}(\text{aq})$  as valid. This bias would then introduce a  $\sim 700 \text{ J}\cdot\text{mol}^{-1}$  bias in  $\Delta_f G^\circ [\text{CdCl}_2\cdot\text{H}_2\text{O}(\text{cr})]$ .

## C. Auxiliary Values Required for Data Pathway

$\Delta_{\text{sol}} G^\circ [\text{CdCl}_2(\text{aq})]$ ;  $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]$ ;  $\Delta_f G^\circ [\text{Cl}^-(\text{aq})]$ ;

$\Delta_f G^\circ [\text{Hg}_2\text{Cl}_2(\text{cr})]$

$\Delta_f G^\circ [\text{PbCl}_2(\text{cr})]$ ;  $\Delta_f G^\circ [\text{Pb}(\text{Hg})]$ ;  $\Delta_f G^\circ [\text{Cd}(\text{Hg})]$

$\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$

$S^\circ [\text{Cl}_2(\text{g})]$ ;  $S^\circ [\text{H}_2(\text{g})]$ ;  $S^\circ [\text{O}_2(\text{g})]$ ;  $S^\circ [\text{Cd}(\text{cr})]$ .

## D. Other Thermodynamic Measurements Considered

None.

## E. More Recent Determinations of the Thermodynamic Properties of $\text{CdCl}_2\cdot\text{H}_2\text{O}(\text{cr})$

84CHU measured the  $T-p$  locus of the  $\text{CdCl}_2\cdot\text{H}_2\text{O}(\text{cr})-\text{CdCl}_2(\text{cr})$  existence curve. These measurements establish a difference in molar volume of the anhydrous and monohydrated forms of the dihalide.

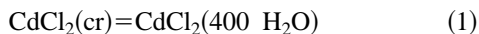
## F. Bibliography

- 1887PIC Pickering, S. U., *J. Chem. Soc.* **51**, 75 (1887).  
 27VOS Vosburgh, W. C., *J. Am. Chem. Soc.* **49**, 2222 (1927).  
 30PRI/VOS Priepeke, R. J., Vosburgh, W. C., *J. Am. Chem. Soc.* **52**, 4831 (1930).  
 84CHU Churagulov, B. R., *Khim. Termodin.* 193 (1984).

## 6. CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr)

### A. Selected Values, NBS Tables

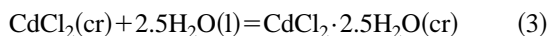
17COH/BRU measured the enthalpy of solution of CdCl<sub>2</sub>(cr) in sufficient water to yield CdCl<sub>2</sub>(400 H<sub>2</sub>O):



at 291.15 K as  $-12.678 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-3.091 \text{ kcal}\cdot\text{mol}^{-1}$ ). They also measured the enthalpy of solution of CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr) in sufficient water to yield CdCl<sub>2</sub>(400 H<sub>2</sub>O):



at 291.15 K as  $12.309 \text{ kJ}\cdot\text{mol}^{-1}$  ( $2.942 \text{ kcal}\cdot\text{mol}^{-1}$ ). The worksheets used these two reaction enthalpies to calculate the enthalpy for:



as  $-25.242 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-6.033 \text{ kcal}\cdot\text{mol}^{-1}$ ). The heat capacity of the reaction was assumed to be  $-92 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-22 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) giving the heat of reaction for 298.15 K as  $-25.886 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-6.187 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value was then used to calculate the enthalpy of formation of CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr) as  $\Delta_f H^\circ + 2.5 \Delta_f H^\circ [\text{H}_2\text{O}(\text{l})] + \Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$ , where  $\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$  was taken to be  $-391.497 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-93.57 \text{ kcal}\cdot\text{mol}^{-1}$ ). Their final value was  $-1131.94 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-270.54 \text{ kcal}\cdot\text{mol}^{-1}$ ).

They obtained  $\Delta_f G^\circ [\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}(\text{cr})]$  as an average of six values that are described under the entry for Cd<sup>2+</sup>(aq), in items 4, 7, 8, 9, and 10 of section A and item 2 of section D. The average was  $\Delta_f G^\circ [\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}(\text{cr})] = -944.094 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-225.644 \text{ kcal}\cdot\text{mol}^{-1}$ ).

The entropy of CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr) was obtained from  $-(\Delta_f G^\circ - \Delta_f H^\circ)/(298.15) + S^\circ(\text{Cd}) + S^\circ[\text{Cl}_2(\text{g})] + 2.5 S^\circ[\text{H}_2(\text{g})] + 1.25 S^\circ[\text{O}_2(\text{g})] = 227.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $54.3 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

### B. Comments

In the enthalpy of formation calculation,  $\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$  was used. This value contained an arithmetic error [see Comments for CdCl<sub>2</sub>(cr), section 4]. Using  $\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$  without the arithmetic error,  $-390.88$  rather than  $-391.497 \text{ kJ}\cdot\text{mol}^{-1}$ , the values for  $\Delta_f H^\circ$ , and  $S^\circ$  would be:  $-1131.34 \text{ kJ}\cdot\text{mol}^{-1}$ , and  $229.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively. Also, a better approximation of the heat capacity for Eq. (3) would be  $-110 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , (from  $-44 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  as the heat capacity change per mol of hydrated water.) Carrying this value through their calculational pathway yields:  $\Delta_f H^\circ = -1131.47 \text{ kJ}\cdot\text{mol}^{-1}$  and  $S^\circ = 229.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , differences of approximately  $500 \text{ J}\cdot\text{mol}^{-1}$  and  $1.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , using the same measurements and calculational pathway.

Additionally, there is a question of thermodynamic consistency that arises due to the use of the enthalpy of solution of CdCl<sub>2</sub>(cr) from 17COH/BRU. The value obtained from 17COH/BRU is not that obtained from  $\Delta_f H^\circ [\text{Cd}^{2+}(\text{aq})]$

$+ 2 \Delta_f H^\circ [\text{Cl}^-(\text{aq})] - 2 \Delta_f H^\circ [\text{CdCl}_2(\text{cr})]$ , where the  $\Delta_f H^\circ$  values would be those tabulated, followed by adjustment of the temperature. The 17COH/BRU enthalpy of solution is also different than that from 1887PIC used in the analogous calculation for CdCl<sub>2</sub>·H<sub>2</sub>O(cr) ( $-12.933 \text{ kJ}\cdot\text{mol}^{-1}$  vs  $-13.435 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively).

### C. Auxiliary Values Required for Data Pathway

$$\Delta_{\text{sol}} G^\circ [\text{CdCl}_2(\text{aq})]; \Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]; \Delta_f G^\circ [\text{Cl}^-(\text{aq})]$$

$$\Delta_f G^\circ [\text{AgCl}(\text{cr})]; \Delta_f G^\circ [\text{PbCl}_2(\text{cr})]; \Delta_f G^\circ [\text{Hg}_2\text{Cl}_2(\text{cr})]$$

$$\Delta_f H^\circ [\text{CdCl}_2(\text{cr})]; \Delta_f H^\circ [\text{H}_2\text{O}(\text{l})]$$

$$S^\circ [\text{Cl}_2(\text{g})]; S^\circ [\text{H}_2(\text{g})]; S^\circ [\text{O}_2(\text{g})]; S^\circ [\text{Cd}(\text{cr})].$$

### D. Other Thermodynamic Measurements Considered

See Cd<sup>2+</sup>(aq) items, in section 3, under section for other determinations of  $\Delta_f G$  for CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr).

### E. More Recent Determinations of the Thermodynamic Properties of CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr)

84CHU measured the  $T-p$  locus of the CdCl<sub>2</sub>·H<sub>2</sub>O(cr)–CdCl<sub>2</sub>·2.5H<sub>2</sub>O(cr) existence curve. These measurements establish a difference in molar volume of the two hydrated forms of the dihalide.

### F. Bibliography

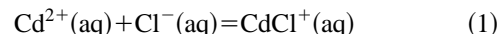
17COH/BRU Cohen, E., Bruins, H. R., Verslag. Gewone Vergader. Afdel. Natuurk., Koninkl. Ned. Akad. Wetenschap. **26**, 587 (1917).

84CHU Churagulov, B. R., Khim. Termodin. **193** (1984).

## 7. CdCl<sup>+</sup>(aq)

### A. Selected Values, NBS Tables

Values of the equilibrium constant for the reaction



for 298.15 K and for ionic strength limiting to 0, only, were taken from 64SIL/MAR. From each of the equilibrium constants was calculated  $\Delta_r G$  and then  $\Delta_f G^\circ$ . Seven of the values, thus calculated, ( $-52.58$ ,  $-52.64$ ,  $-52.57$ ,  $-52.77$ ,  $-52.61$ ,  $-52.64$ ,  $-52.57$ )  $\text{kcal}\cdot\text{mol}^{-1}$  were averaged to obtain  $-224.39 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-53.63 \text{ kcal}\cdot\text{mol}^{-1}$ ).

From 64SIL/MAR's list of values of the enthalpy change for Eq. (1), one value was chosen,  $\Delta_r H^\circ = 2.5 \text{ kJ}\cdot\text{mol}^{-1}$  ( $0.6 \text{ kcal}\cdot\text{mol}^{-1}$ ). [Other values listed were  $5.31$  and  $4.60 \text{ kJ}\cdot\text{mol}^{-1}$  ( $1.27$  and  $1.10 \text{ kcal}\cdot\text{mol}^{-1}$ )]. The chosen  $\Delta_r H^\circ$ , when combined with  $\Delta_f H^\circ [\text{Cd}^{2+}(\text{aq})] = -75.90 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.14 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $\Delta_f H^\circ [\text{Cl}^-(\text{aq})] = -167.159 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-39.952 \text{ kcal}\cdot\text{mol}^{-1}$ ), gave  $\Delta_f H^\circ [\text{CdCl}^+(\text{aq})] = -240.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-57.5 \text{ kcal}\cdot\text{mol}^{-1}$ ).

Finally, the worksheet indicated that the entropy of  $\text{CdCl}^+(\text{aq})$  was calculated to be  $43.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $10.4 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

### B. Comments

An arithmetic error was made in the calculation of the average for  $\Delta_f G^\circ$ ; it should have been  $-52.63$ , not  $-53.63 \text{ kcal}\cdot\text{mol}^{-1}$ . Correction of the mathematical error gives  $\Delta_f G^\circ = -220.20 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $4.18 \text{ kJ}\cdot\text{mol}^{-1}$  different. The net effect of the error is to increase the equilibrium constant by a factor of 5 from  $\sim 100$  to  $\sim 500$ . No reason was given for the particular choice of enthalpy of reaction. Completing the calculation gives  $S^\circ[\text{CdCl}^+(\text{aq})] = 29.53 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ,  $14 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  different than the tabulated value.

Finally, it should be noted that the equilibrium constant is not large and so the thermodynamic properties for the association reaction are model dependent. Choices of values from different models and averages over models were performed. Perhaps relevant is the comment made by 70REI/STO after examining their values and those of others for speciation of Cd-Cl complexes. From 70REI/STO, "The only conclusion possible ... is that the degree of complexing in the cadmium chloride system varies with the author ... ."

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f G^\circ[\text{Cd}^{2+}(\text{aq})]; \Delta_f G^\circ[\text{Cl}^-(\text{aq})]$$

$$\Delta_f H^\circ[\text{Cd}^{2+}(\text{aq})]; \Delta_f H^\circ[\text{Cl}^-(\text{aq})]$$

$$S^\circ[\text{Cl}_2(\text{g})]; S^\circ[\text{Cd}(\text{cr})].$$

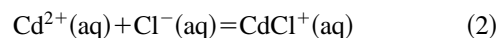
### D. Other Thermodynamic Measurements Considered

Several other values were listed in 64SIL/MAR but were considered no further. No explanation was given why particular values were chosen.

Although included in 64SIL/MAR, special note is made here of a potentiometric study by 53VAN/DAW. They measured the potentials of concentration cells with liquid junctions and cadmium amalgam electrodes. The measurements, not reported, were made at different temperatures and different ionic strengths. They were used as a basis for treatment of measurements described in section E, below.

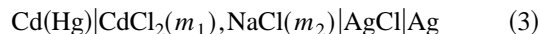
### E. More Recent Determinations of the Thermodynamic Properties of $\text{CdCl}^+(\text{aq})$

70PRO/WUL measured the enthalpy of reaction of an uncharacterized sample of  $\text{CdO} + \text{Cd}(\text{OH})_2 + \gamma\text{-Cd}(\text{OH})_2$  with an aqueous mixture of  $\text{HCl}$  and  $\text{HClO}_4$ . The measurements were made with five different compositions of the acid mixture. From combination of these measurements with equilibrium constant values reported by 53VAN/DAW, and various convoluted methods for nonideality effects, they calculated the standard enthalpy of reaction of



to be  $(3.4 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$  for 298.15 K. Their value is different from that given by 53VAN/DAW,  $2.51 \text{ kJ}\cdot\text{mol}^{-1}$  (298.15 K), by more than 53VAN/DAW's estimated uncertainty of  $0.21 \text{ kJ}\cdot\text{mol}^{-1}$ .

70REI/STO measured the potential of the cell



with varying values of  $m_1$  and  $m_2$  at 298.15 K. From their measurements they extracted stability constants for the four complexation reactions including Eq. (1). Activity coefficients were taken to be functions of ionic strength with adjustable parameters determined in the representation of the measured values. The equilibrium constant they obtained for Eq. (1) was  $85 \pm 1$ , yielding a Gibbs energy of reaction of  $-11.01 \pm 0.03 \text{ kJ}\cdot\text{mol}^{-1}$ .

92SCH/SCH measured the enthalpy of dilution of  $\text{CdCl}_2(\text{aq})$  with a commercial small-celled batch-mixing calorimeter. The dilutions involved an initial molality of approximately  $1 \text{ mol}\cdot\text{kg}^{-1}$  and final molalities ranging from  $0.8$  to  $0.1 \text{ mol}\cdot\text{kg}^{-1}$ . They were able to represent the enthalpies of dilution with an ion-interaction equation and without the assumption of formation of any Cd-Cl complexes in solution.

90STO measured potentials of electrochemical cells with and without transference. His measurements led to activity coefficients for  $\text{CdCl}_2(\text{aq})$  at 0.1, 1.0, 2.0, 3.0, and  $6.0 \text{ mol}\cdot\text{kg}^{-1}$ . They confirm solute activity coefficients obtained from earlier isopiestic molality determinations. Cation transference numbers were also obtained.

85RAR/MIL measured isopiestic ratios of  $\text{CdCl}_2(\text{aq})$  against  $\text{NaCl}(\text{aq})$  for molalities from  $\sim 1.8$  to  $\sim 7.3 \text{ mol}\cdot\text{kg}^{-1}$  and for 298.15 K. Diffusion coefficients were also determined.

68PAN/NI measured isopiestic molalities of cadmium chloride (molalities from 0.183 to  $5.881 \text{ mol}\cdot\text{kg}^{-1}$ ) relative to potassium chloride.

66HUA/PAN measured freezing point depressions of aqueous cadmium chloride for molalities from 0.0056 to  $0.0943 \text{ mol}\cdot\text{kg}^{-1}$ . From these measurements they estimate an equilibrium constant for Eq. (1) at 273.15 K to be  $74 \pm 5$ .

### F. Bibliography

- 53VAN/DAW Vanderzee, C. E., Dawson, H. J., *J. Am. Chem. Soc.* **75**, 5659 (1953).
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- 70PRO/WUL Provost, R. H., Wulff, C. A., *J. Chem. Thermodynam.* **2**, 793 (1970).
- 70REI/STO Reilly, P. J., Stokes, R. H., Aust., *J. Chem.* **23**, 1397 (1970).

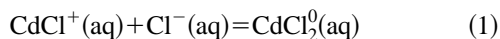


85RAR/MIL	Rard, J. A., Miller, D. G., <i>J. Solution Chem.</i> <b>14</b> , 271 (1985).
90STO	Stokes, R. H., <i>J. Phys. Chem.</i> <b>94</b> , 7769 (1990).
92SCH/SCH	Schreiber, D. R., Schreiber, L. C., <i>J. Solution Chem.</i> <b>21</b> , 249 (1992).

## 8. CdCl<sub>2</sub><sup>0</sup>(aq)

### A. Selected Values, NBS Tables

Values of the equilibrium constant for the reaction



for 298.15 K and for ionic strength limiting to 0, only, were taken from 64SIL/MAR. A value of  $\Delta_r G^\circ$  was calculated from each of the equilibrium constants. A number was written on the worksheet: "85.002". This number is the sum of  $\Delta_r G^\circ [\text{Cl}^-(\text{aq})] = -31.372$  and  $-53.63 \text{ kcal}\cdot\text{mol}^{-1}$ , the supposed  $\Delta_r G^\circ$  for CdCl<sup>+</sup>(aq), with inversion of sign. Such a value was needed because 64SIL/MAR's equilibrium constants are for stepwise addition. The number "85.002" was added to each of three values of  $\Delta_r G^\circ$  for Eq. (1). These three values, thus calculated,  $-85.95$ ,  $-85.87$ ,  $-85.82 \text{ kcal}\cdot\text{mol}^{-1}$ , were averaged to obtain  $\Delta_r G^\circ [\text{CdCl}_2^0(\text{aq})] = -359.322 \text{ kJ}\cdot\text{mol}^{-1} (-85.88 \text{ kcal}\cdot\text{mol}^{-1})$ .

A value of  $\Delta_r H^\circ$  from 64SIL/MAR was found on the worksheet,  $2.5 \text{ kJ}\cdot\text{mol}^{-1}$  ( $0.6 \text{ kcal}\cdot\text{mol}^{-1}$ ).  $\Delta_r H^\circ [\text{CdCl}_2^0(\text{aq})] = -405.0 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-96.8 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated from  $\Delta_r H^\circ [\text{CdCl}^+(\text{aq})] + \Delta_r H^\circ [\text{Cl}^-(\text{aq})] + \Delta_r H^\circ$ .

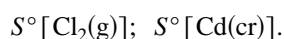
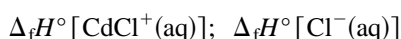
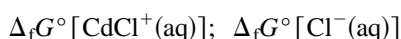
Finally, the worksheet indicated the entropy of CdCl<sub>2</sub>(aq) was calculated to be  $121.75 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $29.1 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

### B. Comments

$\Delta_r G^\circ [\text{CdCl}^+(\text{aq})]$  was calculated incorrectly and that error was passed into the current values. Using  $\Delta_r G^\circ [\text{CdCl}^+(\text{aq})] = -220.20 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_r G^\circ [\text{CdCl}_2^0(\text{aq})]$  was calculated to be  $-355.15 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $4.2 \text{ kJ}\cdot\text{mol}^{-1}$  different. Completing the calculation gives  $S^\circ [\text{CdCl}_2^0(\text{aq})] = 107.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ,  $14 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  different than the tabulated value.

Finally, it should be noted that the equilibrium constant is not large and so the thermodynamic properties for the association reaction are model dependent. Choices of values from different models and averages over models were performed.

### C. Auxiliary Values Required for Data Pathway

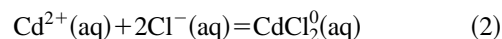


## D. Other Thermodynamic Measurements Considered

None.

## E. More Recent Determinations of the Thermodynamic Properties of CdCl<sub>2</sub><sup>0</sup>(aq)

70PRO/WUL measured the enthalpy of reaction of an uncharacterized sample of CdO + Cd(OH)<sub>2</sub> + γ-Cd(OH)<sub>2</sub> with an aqueous mixture of HCl and HClO<sub>4</sub>. The measurements were made with five different compositions of the acid mixture. From these measurements combined with equilibrium constant values reported by 53VAN/DAW, and various convoluted methods for nonideality composition, they calculated the standard enthalpy of reaction of



to be  $(0.8 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$  for 298.15 K. Their value is different from that given by 53VAN/DAW,  $5.0 \text{ kJ}\cdot\text{mol}^{-1}$  (298.15 K), by more than 53VAN/DAW's estimated uncertainty of  $1.3 \text{ kJ}\cdot\text{mol}^{-1}$ , indicating a significant probability of systematic errors between 53VAN/DAW's and 70PRO/WUL's values.

70REI/STO measured the potential of the cell



with varying values of  $m_1$  and  $m_2$  at 298.15 K. From their measurements they extracted stability constants for the four complexation reactions including Eq. (2). Activity coefficients were taken to be functions of ionic strength with adjustable parameters determined in the representation of the measured values. The equilibrium constant they obtained for Eq. (2) was  $231 \pm 2$ , yielding a Gibbs energy of reaction of  $(-13.491 \pm 0.02) \text{ kJ}\cdot\text{mol}^{-1}$ . Comparative values from 53VAN/DAW were  $500 \pm 20$  and  $(-15.40 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$ .

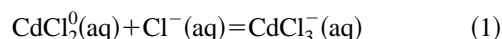
## F. Bibliography

- 53VAN/DAW Vanderzee, C. E., Dawson, H. J., *J. Am. Chem. Soc.* **75**, 5659 (1953).  
 64SIL/MAR Sillen, L. G., Martell, A. E., *Stability Constants of Metal-Ion Complexes* (The Chemical Society, London, 1964).  
 70PRO/WUL Provost, R. H., Wulff, C. A., *J. Chem. Thermodynam.* **2**, 793 (1970).  
 70REI/STO Reilly, P. J., Stokes, R. H., *Aust. J. Chem.* **23**, 1397 (1970).

## 9. CdCl<sub>3</sub><sup>-</sup>(aq)

### A. Selected Values, NBS Tables

Values of the equilibrium constant for the reaction



for 298.15 K and for ionic strength limiting to 0, only, were taken from 64SIL/MAR. From each of the equilibrium constants was calculated  $\Delta_r G^\circ$ . A number was written on the

worksheet as: "117.252". This number is the sum of  $\Delta_f G^\circ [\text{Cl}^-(\text{aq})] = -31.372$  and  $-85.88 \text{ kcal}\cdot\text{mol}^{-1}$ , the supposed  $\Delta_f G^\circ$  for  $\text{CdCl}_2^0(\text{aq})$ , with inversion of sign. Such a value was needed because 64SIL/MAR's equilibrium constants are for stepwise addition. The number "117.252" was added to one of the values of  $\Delta_f G^\circ$  for Eq. (1) given in 64SIL/MAR to give  $\Delta_f G^\circ [\text{CdCl}_3^-(\text{aq})] = -487.0 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-116.4 \text{ kcal}\cdot\text{mol}^{-1}$ ).

A value of  $\Delta_f H^\circ$  from 64SIL/MAR was found on the worksheet,  $11.09 \text{ kJ}\cdot\text{mol}^{-1}$  ( $2.65 \text{ kcal}\cdot\text{mol}^{-1}$ ).  $\Delta_f H^\circ [\text{CdCl}_3^-(\text{aq})] = -561.1 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-134.1 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated as  $\Delta_f H^\circ [\text{CdCl}_2^0(\text{aq})] + \Delta_f H^\circ [\text{Cl}^-(\text{aq})] + \Delta_f H^\circ$ .

Finally, the worksheet indicated the entropy of  $\text{CdCl}_2(\text{aq})$  was calculated to be  $202.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $48.5 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

## B. Comments

$\Delta_f G^\circ [\text{CdCl}_2^0(\text{aq})]$  was incorrect [see entry for  $\text{CdCl}_2^0(\text{aq})$ , section 8] and that error was passed into the current values. Using  $\Delta_f G^\circ [\text{CdCl}_2^0(\text{aq})] = -355.15 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f G^\circ [\text{CdCl}_3^-(\text{aq})]$  was calculated to be  $-482.83 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $4.2 \text{ kJ}\cdot\text{mol}^{-1}$  different. Completing the calculation gives  $S^\circ [\text{CdCl}_3^-(\text{aq})] = 188.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ,  $14 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  different than the tabulated value.

Finally, it should be noted that the equilibrium constant is not large and therefore the thermodynamic properties for the association reaction are model dependent. Choices of values from different models and averages over models were performed.

## C. Auxiliary Values Required for Data Pathway

$$\Delta_f G^\circ [\text{CdCl}_2^0(\text{aq})]; \Delta_f G^\circ [\text{Cl}^-(\text{aq})]$$

$$\Delta_f H^\circ [\text{CdCl}_2^0(\text{aq})]; \Delta_f H^\circ [\text{Cl}^-(\text{aq})]$$

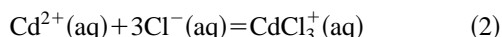
$$S^\circ [\text{Cl}_2(\text{g})]; S^\circ [\text{Cd}(\text{cr})].$$

## D. Other Thermodynamic Measurements Considered

None.

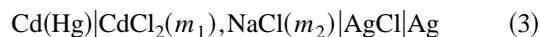
## E. More Recent Determinations of the Thermodynamic Properties of $\text{CdCl}_3^-(\text{aq})$

70PRO/WUL measured the enthalpy of reaction of an uncharacterized sample of  $\text{CdO} + \text{Cd}(\text{OH})_2 + \gamma\text{-Cd}(\text{OH})_2$  with an aqueous mixture of  $\text{HCl}$  and  $\text{HClO}_4$ . The measurements were made with five different compositions of the acid mixture. From these measurements combined with equilibrium constant values reported by 53VAN/DAW, and various convoluted methods for finding nonideality effects, they calculated the standard enthalpy of reaction of



to be  $(17.6 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$  for 298.15 K.

70REI/STO measured the potential of the cell



with varying values of  $m_1$  and  $m_2$  at 298.15 K. From their measurements they extracted stability constants for the four complexation reactions including Eq. (2). Activity coefficients were taken to be functions of ionic strength with adjustable parameters determined in the representation of the measured values. The equilibrium constant they obtained for Eq. (2) was  $122 \pm 1$ , yielding a Gibbs energy of reaction of  $(-11.909 \pm 0.02) \text{ kJ}\cdot\text{mol}^{-1}$ . Comparative values from 53VAN/DAW were  $(130 \pm 10$  and  $-12.0 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ .

## F. Bibliography

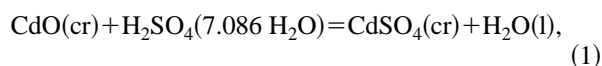
- 53VAN/DAW Vanderzee, C. E., Dawson, H. J., *J. Am. Chem. Soc.* **75**, 5659 (1953).  
 64SIL/MAR Sillen, L. G., Martell, A. E., *Stability Constants of Metal-Ion Complexes* (The Chemical Society, London, 1964).  
 70PRO/WUL Provost, R. H., Wulff, C. A., *J. Chem. Thermodynam.* **2**, 793 (1970).  
 70REI/STO Reilly, P. J., Stokes, R. H., *Aust. J. Chem.* **23**, 1397 (1970).

## 10. CdO(cr)

### A. Selected Values, NBS Tables

The 298.15 K entropy and heat capacity of  $\text{CdO}(\text{cr})$  were taken from 61KEL/KIN to be  $S^\circ = 54.81 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $13.1 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and  $C_p^\circ = 43.43 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $10.38 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

The enthalpy of formation of cadmium oxide was calculated from the measured enthalpy of dissolution of cadmium oxide in sulfuric acid. Manipulation of that reaction's enthalpy with other measured enthalpies gave the enthalpy for the reaction:



for 303.15 K (65ADA/KIN) as  $-84.01 \text{ kJ}\cdot\text{mol}^{-1}$ . The enthalpy of Eq. (1), adjusted by 65ADA/KIN to 298.15 K, was  $(-84.27 \pm 0.33) \text{ kJ}\cdot\text{mol}^{-1}$ . Combination of  $\Delta_f H^\circ$  for Eq. (1) with the  $\Delta_f H^\circ$  of  $\text{H}_2\text{O}(\text{l})$ ,  $-285.830 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $\text{CdSO}_4(\text{cr})$ ,  $-933.28 \text{ kJ}\cdot\text{mol}^{-1}$ , and  $\text{H}_2\text{SO}_4(7.086 \text{ H}_2\text{O})$ ,  $876.518 \text{ kJ}\cdot\text{mol}^{-1}$  gave an enthalpy of formation of  $\text{CdO}(\text{cr})$  of  $-258.2 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-61.7 \text{ kcal}\cdot\text{mol}^{-1}$ ).

The Gibbs energy of formation,  $-228.4 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-54.6 \text{ kcal}\cdot\text{mol}^{-1}$ ), was calculated from the usual manipulation of the above values.

### B. Comments

None.

### C. Auxiliary Values Required for Data Pathway

$$S^\circ [\text{O}_2(\text{g})]; S^\circ [\text{Cd}(\text{cr})]; S^\circ [\text{H}_2\text{O}(\text{l})]$$

$$\Delta_f H^\circ [\text{H}_2\text{O}(\text{l})]; \Delta_f H^\circ [\text{CdSO}_4(\text{cr})];$$

$$\Delta_f H^\circ [\text{H}_2\text{SO}_4(7.086 \text{ H}_2\text{O})]$$

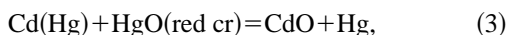
$$\Delta_f H^\circ [\text{H}_2\text{O}(l)].$$

#### D. Other Thermodynamic Measurements Considered

The emf of the electrochemical cell:



was determined to be  $-0.85858$  abs. V  $-0.000188$  abs. V/K ( $T-297.98$  K) by 29MAI. This emf was used to calculate the 298.15 K emf for the reaction,



as  $0.85889$  V, giving a  $\Delta_r G^\circ$  of  $-165.745$  kJ·mol<sup>-1</sup>. Combination of this value with the  $\Delta_f G^\circ$  of Cd(Hg),  $-9.740$  kJ·mol<sup>-1</sup>; and HgO(red cr)  $-58.555$  kJ·mol<sup>-1</sup> yielded a value of  $-234.0$  kJ·mol<sup>-1</sup> for the  $\Delta_f G^\circ$  of CdO.

For 42MAK an indication of "some cell" or "same cell" appeared along with "metallic Cd" and " $E_{25} = -0.0353$ ." The indication was that this led to a  $\Delta_f G^\circ$  of CdO(cr) of  $-230.4$  kJ·mol<sup>-1</sup>.

56GIL/KIT measured the partial pressure of cadmium over cadmium oxide from 1153 to 1373 K. These measurements gave the Gibbs energy of reaction,  $\Delta_r G^\circ = 360.33$  kJ·mol<sup>-1</sup>  $-0.2044T$  J·mol<sup>-1</sup>. From this equation they calculated the 298.15 K entropy of CdO as  $60.7$  J·K<sup>-1</sup>·mol<sup>-1</sup> and the enthalpy of formation as  $-254.0$  kJ·mol<sup>-1</sup>.

Decomposition pressures over cadmium oxide were also measured by 63GLE/STO. The Gibbs energy that 63GLE/STO obtained was  $\Delta_r G^\circ = 365.01$  kJ·mol<sup>-1</sup>  $-0.2090T$  J·mol<sup>-1</sup> for temperatures from 1242 to 1379 K. The 298.15 K enthalpy of formation and entropy for CdO(cr) calculated from these values were  $-258.6$  kJ·mol<sup>-1</sup> and  $52.3$  J·K<sup>-1</sup>·mol<sup>-1</sup>, respectively.

The enthalpy of formation was determined by combustion calorimetry by 54MAH. The enthalpy of formation value 54MAH calculated from the measurements was  $(-256.1 \pm 0.8)$  kJ·mol<sup>-1</sup>.

33BEC/ROT also measured the enthalpy of combustion of Cd(cr) to give CdO(cr). The NBS Tables staff calculated a value of the enthalpy of formation of  $-260.9$  kJ·mol<sup>-1</sup> from the 33BEC/ROT measurements.

Yet another determination of the combustion of cadmium in oxygen [24MOO/PAR] was used to derive an enthalpy of formation of  $-274.0$  kJ·mol<sup>-1</sup>.

40FRI/BLA measured the dissolution of CdO(cr) and Cd(OH)<sub>2</sub> in a mixture of HF, HCl, and H<sub>3</sub>PO<sub>4</sub> at 319.15 K (different measurements). These values, when combined with the enthalpy of formation of Cd(OH)<sub>2</sub>(cr) and H<sub>2</sub>O(l), gave an enthalpy of formation of  $-255.2$  kJ·mol<sup>-1</sup>.

59SHC/LIL measured the heat of solution of CdO(cr) in different strengths of different aqueous acids. From these measurements NBS staff calculated an average enthalpy of formation of  $-259.8$  kJ·mol<sup>-1</sup>.

#### E. More Recent Determinations of the Thermodynamic Properties of CdO(cr)

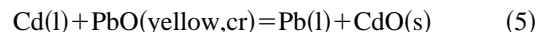
70PRO/WUL measured the enthalpy of dissolution of CdO(cr) in aqueous HClO<sub>4</sub>. They did not report the values of measurements at finite concentration and gave the standard-state enthalpy of reaction of  $(-103.39 \pm 0.8)$  kJ·mol<sup>-1</sup>. Their analysis of their crystalline sample indicated it contained 0.47 mol H<sub>2</sub>O for each mole of Cd(OH)<sub>2</sub>(cr). Any correction for the enthalpy change due to this level of water content was not described, if applied.

71VOR/BRO claimed a value of the enthalpy of formation of CdO(cr) exists "from electrochemical measurements" but gave no other information. The value they claimed was  $(-259.8 \pm 0.6)$  kJ·mol<sup>-1</sup>.

74COY/LEW made Knudsen effusion measurements on a sample of CdO(cr) from approximately 900–1100 K with different orifice diameters. Their measurements corresponded to the reaction



81SCH/BAL made equilibrium measurements of the reaction



for temperatures from 743 to 1051 K. From these measurements, 81SCH/BAL obtained  $\Delta_r G^\circ(800 \text{ K}) = (-37.24 \pm 0.22)$  kJ·mol<sup>-1</sup>. They also made enthalpy of reaction measurements for dropping liquid cadmium on yellow lead oxide at 785 and 811 K. From these measurements, they obtained  $\Delta_r H^\circ(800 \text{ K}) = (-39.15 \pm 1.6)$  kJ·mol<sup>-1</sup>. They then extrapolated these values to 298.15 K, by means of tabulated thermodynamic properties for lead, cadmium, lead oxide, and cadmium oxide, and combined that result with an enthalpy of formation of yellow lead oxide; they obtained  $\Delta_f H^\circ = (-255.7 \pm 1.6)$  kJ·mol<sup>-1</sup>.

#### F. Bibliography

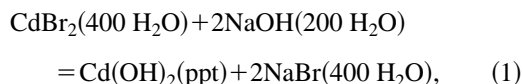
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- 29MAI Maier, C. G., J. Am. Chem. Soc. **51**, 194 (1929).
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- 54MAH Mah, A. D., J. Am. Chem. Soc. **76**, 3363 (1954).
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- 65ADA/KIN Adami, L. H., King, E. G., Heats of Formation of Anhydrous Sulfates of Cadmium, Cobalt, Copper, Nickel, and Zinc (U.S. Gov. Printing Office, U.S.B.M. RI 6617, 1965).
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- 71VOR/BRO Vorob'ev, A. F., Broier, A. F., Russ. J. Phys. Chem. **45**, 2390 (1971).
- 74COY/LEW Coyle, R. T., Lewis, G., J. Am. Ceram. Soc. **57**, 398 (1974).
- 81SCH/BAL Schuffenecker, L., Balesdent, D., Houriez, J., J. Chem. Thermodyn. **13**, 849 (1981).

## 11. Cd(OH)<sub>2</sub>(cr)

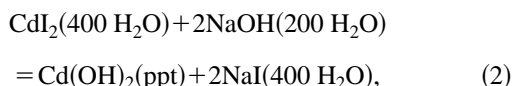
### A. Selected Values, NBS Tables

1882THO measured the enthalpy change for the following reaction:



at 291.15 K and obtained  $-24.85 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-5.94 \text{ kcal}\cdot\text{mol}^{-1}$ ). The heat capacity change for this reaction was written on the worksheets as  $+188 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $45 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), crossed out, and  $+251 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $60 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) then written. Their value for the 298.15 K enthalpy of reaction,  $-23.14 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-5.53 \text{ kcal}\cdot\text{mol}^{-1}$ ), was combined with the enthalpies of formation of  $\text{CdBr}_2(400 \text{ H}_2\text{O})$ ,  $\text{NaOH}(200 \text{ H}_2\text{O})$ , and  $\text{NaBr}(400 \text{ H}_2\text{O})$  of  $-319.373 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-76.332 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-470.700 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-112.50 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-361.351 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-86.365 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively, to give the enthalpy of formation of  $-561.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

1882THO also reported measurement of the enthalpy change for the reaction:



at 291.15 K as  $\Delta_f H^\circ = -13.14 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-3.14 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value was indicated as leading to a 298.15 K  $\Delta_f H^\circ = -11.38 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.72 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with the enthalpies of formation of  $\text{NaI}(400 \text{ H}_2\text{O})$ ,  $\text{NaOH}(200 \text{ H}_2\text{O})$ , and  $\text{CdI}_2(400 \text{ H}_2\text{O})$  of  $-295.010 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-70.509 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-470.700 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-112.50 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-198.008 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-47.325 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively, gave  $\Delta_f H^\circ = -560.7 \text{ kJ}\cdot\text{mol}^{-1}$ . The difference of values obtained from the two different Thomsen measurements is smaller than the errors

introduced in the data manipulations (see Comments). The value from Eq. (2) was entered into the NBS Tables.

Solubility product values (as  $\text{pK}_{\text{sp}}$ ) of 14.22, 13.93, 14.61, 13.66, 14.23, 14.39, and 14.4 were taken from the compilation by 64SIL/MAR. An additional solubility product, 14.09, was taken from 64SPI/MAI. These values were each converted into the Gibbs energy of solution and the average taken to be  $81.38 \text{ kJ}\cdot\text{mol}^{-1}$  ( $19.45 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value was combined with  $\Delta_f G^\circ$  values for  $\text{Cd}^{2+}(\text{aq})$  and  $\text{OH}^-(\text{aq})$  of  $-77.580 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-18.542 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $-157.293 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-37.594 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively, to obtain  $\Delta_f G^\circ$  for  $\text{Cd}(\text{OH})_2(\text{cr}) = -473.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-113.21 \text{ kcal}\cdot\text{mol}^{-1}$ ).

The difference of these two values gave the entropy of formation which, when combined with the entropies of the elements, gave an entropy of  $96 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $23 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

### B. Comments

The heat capacity change for the reaction appears too large. Estimating the maximum heat capacity for  $\text{Cd}(\text{OH})_2$  by the DuLong–Petit rule as  $120 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , recognizing an approximate cancelation of contributions from the  $\text{Na}^+$  and  $\text{Br}^-$  aqueous ions on both sides of the reaction and using standard-state values for  $\text{Cd}^{2+}(\text{aq})$  and  $\text{OH}^-(\text{aq})$  ions of  $+54$  and  $-57 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (sum =  $-60 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), the maximum reasonable  $\Delta_f C_p$  would be  $180 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Concentration effects for the aqueous ions would shift the  $-60 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  value to a less negative value which reduces the  $180 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  value to a smaller value. Thus, their crossed out value for  $\Delta_f C_p$  was more correct. The difference in  $\Delta_f C_p$  causes a  $0.5 \text{ kJ}\cdot\text{mol}^{-1}$  error in the 298.15 K enthalpy of reaction used in subsequent calculations. The enthalpy of formation used for  $\text{NaOH}(200 \text{ H}_2\text{O})$   $-470.700 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-112.50 \text{ kcal}\cdot\text{mol}^{-1}$ ) does not match the value given in the NBS Tables of  $-469.608 \text{ kJ}\cdot\text{mol}^{-1}$ . Using both of these changes and Eq. (1) gives an enthalpy of formation of  $-559.5 \text{ kJ}\cdot\text{mol}^{-1}$ , different by  $1.6 \text{ kJ}\cdot\text{mol}^{-1}$ .

The standard deviation of the Gibbs energies of solution averaged above is approximately  $1.3 \text{ kJ}\cdot\text{mol}^{-1}$ .

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H^\circ [\text{CdI}_2(400 \text{ H}_2\text{O})]; \quad \Delta_f H^\circ [\text{NaOH}(200 \text{ H}_2\text{O})];$$

$$\Delta_f H^\circ [\text{NaI}(400 \text{ H}_2\text{O})]$$

$$\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]; \quad \Delta_f G^\circ [\text{OH}^-(\text{aq})];$$

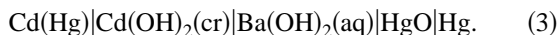
$$S^\circ [\text{Cd}(\text{cr})]; \quad S^\circ [\text{O}_2(\text{g})]; \quad S^\circ [\text{H}_2(\text{g})].$$

### D. Other Thermodynamic Measurements Considered

Also found on the sheets was: “ $\text{Cd}(\text{OH})_2(\text{c}) = -113.2$   
 $\Delta_f H^\circ =$  (crossed out)  $-132.2$  for aged, (illegible)  
 $\Delta_f S^\circ = -63.7$ ”

$S = 28.9$  eu This is high, if  $\text{CdO} = 13.1$ .

The source of all but the first of these values was not listed. 29MAI measured the emf of the electrochemical cell:



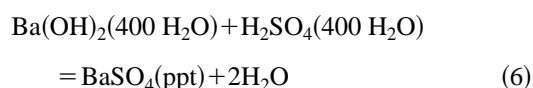
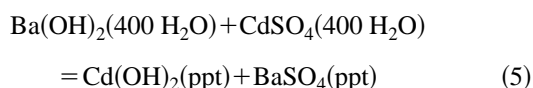
Treatment of this potential led to a  $\Delta_f G^\circ$  value of  $-468.909 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-112.072 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value was not considered further as they believed the reaction to have been uncertain, in other words, they thought it possible that the  $\text{Cd(OH)}_2$  was in actuality  $\text{CdO}(\text{cr})$  in Eq. (3).

27ISH/SHI measured the emf of the electrochemical cell:



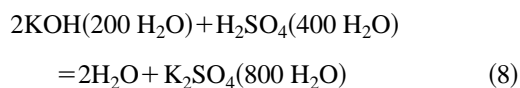
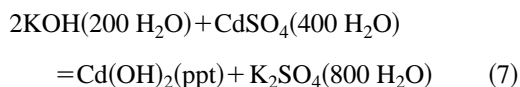
and obtained a voltage of  $0.8598 \text{ V}$  which was used to obtain a Gibbs energy of reaction of  $-165.979 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-39.670 \text{ kcal}\cdot\text{mol}^{-1}$ ). This led to a value of  $\Delta_f G^\circ$  equal to  $-471.081 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-112.591 \text{ kcal}\cdot\text{mol}^{-1}$ ).

1882THO measured the enthalpy change of the reactions



at  $291.15 \text{ K}$  as  $-54.693 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-13.072 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $-154.373 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-36.896 \text{ kcal}\cdot\text{mol}^{-1}$ ). They assumed that no enthalpy change occurred for the correction to  $298.15 \text{ K}$ ; from that assumption and the measured values, they calculated  $\Delta_f H^\circ = -561.242 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-134.14 \text{ kcal}\cdot\text{mol}^{-1}$ ). Use of a reasonable value of  $\Delta_f C_p$  gives  $\Delta_f H = -559.4 \text{ kJ}\cdot\text{mol}^{-1}$ .

1882THO also measured the enthalpy change for the reactions:

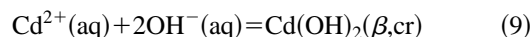


at  $291.15 \text{ K}$  as  $-29.564 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-7.066 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $-130.909 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-31.288 \text{ kcal}\cdot\text{mol}^{-1}$ ). They assumed that no enthalpy change occurred for the correction to  $298.15 \text{ K}$ ; from that assumption and the measured values they calculated  $\Delta_f H^\circ = -559.568 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-133.74 \text{ kcal}\cdot\text{mol}^{-1}$ ). Use of a reasonable value of  $\Delta_f C_p$  gives  $\Delta_f H = -561.4 \text{ kJ}\cdot\text{mol}^{-1}$ .

### E. More Recent Determinations of the Thermodynamic Properties of $\text{Cd(OH)}_2(\text{cr})$

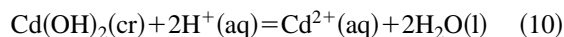
91RAI/FEL measured the solubility of  $\text{Cd(OH)}_2(\text{cr})$  as a function of pH and at low ionic strength [ $0.01 \text{ NaClO}_4(\text{aq})$ ]. The measurements were treated with a chemical equilibrium model that included precipitation of  $\beta\text{-Cd(OH)}_2(\text{cr})$  and formation of the aqueous species  $\text{Cd(OH)}_2^0(\text{aq})$  and

$\text{Cd(OH)}_4^{2-}(\text{aq})$ . Their measurements and subsequent treatment led to a value of the Gibbs energy for the reaction



of  $-80.712 \pm 1.2 \text{ kJ}\cdot\text{mol}^{-1}$ . Using NBS Tables values for the Gibbs energy of formation of  $\text{Cd}^{2+}(\text{aq})$  and  $\text{OH}^-(\text{aq})$ , this value would lead to a Gibbs energy of formation of  $-472.81 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{Cd(OH)}_2(\beta, \text{cr})$ .

70PRO/WUL measured dissolution of a sample of  $\text{Cd(OH)}_2(\text{cr})$  in different concentrations of perchloric acid, ranging from  $0.1$  to  $1.0 \text{ mol}\cdot\text{kg}^{-1}$ . They gave a value of the standard state enthalpy change for the reaction



as  $-85.19 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$ . Their analysis of their crystalline sample indicated it contained  $0.25 \text{ mol H}_2\text{O}$  for each mole of  $\text{Cd(OH)}_2(\text{cr})$ . Any correction for the enthalpy change due to this level of water content was not described, if applied.

### F. Bibliography

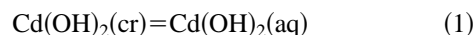
- 1882THO Thomsen, J., *Thermochemische Untersuchungen* (J. Barth, Leipzig, 1882–1886).
- 27ISH/SHI Ishikawa, F., Shibata, E., *Nippon Kagaku Zasshi* **48**, 279 (1927).
- 29MAI Maier, C. G., *J. Am. Chem. Soc.* **51**, 194 (1929).
- 64SIL/MAR Sillen, L. G., Martell, A. E., *Stability Constants of Metal-Ion Complexes* (The Chemical Society, London, 1964).
- 64SPI/MAI Spivakovskii, V. B., Maisa, L. P., Zhur. Neorg. Khim. **9**, 2287 (1964).
- 70PRO/WUL Provost, R. H., Wulff, C. A., *J. Chem. Thermodynam.* **2**, 655 (1970).
- 91RAI/FEL Rai D., Felmy, A. R., Szelmezcza, R. W., *J. Solution Chem.* **20**, 375 (1991).

## 12. $\text{Cd(OH)}_2^0(\text{aq})$

### A. Selected Values, NBS Tables

64SPI/MAI calculated a series of stability constants from measurements of pH as a function of the concentrations of  $\text{Cd}^{2+}$  and  $\text{Br}^-$  in basic solutions. From the solubility of  $\text{Cd(OH)}_2$  and the stability constants, a  $\Delta_f G^\circ$  value for  $\text{Cd(OH)}_2^0(\text{aq})$  of  $-441.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-105.6 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated.

The solubility of  $\text{Cd(OH)}_2(\text{cr})$  as a function of concentration of  $\text{HClO}_4(\text{aq})$  and  $\text{NaOH}(\text{aq})$  was measured by 57GAY/WOO. The assumption of the reaction:



and the measurements led to an equilibrium constant for reaction (1) of  $4.3 \times 10^{-6}$ . When combined with the  $\Delta_f G^\circ$  value for  $\text{Cd(OH)}_2(\text{cr})$ , the  $\Delta_f G^\circ$  reaction (1) yielded a  $\Delta_f G^\circ$  value for  $\text{Cd(OH)}_2(\text{aq})$  of  $-443.5 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-106.0 \text{ kcal}\cdot\text{mol}^{-1}$ ). These measurements were also used to determine properties of  $\text{Cd(OH)}^+(\text{aq})$  and  $\text{HCdO}_2^-(\text{aq})$ .

The Gibbs energy of formation was taken to be the un-weighted average of the two values given above, namely  $-442.7 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-105.8 \text{ kcal}\cdot\text{mol}^{-1}$ ).

### B. Comments

In the treatment of multiple equilibria in solution, results one obtains for any particular species can depend on which species were assumed to exist in the solution. The studies described in section A assumed different distributions of species. It is possible that some of the differences in values observed above were due to the differences in assumed chemical models. Thus, the validity of statistical improvement due to averaging may be suspect.

### C. Auxiliary Values Required for Data Pathway

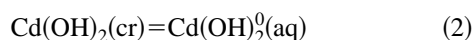
$$\Delta_f G_m^\circ[\text{Cd}(\text{OH})_2(\text{cr})].$$

### D. Other Thermodynamic Measurements Considered

None.

### E. More Recent Determinations of the Thermodynamic Properties of $\text{Cd}(\text{OH})_2^0(\text{aq})$

91RAI/FEL measured the solubility of  $\text{Cd}(\text{OH})_2(\text{cr})$  as a function of pH and at low ionic strength [ $0.01 \text{ NaClO}_4(\text{aq})$ ]. The measurements were treated with a chemical equilibrium model that included precipitation of  $\beta\text{-Cd}(\text{OH})_2(\text{cr})$  and formation of the aqueous species  $\text{Cd}(\text{OH})_2^0(\text{aq})$  and  $\text{Cd}(\text{OH})_4^{2-}(\text{aq})$ . Their measurements and subsequent treatment led to a value of the Gibbs energy for the reaction



of  $40.18 \pm 1.2 \text{ kJ}\cdot\text{mol}^{-1}$ . This value would lead to a Gibbs energy of formation of  $-432.3 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{Cd}(\text{OH})_2^0(\text{aq})$ .

### F. Bibliography

- 57GAY/WOO Gayer, K. H., Woontner, L., *J. Phys. Chem.* **61**, 364 (1957).  
 64SPI/MAI Spivakovskii, V. B., Maisa, L. P., Zhur. *Neorg. Khim.* **9**, 2287 (1964).  
 91RAI/FEL Rai D., Felmy, A. R., Szelmeczka, R. W., *J. Solution Chem.* **20**, 375 (1991).

## 13. $\text{CdOH}^+(\text{aq})$

### A. Selected Values, NBS Tables

57MAR used a potentiometric titration of  $\text{Cd}^{2+}(\text{aq})$  with  $\text{NaOH}$  in  $3 \text{ M NaClO}_4(\text{aq})$  using a glass electrode. The reaction was assumed to be:

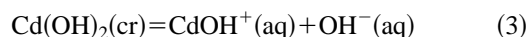
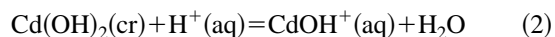


The logarithm (base 10) of the equilibrium constant was reported to be  $-9.0 \pm 0.2$  yielding  $-51.4 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\Delta_r G^\circ$ . This value resulted in a  $\Delta_f G^\circ$  value for  $\text{CdOH}^+(\text{aq})$  of  $-263.2 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-62.9 \text{ kcal}\cdot\text{mol}^{-1}$ ).

62BIE/CIA also made potentiometric measurements using either a glass electrode or a quinhydrone electrode. The value of  $\Delta_r G^\circ$  obtained from these measurements was  $-58.2 \text{ kJ}\cdot\text{mol}^{-1}$  yielding a  $\Delta_f G^\circ$  value for  $\text{CdOH}^+(\text{aq})$  of  $-256.5 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-61.3 \text{ kcal}\cdot\text{mol}^{-1}$ ).

64SPI/MAI calculated a series of stability constants from measurements of pH as a function of the concentrations of  $\text{Cd}^{2+}$  and  $\text{Br}^-$  in basic solutions. From the solubility of  $\text{Cd}(\text{OH})_2$  and the stability constant, a  $\Delta_f G^\circ$  value for  $\text{CdOH}^+(\text{aq})$  of  $-269.4 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-64.4 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated.

The solubility of  $\text{Cd}(\text{OH})_2(\text{cr})$  as a function of concentration of  $\text{HClO}_4(\text{aq})$  and  $\text{NaOH}(\text{aq})$  was measured by 57GAY/WOO. The assumption of the reactions:



and the measurements led to equilibrium constants for Eqs. (2) and (3) of  $4.3 \times 10^{-4}$  and  $1.5 \times 10^{-5}$ , respectively. When combined with the  $\Delta_f G^\circ$  values for  $\text{Cd}(\text{OH})_2(\text{cr})$  and  $\text{OH}^-(\text{aq})$ , Eqs. (2) and (3) yielded  $\Delta_f G^\circ$  values for  $\text{CdOH}^+(\text{aq})$  of  $-255.64 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-61.1 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $-260.24 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-62.2 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively.

The Gibbs energy of formation was taken to be the un-weighted average of the five values given above, namely  $-261.1 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-62.4 \text{ kcal}\cdot\text{mol}^{-1}$ ).

### B. Comments

The standard deviation of the average used for the Gibbs energy is  $5.6 \text{ kJ}\cdot\text{mol}^{-1}$ . In the treatment of multiple equilibria in solution, the results one obtains for any particular species can depend on which species were assumed to exist in the solution. The studies described in section A assumed different distributions of species. It is possible that some of the differences in values for  $\text{CdOH}^+(\text{aq})$  observed above were due to the differences in assumed chemical models. Thus, the validity of statistical improvement due to averaging may be suspect.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f G^\circ[\text{Cd}(\text{OH})_2(\text{cr})]; \quad \Delta_f G^\circ[\text{Cd}^{2+}(\text{aq})]$$

$$\Delta_f G^\circ[\text{H}_2\text{O}(\text{l})]; \quad \Delta_f G^\circ[\text{OH}^-(\text{aq})].$$

### D. Other Thermodynamic Measurements Considered

None.

### E. More Recent Determinations of the Thermodynamic Properties of $\text{Cd}(\text{OH})^+(\text{aq})$

None.

**F. Bibliography**

- 57GAY/WOO Gayer, K. H., Woontner, L., *J. Phys. Chem.* **61**, 364 (1957).  
 57MAR Marcus, Y., *Acta Chem. Scand.* **11**, 690 (1957).  
 62BIE/CIA Biedermann, G., Ciavatta, L., *Acta Chem. Scand.* **16**, 2221 (1962).  
 64SPI/MAI Spivakovskii, V. B., Maisa, L. P., Zhur. Neorg. Khim. **9**, 2287 (1964).

**14. Cd(OH)<sub>3</sub><sup>-</sup>(aq)****A. Selected Values, NBS Tables**

64SPI/MAI calculated a series of stability constants from measurements of pH as a function of the concentrations of Cd<sup>2+</sup> and Br<sup>-</sup> in basic solutions. From the solubility of Cd(OH)<sub>2</sub> and the stability constants, a  $\Delta_f G^\circ$  value for Cd(OH)<sub>3</sub><sup>-</sup>(aq) of  $-597.5 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-142.8 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated.

The solubility of Cd(OH)<sub>2</sub>(cr) as a function of concentration of HClO<sub>4</sub>(aq) and NaOH(aq) was measured by 57GAY/WOO. They reported no value for, or assumption of, a distinct Cd(OH)<sub>3</sub><sup>-</sup>(aq). The value listed on the worksheet and attributed to this reference is only the sum of the properties of HCdO<sub>2</sub><sup>-</sup>(aq) and H<sub>2</sub>O(l). That value was  $-604.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-144.5 \text{ kcal}\cdot\text{mol}^{-1}$ ).

The Gibbs energy of formation was taken to be the unweighted average of the two values given above, namely  $-600.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-143.6 \text{ kcal}\cdot\text{mol}^{-1}$ ).

**B. Comments**

In the treatment of multiple equilibria in solution, the results one obtains for any particular species can depend on which species were assumed to exist in the solution. The studies described in section A assumed different distributions of species. It is possible that some of the differences in values observed above were due to the differences in assumed chemical models. Thus, the validity of any expected statistical improvement due to averaging may be suspect.

**C. Auxiliary Values Required for Data Pathway**

$\Delta_f G^\circ [\text{Cd(OH)}_2(\text{cr})]$ ;  $\Delta_f G^\circ [\text{HCdO}_2^-(\text{aq})]$ ;  $\Delta_f G^\circ [\text{H}_2\text{O}(\text{l})]$ .

**D. Other Thermodynamic Measurements Considered**

None.

**E. More Recent Determinations of the Thermodynamic Properties of Cd(OH)<sub>3</sub><sup>-</sup>(aq)**

None.

**F. Bibliography**

- 57GAY/WOO Gayer, K. H., Woontner, L., *J. Phys. Chem.* **61**, 364 (1957).

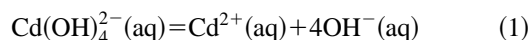
- 64SPI/MAI Spivakovskii, V. B., Maisa, L. P., Zhur. Neorg. Khim. **9**, 2287 (1964).

**15. Cd(OH)<sub>4</sub><sup>2-</sup>(aq)****A. Selected Values, NBS Tables**

64SPI/MAI calculated a series of stability constants from measurements of pH as a function of the concentrations of Cd<sup>2+</sup> and Br<sup>-</sup> in basic solutions. From the solubility of Cd(OH)<sub>2</sub> and the stability constant, a  $\Delta_f G^\circ$  value for Cd(OH)<sub>4</sub><sup>2-</sup>(aq) of  $-754.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-180.4 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated.

The solubility of Cd(OH)<sub>2</sub>(cr) as a function of concentration of HClO<sub>4</sub>(aq) and NaOH(aq) was measured by 57GAY/WOO. They reported no value for, or assumption of, a distinct Cd(OH)<sub>4</sub><sup>2-</sup>(aq). The value listed on the worksheet and attributed to this reference is only the sum of the properties of CdO<sub>2</sub><sup>2-</sup>(aq) and H<sub>2</sub>O(l). That value was  $-759.4 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-181.5 \text{ kcal}\cdot\text{mol}^{-1}$ ).

58LAK/GOO conducted a polarographic study of cadmium ions in hydroxide solutions. The average of 11 equilibrium constant values they obtained for the reaction



was  $2 \times 10^{-10}$ . From this, the  $\Delta_f G^\circ$  value for Cd(OH)<sub>4</sub><sup>2-</sup>(aq) of  $-761.9 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-182.1 \text{ kcal}\cdot\text{mol}^{-1}$ ) was calculated.

The Gibbs energy of formation was taken to be the unweighted average of the three values given above, namely  $-758.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-181.3 \text{ kcal}\cdot\text{mol}^{-1}$ ).

**B. Comments**

In the treatment of multiple equilibria in solution, results one obtains for any particular species can depend on which species were assumed to exist in the solution. The studies described in section A assumed different distributions of species. It is possible that some of the differences in values observed above were due to the differences in assumed chemical models. Thus, the validity of any expected statistical improvement due to averaging may be suspect.

**C. Auxiliary Values Required for Data Pathway**

$\Delta_f G^\circ [\text{Cd(OH)}_2(\text{cr})]$ ;  $\Delta_f G^\circ [\text{CdO}_2^{2-}(\text{aq})]$ ;  
 $\Delta_f G^\circ [\text{Cd}^{2+}(\text{aq})]$   $\Delta_f G^\circ [\text{OH}^-(\text{aq})]$ ;  $\Delta_f G^\circ [\text{H}_2\text{O}(\text{l})]$ .

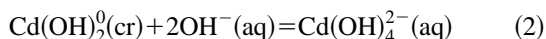
**D. Other Thermodynamic Measurements Considered**

None.

**E. More Recent Determinations of the Thermodynamic Properties of Cd(OH)<sub>4</sub><sup>2-</sup>(aq)**

91RAI/FEL measured the solubility of Cd(OH)<sub>2</sub>(cr) as a function of pH and at low ionic strength [ $0.01 \text{ mol}\cdot\text{kg}^{-1}$  NaClO<sub>4</sub>(aq)]. The measurements were treated with a chemical equilibrium model that included precipitation of

$\beta$ -Cd(OH)<sub>2</sub>(cr) and formation of the aqueous species Cd(OH)<sub>2</sub><sup>0</sup>(aq) and Cd(OH)<sub>4</sub><sup>2-</sup>(aq). Their measurements and subsequent treatment led to a value of the Gibbs energy for the reaction



of  $32.08 \pm 1.8 \text{ kJ} \cdot \text{mol}^{-1}$ . This value would lead to a Gibbs energy of formation of  $-755.2 \text{ kJ} \cdot \text{mol}^{-1}$  for Cd(OH)<sub>4</sub><sup>2-</sup>(aq).

### F. Bibliography

- 57GAY/WOO Gayer, K. H., Woontner, L., J. Phys. Chem. **61**, 364 (1957).  
 58LAK/GOO Lake, P. E., Goodings, J. M., Can. J. Chem. **36**, 1089 (1958).  
 64SPI/MAI Spivakovskii, V. B., Maisa, L. P., Zhur. Neorg. Khim. **9**, 2287 (1964).  
 91RAI/FEL Rai, D., Felmy, A. R., Szelmezcza, R. W., J. Solution Chem. **20**, 375 (1991).

## 16. HCdO<sub>2</sub><sup>-</sup>(aq)

### A. Selected Values, NBS Tables

The  $\Delta_f G^\circ$  value listed on the worksheet was the difference of the  $\Delta_f G^\circ$  values of Cd(OH)<sub>3</sub><sup>-</sup>(aq) and H<sub>2</sub>O(l). That value was  $-363.6 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-86.9 \text{ kcal} \cdot \text{mol}^{-1}$ ).

### B. Comments

The Gibbs energy of formation for HCdO<sub>2</sub><sup>-</sup>(aq) calculated by the NBS Tables staff was the difference of values for Cd(OH)<sub>3</sub><sup>-</sup>(aq) and H<sub>2</sub>O(l). The value for HCdO<sub>2</sub><sup>-</sup>(aq) was used for calculation of one of the  $\Delta_f G^\circ$  for Cd(OH)<sub>3</sub><sup>-</sup>(aq). Thus, this is a circular pathway, resulting in values whose uniqueness does not really exist.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f G^\circ [\text{Cd(OH)}_3^-(\text{aq})]; \quad \Delta_f G^\circ [\text{H}_2\text{O}(\text{l})].$$

### D. Other Thermodynamic Measurements Considered

None.

### E. More Recent Determinations of the Thermodynamic Properties of HCdO<sub>2</sub><sup>-</sup>(aq)

None.

### F. Bibliography

None.

## 17. CdO<sub>2</sub><sup>2-</sup>(aq)

### A. Selected Values, NBS Tables

The  $\Delta_f G^\circ$  value listed on the worksheet was the difference of the  $\Delta_f G^\circ$  values of Cd(OH)<sub>4</sub><sup>2-</sup>(aq) and H<sub>2</sub>O(l). That value was  $-284.5 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-68.0 \text{ kcal} \cdot \text{mol}^{-1}$ ).

### B. Comments

The value for CdO<sub>2</sub><sup>2-</sup>(aq) was calculated by the NBS Tables staff as the difference of values for Cd(OH)<sub>4</sub><sup>2-</sup>(aq) and for 2H<sub>2</sub>O(l). The so-calculated value for CdO<sub>2</sub><sup>2-</sup>(aq) was then used for calculation of one of the  $\Delta_f G^\circ$  values for Cd(OH)<sub>4</sub><sup>2-</sup>(aq). Thus, this is a circular pathway, resulting in values whose uniqueness does not really exist.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f G^\circ [\text{Cd(OH)}_4^{2-}(\text{aq})]; \quad \Delta_f G^\circ [\text{H}_2\text{O}(\text{l})].$$

### D. Other Thermodynamic Measurements Considered

None.

### E. More Recent Determinations of the Thermodynamic Properties of Cd(OH)<sub>3</sub><sup>-</sup>(aq)

None.

### F. Bibliography

None.

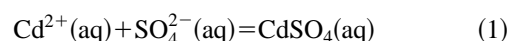
## 18. CdSO<sub>4</sub><sup>0</sup>(aq)

### A. Selected Values, NBS Tables

No values given.

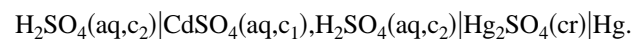
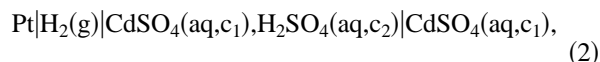
### E. More Recent Determinations of the Thermodynamic Properties of CdSO<sub>4</sub>(aq)

77KAT gave equilibrium constants, determined from conductivity measurements, for the ion-association reaction



as a function of temperature from 273.15 to 318.15 K. A Bjerrum model was used for the nonideality contribution to the solution. In their Bjerrum model, a temperature-dependent value of the closest approach distance of ions was used. The values given for Eq. (1) at 298.15 K were  $\Delta_f G^\circ = (-13.28 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta_f H^\circ = (8.39 \pm 0.65) \text{ kJ} \cdot \text{mol}^{-1}$ , and  $\Delta_f S^\circ = (72.7 \pm 2.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

89AHA/GHO measured emfs of the cell:



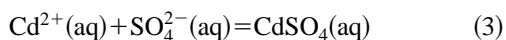


With an ion interaction nonideality model of the Bronsted type, they attempted to extract changes in thermodynamic properties for Eq. (1). Their measurements spanned temperatures of 293.15 K–308.15 K. They gave  $\Delta_r G^\circ$ ,  $\Delta_r H^\circ$ , and  $\Delta_r S^\circ$  of  $(-17.1 \pm 0.4)$  kJ·mol<sup>-1</sup>,  $(64.3 \pm 3.0)$  kJ·mol<sup>-1</sup> and  $(273.2 \pm 6.4)$  J·K<sup>-1</sup>·mol<sup>-1</sup>, respectively. The  $\Delta_r G$  corresponds to ( $K_a = 1000.0$ ) They also gave association constants and thermodynamic properties for the complexation of two sulfate ions with two cadmium ions. We don't reproduce those values here.

81WAC/RIE measured enthalpies of dilution ( $\Delta L_\phi$ ) for cadmium sulfate but did not report the measured values. They extracted an equilibrium constant and an enthalpy of association from their measurements by treating these quantities as parameters. In their model they also treated as a variable parameter the distance under which a pair of ions was defined as an ion pair. Using these three adjustable parameters and a Coulombic potential for free ions, they obtained  $\Delta_r G = -13.57$  kJ·mol<sup>-1</sup> (from  $K_a = 238.8$ ) and  $\Delta_r H = 8.389 \pm 0.004$  kJ·mol<sup>-1</sup>.

69IZA/EAT titrated solutions of  $[(\text{CH}_3)_4\text{N}]_2\text{SO}_4(\text{aq})$  into 0.02 M  $\text{Cd}(\text{ClO}_4)_2(\text{aq})$  in a calorimetric vessel. Measured values were not given. They represented the nonideality of the free ions as a sum of an electrostatic contribution and an ionic-strength independent second virial coefficient of fixed value. Their "log K" value of 2.55 ( $K_a = 355$ ) for Eq. (1) gives  $\Delta_r G = -14.56 \pm 0.06$  kJ·mol<sup>-1</sup> and they gave  $\Delta_r H = 4.10 \pm 0.17$  kJ·mol<sup>-1</sup> and  $\Delta_r S = 62.8 \pm 0.04$  J·K<sup>-1</sup>·mol<sup>-1</sup>.

69BEC/GRU measured the enthalpy change for mixing  $\text{Cd}(\text{ClO}_4)_2(\text{aq})$  with  $\text{Na}_2\text{SO}_4(\text{aq})$  in 2 mol·l<sup>-1</sup>  $\text{NaClO}_4(\text{aq})$  by means of a titration calorimeter. They gave thermodynamic parameters for the reaction



as " $K = 4.3 \pm 0.2$  l·mol<sup>-1</sup>" and  $\Delta_r H = 8.0 \pm 0.8$  kJ·mol<sup>-1</sup>.

38DAV from the treatment of conductivity measurements gave  $K_a = 195$  and thus  $\Delta_r G = -13.07$  kJ·mol<sup>-1</sup> for Eq. (1).

72PIT used a multiple equilibrium model to analyze emf measurements from 31LAM/PAR and osmotic coefficients, probably from 59ROB/STO. The equilibrium constant so obtained was  $K_a = 250$ , corresponding to  $\Delta_r G = -13.7$  kJ·mol<sup>-1</sup> for Eq. (1).

70LAR assumed from other literature sources an equilibrium constant for ion-pair formation,  $K_a = 204$ , and treated the enthalpy of dilution measurements described in 33LAN/MON to obtain an enthalpy change for ion-pair formation, Eq. (3), of  $(9.0 \pm 0.7)$  kJ·mol<sup>-1</sup>.

## F. Bibliography

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 33LAN/MON Lange, E., Monheim, J., Robinson, A. L., J. Am. Chem. Soc. **55**, 4733 (1933).  
 38DAV Davies, C. W., J. Chem. Soc. 2093 (1938).

- 59ROB/STO Robinson, R. A., Stokes, R. H., *Electrolyte Solutions*, 2nd ed. (Butterworths, London, 1959).  
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 72PIT Pitzer, K. S., J. Chem. Soc., Faraday Trans. 2 **1972**, 101 (1972).  
 77KAT Katayama, S., Rikagaku, Kenkyusho Hokoku **53**, 212 (1977).  
 81WAC/RIE Wachter, R., Riederer, K., Pure Appl. Chem. **53**, 1301 (1981).  
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## 19. CdSO<sub>4</sub>(cr)

### A. Selected Values, NBS Tables

The 298.15 K entropy, 123.039 J·K<sup>-1</sup>·mol<sup>-1</sup> (29.407 cal·K<sup>-1</sup>·mol<sup>-1</sup>), the enthalpy difference between 0 and 298.15 K, 18.217 kJ·mol<sup>-1</sup> (4.354 kcal·mol<sup>-1</sup>), and the 298.15 K heat capacity, 99.58 J·K<sup>-1</sup>·mol<sup>-1</sup> (23.805 cal·K<sup>-1</sup>·mol<sup>-1</sup>), were all taken from 55PAP/GIA.

55PAP/GIA also measured the enthalpy of solution of anhydrous cadmium sulfate in water and obtained a value of  $-45.928$  kJ·mol<sup>-1</sup> ( $-10.977$  kcal·mol<sup>-1</sup>) at 298.15 K for a final state of  $\text{CdSO}_4(400 \text{ H}_2\text{O})$ .

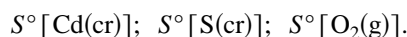
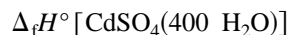


This enthalpy of solution, when combined with the enthalpy of formation of  $\text{CdSO}_4(400 \text{ H}_2\text{O})$ ,  $-979.223$  kJ·mol<sup>-1</sup> ( $-234.040$  kcal·mol<sup>-1</sup>), gave an enthalpy of formation of  $-933.28$  kJ·mol<sup>-1</sup> ( $-234.040$  kcal·mol<sup>-1</sup>). The usual combination of the enthalpy of formation and the entropy of formation gave  $\Delta_r G^\circ = -822.825$  kJ·mol<sup>-1</sup> ( $-196.66$  kcal·mol<sup>-1</sup>).

### B. Comments

80MAR/DOW demonstrated that thermal property measurements from Giauque's laboratory for both copper and aluminum bore similar discrepancies from more modern measurements. These discrepancies suggested the possibility of a systematic bias for measurements made with Giauque's calorimeter. If so, then the uncertainty assigned to the entropy of  $\text{CdSO}_4(\text{cr})$  should include this systematic effect. The cadmium sulfate sample was prepared by dehydration of precipitated crystals of the hydrate.

### C. Auxiliary Values Required for Data Pathway



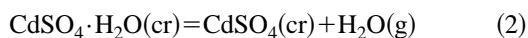
### D. Other Thermodynamic Measurements Considered

1882THO measured the enthalpy of Eq. (1) for 291.15 K. The value he obtained was  $-44.936 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-10.740 \text{ kcal}\cdot\text{mol}^{-1}$ ). The later adjustment to 298.15 K gave the value  $-46.82 \text{ kJ}\cdot\text{mol}^{-1}$  and an enthalpy of formation of  $-932.404 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-222.85 \text{ kcal}\cdot\text{mol}^{-1}$ ). No source for the reaction heat capacity was identified on the worksheets. The value used corresponds to approximately  $-272 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

1882THO also measured the enthalpy of solution of the hydrate  $\text{CdSO}_4\cdot(\text{H}_2\text{O})_{8/3}$  in sufficient water to yield  $\text{CdSO}_4(400 \text{ H}_2\text{O})$ , also at 291.15 K,  $\Delta_f H = -11.13 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.66 \text{ kcal}\cdot\text{mol}^{-1}$ ). Adjustment of this value to 298.15 K and combination with the enthalpy of formation of the hydrate, the enthalpy of formation of 8/3 mol of water and 1882THO's measured value for Eq. (1) gave an enthalpy of formation of  $-933.911 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-223.21 \text{ kcal}\cdot\text{mol}^{-1}$ ).

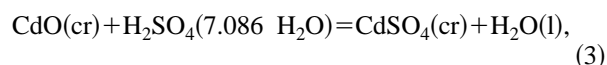
20COH/HEL measured the enthalpy of Eq. (1) for 291.15 K. 20COH/HEL's measured value,  $-44.730 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-10.690 \text{ kcal}\cdot\text{mol}^{-1}$ ), was in good agreement with that of 1882THO. Further calculations were performed on the worksheets and then crossed out so as to be illegible.

33ISH/MUR measured the vapor pressure of the decomposition reaction for the monohydrate



at 298.15 K. The measured vapor pressure for 298.15 K gave a Gibbs energy change for the reaction of  $17.61 \text{ kJ}\cdot\text{mol}^{-1}$  ( $4.21 \text{ kcal}\cdot\text{mol}^{-1}$ ). Combination of this value with the Gibbs energy of formation of water vapor (uncorrected for nonideality) and the Gibbs energy of formation of the monohydrate crystal gave a Gibbs energy of formation of  $-822.616 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-196.61 \text{ kcal}\cdot\text{mol}^{-1}$ ). (The worksheets indicated this value was to be used for the Gibbs energy of formation entry in the table. Those same worksheets also indicated  $\Delta_f H^\circ$  and  $S^\circ$  were to be taken as described in section A.)

65ADA/KIN determined the enthalpy of the reaction:



measured at 303.15 K and adjusted to 298.15 K. From their value of the enthalpy of the reaction, the worksheets indicated that a value of the heat of formation of  $\text{CdSO}_4(\text{cr})$  was calculated to be  $-931.11 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-222.54 \text{ kcal}\cdot\text{mol}^{-1}$ ). The enthalpy of reaction for Eq. (3) was used in conjunction with the  $\Delta_f H^\circ$  for  $\text{CdSO}_4(\text{cr})$  to obtain the enthalpy of formation of  $\text{CdO}(\text{cr})$ . That value of  $\Delta_f H^\circ$  for  $\text{CdO}(\text{cr})$  was then used with the same measurement to obtain the enthalpy of formation of  $\text{CdSO}_4(\text{cr})$ . This was a circular argument.

### E. More Recent Determinations of the Thermodynamic Properties of $\text{CdSO}_4(\text{cr})$

68LAR/CER measured the enthalpy of solution of  $\text{CdSO}_4(\text{cr})$  in water for 298.15 K. Their standard enthalpy of solution was  $-51.92 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-12.41 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value is about  $50 \text{ J}\cdot\text{mol}^{-1}$  different from that used to determine the NBS Tables of enthalpy of formation.

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- 33ISH/MUR Ishikawa, F., Murooka, H., *Bull. Inst. Phys. Chem. Res. (Tokyo)* **9**, 781 (1933).
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## 20. $\text{CdSO}_4\cdot\text{H}_2\text{O}(\text{cr})$

### A. Selected Values, NBS Tables

The 298.15 K entropy,  $154.030 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $36.814 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), the enthalpy difference between 0 and 298.15 K,  $23.356 \text{ kJ}\cdot\text{mol}^{-1}$  ( $5.582 \text{ kcal}\cdot\text{mol}^{-1}$ ), and the 298.15 K heat capacity,  $134.54 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $32.156 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), were all taken from 55PAP/GIA.

55PAP/GIA also measured the enthalpy of solution of cadmium sulfate monohydrate in water and obtained a value of  $-25.497 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-6.094 \text{ kcal}\cdot\text{mol}^{-1}$ ) at 298.15 K for a final state of  $\text{CdSO}_4(400 \text{ H}_2\text{O})$ .



This enthalpy of solution, when combined with the enthalpy of formation of  $\text{CdSO}_4(400 \text{ H}_2\text{O})$ ,  $-979.223 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-234.040 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $\text{H}_2\text{O}(\text{l})$ , gave an enthalpy of formation of  $-1239.55 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-296.26 \text{ kcal}\cdot\text{mol}^{-1}$ ). The Gibbs energy of formation was calculated from the enthalpy of formation and the entropy by the usual manipulation [ $\Delta_f G^\circ = -1068.84 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-255.46 \text{ kcal}\cdot\text{mol}^{-1}$ )].

### B. Comments

80MAR/DOW demonstrated that thermal property measurements from Giaque's laboratory for both copper and aluminum bore similar discrepancies from more modern measurements. These discrepancies suggested the possibility

of a systematic bias for measurements made with Giauque's calorimeter. If so, then the uncertainty assigned to the entropy of  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  should include this systematic effect.

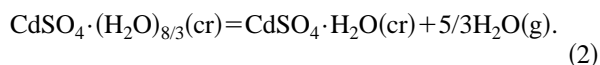
### C. Auxiliary Values Required for Data Pathway

$$\Delta_f H^\circ [\text{CdSO}_4(400 \text{ H}_2\text{O})]$$

$$S^\circ [\text{Cd}(\text{cr})]; S^\circ [\text{S}(\text{cr})]; S^\circ [\text{O}_2(\text{g})]; S^\circ [\text{H}_2(\text{g})].$$

### D. Other Thermodynamic Measurements Considered

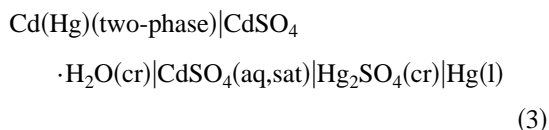
23CAR/JET measured the vapor pressure of water over the hydrate,  $\text{CdSO}_4 \cdot (\text{H}_2\text{O})_{8/3}$ , from 298.15 to 363.19 K as it decomposed into  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ :



These vapor pressures were used to calculate the Gibbs energy and enthalpy changes for Eq. (2), but not by model representation. In other words, the Gibbs energy change was based on the 298.15 K measurement alone and the enthalpy was obtained from a line drawn through some of the measurements. The Gibbs energy and enthalpy changes for Eq. (2) were then combined with the enthalpy and Gibbs energy of formation for  $\text{CdSO}_4 \cdot (\text{H}_2\text{O})_{8/3}$ ,  $-1729.33$  and  $-1465.337 \text{ kJ} \cdot \text{mol}^{-1}$ , ( $-413.32$  and  $-350.224 \text{ kcal} \cdot \text{mol}^{-1}$ ) to obtain the enthalpy and Gibbs energy of formation for  $\text{CdSO}_4 \cdot \text{H}_2\text{O}(\text{cr})$  of  $-1241.18$  and  $-1068.815 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-296.65$  and  $-255.453 \text{ kcal} \cdot \text{mol}^{-1}$ ).

1882THO measured the enthalpy of Eq. (1) for 291.15 K. The value he obtained was  $-25.31 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-6.05 \text{ kcal} \cdot \text{mol}^{-1}$ ). The later adjustment to 298.15 K gave the value  $-26.94 \text{ kJ} \cdot \text{mol}^{-1}$  and an enthalpy of formation of  $-1238.13 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-295.92 \text{ kcal} \cdot \text{mol}^{-1}$ ).

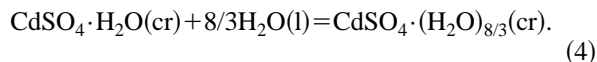
41VIN/BRI measured the emf of the electrochemical cell:



from 293.15 to 323.15 K. The worksheets indicated the Gibbs energy change for Eq. (3) at 298.15 K to be  $-195.711 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-46.776 \text{ kcal} \cdot \text{mol}^{-1}$ ). Also involved in the worksheet calculation was a quantity  $0.314 \text{ kJ} \cdot \text{mol}^{-1}$  ( $0.075 \text{ kcal} \cdot \text{mol}^{-1}$ ). This quantity was related to the nonideality of water vapor over saturated  $\text{CdSO}_4(\text{aq})$ . The quantities that would have entered into that correction are the molality and the osmotic coefficient of the saturated solution and the vapor pressure of water at 298.15 K. However, the monohydrate is not stable at 298.15 K, the 8/3 hydrate is. The Gibbs energy of formation was then calculated to be  $-1068.828 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-255.456 \text{ kcal} \cdot \text{mol}^{-1}$ ).

1882THO also measured the enthalpy of solution of the two hydrates  $\text{CdSO}_4 \cdot \text{H}_2\text{O}(\text{cr})$  and  $\text{CdSO}_4 \cdot (\text{H}_2\text{O})_{8/3}(\text{cr})$  in

sufficient water to yield  $\text{CdSO}_4(400 \text{ H}_2\text{O})$ , at 291.15 K. The difference of these two enthalpies was used as the enthalpy of the reaction:



Adjustment of this value to 298.15 K, using a heat capacity change for the reaction of  $-46 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , and combination with the enthalpy of formation of  $\text{CdSO}_4 \cdot (\text{H}_2\text{O})_{8/3}(\text{cr})$ , the enthalpy of formation of 5/3 mol of water gave an enthalpy of formation for the monohydrate of  $-1238.42 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-295.99 \text{ kcal} \cdot \text{mol}^{-1}$ ).

### E. More Recent Determinations of the Thermodynamic Properties of $\text{CdSO}_4 \cdot \text{H}_2\text{O}(\text{cr})$

68LAR/CER measured the enthalpy of solution of  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  in water for 298.15 K.

Their standard enthalpy of solution was  $-32.05 \text{ kJ} \cdot \text{mol}^{-1}$  ( $-7.66 \text{ kcal} \cdot \text{mol}^{-1}$ ).

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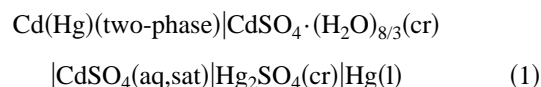
## 21. $\text{CdSO}_4 \cdot (\text{H}_2\text{O})_{8/3}(\text{cr})$

### A. Selected Values, NBS Tables

The 298.15 K entropy,  $229.635 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  ( $54.884 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ), the difference in enthalpy between 0 and 298.15 K,  $35.551 \text{ kJ} \cdot \text{mol}^{-1}$  ( $8.497 \text{ kcal} \cdot \text{mol}^{-1}$ ), and the 298.15 K heat capacity,  $213.260 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  ( $50.970 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ), were all taken from 55PAP/GIA.

The worksheets indicated  $\Delta_f G^\circ$  was " $-350.224 \text{ kcal} \cdot \text{mol}^{-1}$  (see  $\text{Cd}^{2+}$ )," but that value does not appear on the  $\text{Cd}^{2+}(\text{aq})$  worksheets. It may have been calculated from the quantity  $[3 \cdot (-350.219 \text{ kcal} \cdot \text{mol}^{-1})$  (obtained from the measurements from 41VIN/BRI) +  $(-350.240 \text{ kcal} \cdot \text{mol}^{-1})$  (obtained from the measurements of 33ISH/MUR)]/4. No rationale for this calculation was listed.

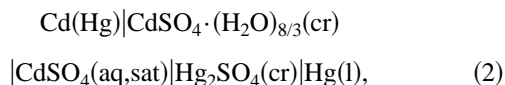
41VIN/BRI measured the emf of the electrochemical cell



from 293.15 to 323.15 K. The worksheets indicated the Gibbs energy change for Eq. (1) at 298.15 K to be

$-196.447 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-46.952 \text{ kcal}\cdot\text{mol}^{-1}$ ) calculated from the emf of 1.01844 abs. V. Also involved in the worksheet calculation was a quantity  $0.761 \text{ kJ}\cdot\text{mol}^{-1}$  ( $0.182 \text{ kcal}\cdot\text{mol}^{-1}$ ). This quantity was related to the nonideality of water vapor over saturated  $\text{CdSO}_4(\text{aq})$  multiplied by 8/3. The quantities that would have entered into that correction are the molality and the osmotic coefficient of the saturated solution and the vapor pressure of water at 298.15 K. The Gibbs energy of formation was calculated to be  $-1465.316 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-350.219 \text{ kcal}\cdot\text{mol}^{-1}$ ).

33ISH/MUR measured the emf of the electrochemical cell:



obtaining 1.01845 int. V for 298.15 K. This value was used to obtain a Gibbs energy of formation of  $-1465.404 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-350.240 \text{ kcal}\cdot\text{mol}^{-1}$ ). The pathway of the calculation was similar to that described in the preceding paragraph.

The enthalpy of formation [ $\Delta_f H^\circ = -1729.37 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-413.33 \text{ kcal}\cdot\text{mol}^{-1}$ )] was calculated from the usual manipulation of the entropy and the Gibbs energy of formation.

### B. Comments

80MAR/DOW demonstrated that thermal property measurements from Giauque's laboratory for both copper and aluminum bore similar discrepancies from more modern measurements. These discrepancies suggested the possibility of a systematic bias for measurements made with Giauque's calorimeter. If so, then the uncertainty assigned to the entropy of  $\text{CdSO}_4\cdot(\text{H}_2\text{O})_{8/3}$  should include this systematic effect.

### C. Auxiliary Values Required for Data Pathway

$$\Delta_f G^\circ[\text{Hg}_2\text{SO}_4(\text{cr})]; \Delta_f G^\circ[\text{H}_2\text{O}(\text{l})]; \Delta_f G^\circ[\text{Cd}(\text{Hg})]$$

$$m_{\text{sat}}[\text{CdSO}_4(\text{aq})]$$

$$\phi_{\text{sat}}[\text{CdSO}_4(\text{aq})]$$

$$p_{\text{sat}}(\text{H}_2\text{O})$$

$$S^\circ[\text{Cd}(\text{cr})]; S^\circ[\text{S}(\text{cr})]; S^\circ[\text{O}_2(\text{g})]; S^\circ[\text{H}_2(\text{g})].$$

### D. Other Thermodynamic Measurements Considered

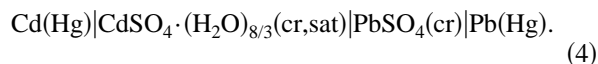
55PAP/GIA measured the enthalpy of solution of  $\text{CdSO}_4\cdot(\text{H}_2\text{O})_{8/3}(\text{cr})$  and obtained a value of  $-12.129 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.899 \text{ kcal}\cdot\text{mol}^{-1}$ ) at 298.15 K for a final state of  $\text{CdSO}_4(400 \text{ H}_2\text{O})$



This enthalpy of solution when combined with the enthalpy of formation of  $\text{CdSO}_4(400 \text{ H}_2\text{O})$ ,  $-979.223 \text{ kJ}\cdot\text{mol}^{-1}$

( $-234.040 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $\text{H}_2\text{O}(\text{l})$  gave an enthalpy of formation of  $-1729.306 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-413.314 \text{ kcal}\cdot\text{mol}^{-1}$ ).

210BA measured the emf of the electrochemical cell:



The worksheets indicate this cell yielded a value of the Gibbs energy of formation of  $-1467.542 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-350.751 \text{ kcal}\cdot\text{mol}^{-1}$ ).

31LAM/PAR measured the emf of the electrochemical cell:



The worksheets indicate this cell yielded a value of the Gibbs energy of formation of  $-1464.019 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-349.909 \text{ kcal}\cdot\text{mol}^{-1}$ ).

20COH/HEL measured the enthalpy change for the solution of the 8/3 hydrate into water:



The enthalpy change for Eq. (6) at 291.15 K was  $-10.623 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.539 \text{ kcal}\cdot\text{mol}^{-1}$ ). A heat capacity change of  $-188 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-45 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) was assumed. The resultant 298.15 K heat of solution was  $-11.92 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.85 \text{ kcal}\cdot\text{mol}^{-1}$ ). The *assumed* heat capacity change is discordant with the value measured by 55PAP/GIA. Using 55PAP/GIA's measured value of heat capacity, 20COH/HEL's enthalpy of solution becomes instead  $-12.209 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.918 \text{ kcal}\cdot\text{mol}^{-1}$ ), in good agreement with values from 55PAP/GIA and 68LAR/CER (discussed in section E).

1882THO measured the enthalpy of Eq. (6) at 291.15 K as  $-11.12 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.66 \text{ kcal}\cdot\text{mol}^{-1}$ ). A heat capacity change of  $-188 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-45 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) was assumed. The resultant 298.15 K heat of solution was  $-12.42 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.98 \text{ kcal}\cdot\text{mol}^{-1}$ ).

### E. More Recent Determinations of the Thermodynamic Properties of $\text{CdSO}_4\cdot(\text{H}_2\text{O})_{8/3}(\text{cr})$

68LAR/CER measured the enthalpy of solution of  $\text{CdSO}_4\cdot(\text{H}_2\text{O})_{8/3}$  in water for 298.15 K. Their standard enthalpy of solution was  $-18.08 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-4.32 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value is within 10 and 70  $\text{J}\cdot\text{mol}^{-1}$  of the values obtained by 55PAP/GIA and 20COH/HEL, respectively, after calculating the changes of the earlier values from  $0.1388 \text{ mol}\cdot\text{kg}^{-1}$  to standard state using the NBS Tables value for this enthalpy effect.

### F. Bibliography

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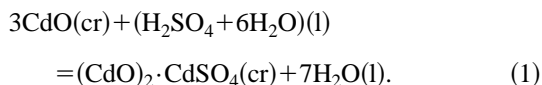
## 22. (CdO)<sub>2</sub>·CdSO<sub>4</sub>(cr)

### A. Selected Values, NBS Tables

No values given.

### E. More Recent Determinations of the Thermodynamic Properties of (CdO)<sub>2</sub>·CdSO<sub>4</sub>(cr)

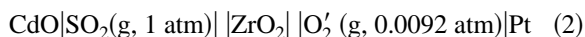
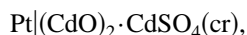
83KO/BRO determined the enthalpy of formation of (CdO)<sub>2</sub>·CdSO<sub>4</sub>(cr) through a calorimetric procedure. By conducting a series of enthalpies of solution measurements and manipulating the measured values, they obtained an enthalpy of reaction of  $-83.178 \pm 0.16 \text{ kJ}\cdot\text{mol}^{-1}$  for the reaction



Combination of this enthalpy with enthalpies of formation of H<sub>2</sub>O(l) and (H<sub>2</sub>SO<sub>4</sub>+6H<sub>2</sub>O)(l) ( $-285.830 \pm 0.042$ ) and ( $-874.556 \pm 0.42$ )  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively) from the NBS Tables, and with the enthalpy of formation of CdO(cr) [ $(-258.15 \pm 0.84) \text{ kJ}\cdot\text{mol}^{-1}$ ] from 77COD gave the resultant enthalpy of formation for (CdO)<sub>2</sub>·CdSO<sub>4</sub>(cr) as ( $-1446.4 \pm 2.6$ )  $\text{kJ}\cdot\text{mol}^{-1}$ .

86BEY/FER measured the heat capacity of (CdO)<sub>2</sub>·CdSO<sub>4</sub>(cr) from near 5 to 300.7 K. The sample was the same as that of 83KO/BRO. 86BEY/FER also made enthalpy-increment determinations between temperatures ranging to 1001.5 and 298.15 K. They reported the existence of a ‘nonisothermal transition’ in the temperature range of 245–260 K. Their value for the 298.15 K entropy was  $246.588 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

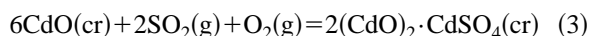
83SCH measured the emf of the electrochemical cell



from 1037 to 1208 K. From these measurements and knowledge of the zirconia electrode's thermodynamic properties, they gave a Gibbs energy of formation of [ $(-1812.76 + 0.92989 T) \pm 2.55$ ]  $\text{kJ}\cdot\text{mol}^{-1}$  and an enthalpy of formation of ( $-1812.76 \pm 2.55$ )  $\text{kJ}\cdot\text{mol}^{-1}$  for the temperature range of 1036.8–1208 K. 86BEY/FER used their own values

for the relative enthalpy of (CdO)<sub>2</sub>·CdSO<sub>4</sub>(cr) and auxiliary values of the enthalpy of SO<sub>2</sub>(g), O<sub>2</sub>(g) and CdO(cr) to calculate a 298.15 K enthalpy of formation [ $(-1441.0 \pm 2.6) \text{ kJ}\cdot\text{mol}^{-1}$ ] from 83SCH's high temperature value, in good agreement with  $-1446.4 \pm 2.6 \text{ kJ}\cdot\text{mol}^{-1}$ . Note that 86BEY/FER did not increase 83SCH's uncertainty estimate; this assumes no uncertainty to be introduced in the extrapolation from 1100 to 298.15 K, which would be rather unlikely.

88FUK/SAI measured oxygen activity over the Cd+S+O system with a stabilized zirconia as the electrolyte for the galvanic cell. Their measurements are in good agreement with values from 83SCH. For example, 88FUK/SAI give an equation for the standard-state Gibbs energy change of the reaction



that gives a value of  $-202.9 \text{ kJ}\cdot\text{mol}^{-1}$  which compares with 83SCH's value calculated from his measurements at that temperature of  $-203.04 \text{ kJ}\cdot\text{mol}^{-1}$ .

### F. Bibliography

- 77COD CODATA Bull. **28**, 18 (1977).
- 83KO/BRO Ko, H. C., Brown, R. R., *Enthalpy of Formation of 2CdO·CdSO<sub>4</sub>* (U.S. Bureau of Mines RI 8751, 1983).
- 83SCH Schaefer, S. C., *Electrochemical Determination of Thermodynamic Properties of Manganese Sulfate and Cadmium Oxysulfate* (U.S. Bureau of Mines RI 8309, 1983).
- 86BEY/FER Beyer, R. P., Ferrante, M. J., *J. Chem. Thermodynam.* **18**, 365 (1986).
- 88FUK/SAI Fukatsu, N., Saito, A., Noboru, S., Ohashi, T., *J. Electrochem. Soc.* **135**, 997 (1988).

## 23. CdCO<sub>3</sub>(cr)

### A. Selected Values, NBS Tables

The Gibbs energy of formation was taken from the electrochemical cell measurements described by Saegusa (50SAE). The cell reaction was:

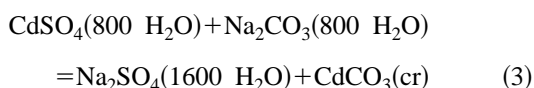


The emf for this cell was 1.1540 abs. V at 298.15 K. This value yields a standard-state Gibbs energy change for the reaction



of  $-222.67 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-53.22 \text{ kcal}\cdot\text{mol}^{-1}$ ). This value of  $\Delta_r G^\circ$  was combined with the evaluator's values of  $\Delta_f G^\circ$  for Ag<sub>2</sub>CO<sub>3</sub>(cr) and Cd(Hg),  $-436.8 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-104.4 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $-9.740 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-2.328 \text{ kcal}\cdot\text{mol}^{-1}$ ), respectively. These values resulted in  $-669.4 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-160.0 \text{ kcal}\cdot\text{mol}^{-1}$ ) for  $\Delta_f G^\circ$  for CdCO<sub>3</sub>(cr).

The enthalpy of formation was taken from Thomsen's (1882THO) measurement of the enthalpy change for the reaction



occurring at 291.15 K. The observed enthalpy change for 291.15 K,  $-1.55 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.37 \text{ kcal}\cdot\text{mol}^{-1}$ ) was converted to an enthalpy change for 298.15 K by assuming the heat capacity change for Eq. (3) was  $-125 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-30 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). This gave a 298.15 K enthalpy change for Eq. (3) of  $-2.43 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-0.58 \text{ kcal}\cdot\text{mol}^{-1}$ ). This enthalpy of reaction was then combined with values of the heats of formation of  $\text{Na}_2\text{SO}_4(1600 \text{ H}_2\text{O})$ ,  $\text{Na}_2\text{CO}_3(800 \text{ H}_2\text{O})$ , and  $\text{CdSO}_4(800 \text{ H}_2\text{O})$ , of  $-1388.67 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-331.90 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $-1157.09 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-276.55 \text{ kcal}\cdot\text{mol}^{-1}$ ), and  $-979.884 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-234.198 \text{ kcal}\cdot\text{mol}^{-1}$ ) to give the enthalpy of formation of  $\text{CdCO}_3(\text{cr})$  equal to  $-750.6 \text{ kJ}\cdot\text{mol}^{-1}$  ( $-179.4 \text{ kcal}\cdot\text{mol}^{-1}$ ).

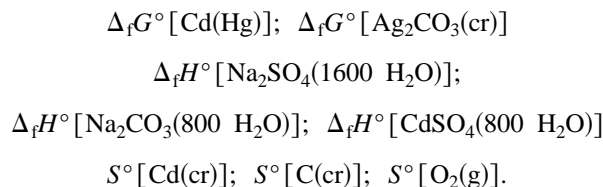
The usual manipulation of these two values gave an entropy of formation of  $-272.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $-65.1 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). Combination of this value with the entropies of formation of the elements yielded an entropy of  $\text{CdCO}_3(\text{cr})$  of  $92.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $22.1 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

### B. Comments

The heat capacity change for Eq. (3) is obviously wrong. (The crystal phase has a positive heat capacity and the electrolytes possess negative heat capacities. Thus, the heat capacity change for the reaction should be positive, not negative.) The enthalpies of formation used in the calculations for  $\text{Na}_2\text{CO}_3(800 \text{ H}_2\text{O})$  and for  $\text{Na}_2\text{SO}_4(1600 \text{ H}_2\text{O})$  do not match the values given in the NBS Tables ( $-1154.64$  and  $-1388.52 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively).

According to their own descriptions of their methods, the  $\Delta_f G^\circ [\text{Ag}_2\text{CO}_3(\text{cr})]$  value used by them for this calculation did not exist at the time they performed the calculation, yet there it was. Thus, the sequential method, with certain selected exceptions which they described, was not in agreement with their calculation for this substance.

### C. Auxiliary Values Required for Data Pathway



### D. Other Thermodynamic Measurements Considered

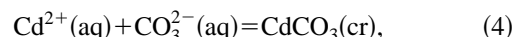
Several sets of measurements of the vapor pressure of  $\text{CO}_2(\text{g})$  over  $\text{CdCO}_3(\text{cr})$  were examined but were not included in the final analysis. These measurements are not in particularly good agreement with each other. They also require auxiliary high temperature thermodynamic properties to adjust from high temperature to 298.15 K; apparently these values were not thought to be well enough known to

make a reliable adjustment. Additionally, in gas decomposition studies the establishment of true equilibrium introduces a complicating factor. The  $\text{CO}_2(\text{g})$  decomposition pressure studies were from 25AND, 63BER/KOV, 24CEN/AND, 27JAN, and 56BER/RAS. The values of  $\Delta_f G^\circ$ ,  $\Delta_f H^\circ$ , and  $S^\circ$  deduced from these measurements were  $-675.3 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $-754.4 \text{ kJ}\cdot\text{mol}^{-1}$ , and  $100.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

### E. More Recent Determinations of the Thermodynamic Properties of $\text{CdCO}_3(\text{cr})$

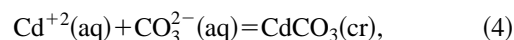
96ARC determined the entropy and other thermal properties of  $\text{CdCO}_3(\text{cr})$  from enthalpy-increment measurements determined from 4.5 to 350 K (temperature basis, ITS-90) and the assumption of a zero-valued configurational entropy. Measurements were made with an adiabatic calorimeter with a previously demonstrated high degree of reliability. The 298.15 K entropy,  $S^\circ$ , was determined to be  $(103.88 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

93STI/PAR measured the solubility of cadmium in water as a function of pH,  $\text{pCO}_2$ ,  $\text{pClO}_4$  (inert electrolyte in the form of  $\text{KClO}_4$ ) and temperature. These measurements were regressed with a chemical equilibrium model that accounted for hydrolysis reactions and ion-pairing reactions. The statistical treatment of the measurements required assumption of knowledge of thermodynamic properties of all these other reactions, including but not limited to cadmium hydroxides. From these measurements and calculations, they obtained a 298.15 K standard-state Gibbs energy and enthalpy of the reaction,



of  $-69.08$  and  $0.74 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. They combined those values with auxiliary values from 89COX/WAG to obtain  $\Delta_f G^\circ$ ,  $\Delta_f H^\circ$ , and  $S^\circ$  values of  $-674.7 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $-751.9 \text{ kJ}\cdot\text{mol}^{-1}$ , and  $106 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

91RAI/FEL measured the solubility of cadmium in water as a function of pH,  $\text{pCO}_2$ , and varying concentrations of  $\text{Na}_2\text{CO}_3(\text{aq})$ . These measurements were regressed with a chemical equilibrium model that accounted for hydrolysis reactions and ion-pairing reactions. The statistical treatment of the measurements required assumption of knowledge of thermodynamic properties of other reactions, including but not limited to cadmium hydroxides. The Gibbs energy of formation for  $\text{CdCO}_3(\text{aq})$  and  $\text{Cd}(\text{CO}_3)_2^{2-}(\text{aq})$  were also obtained from the treatment of the measured solubilities. From these measurements and calculations they obtained a 298.15 K standard-state Gibbs energy of the reaction,



of  $-69.87 \text{ kJ}\cdot\text{mol}^{-1}$ . They combined those values with auxiliary values from the NBS Tables [ $\text{Cd}^{2+}(\text{aq})$ ] and 84HAR/MOL [ $\text{CO}_3^{2-}(\text{aq})$ ] to obtain  $\Delta_f G^\circ$  of  $-675.37 \text{ kJ}\cdot\text{mol}^{-1}$ .

77GOR/CHE measured decomposition pressures from 512 to 625 K. Results were in reasonably good agreement with the earlier measurements from 25AND.

76MAR/POU measured the equilibrium pressure of  $\text{CO}_2(\text{g})$  with  $\text{CdCO}_3(\text{cr})$  and  $\text{CdO}(\text{cr})$  from about 700 to 900 K and pressures to 30 MPa. From these measurements and the van't Hoff relation they gave the enthalpy of the reaction to be  $96 \pm 4 \text{ kJ} \cdot \text{mol}^{-1}$ . They also measured the enthalpy of the decomposition reaction by means of differential thermal analysis. From that method they gave a value of  $103 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$ .

75POU/MAR was the same as 76MAR/POU.

65GAM/STU measured solubilities of cadmium carbonate under pH and  $\text{pCO}_2$  control. Their solubility product led them to a Gibbs energy of formation of  $-674.34 \text{ kJ} \cdot \text{mol}^{-1}$ .

## F. Bibliography

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- 25AND Andrussow, L., *Z. Phys. Chem.* **115**, 273 (1925).
- 27JAN Jander, W., *Z. Anorg. Chem.* **168**, 113 (1927).
- 50SAE Saegusa, F., *Sci. Rep. Tohoku Univ. I Ser.* **34**, 55 (1950).
- 56BER/RAS Berg, L. G., Rassonskaya, I. S., Buris, E. V., *Akad. Nauk SSSR, Izvest. Sect. Fiz. Khim. Anal., Inst. Obsh. Neorg. Khim.* **27**, 239 (1956).
- 63BER/KOV Berg, L. G., Kovyrzina, V. P., *Dokl. Akad. Nauk SSSR* **151**, 117 (1963).
- 65GAM/STU Gamsjäger, H., Stuber, H. U., Schindler, P., *Helv. Chim. Acta* **48**, 723 (1965).
- 75POU/MAR Pouillen, P., Martre, A.-M., *Conf. Int. Thermodynam. Chem.* **4**, 14 (1975).
- 76MAR/POU Martre, A. M., Pouillen, P., Petot, C., *J. Therm. Anal.* **9**, 271 (1976).
- 77GOR/CHE Gorban, N.D., Chernyshov, A. A., *Vestn. Kharkov Un-ta.* **161**, 42 (1977).
- 84HAR/MOL Harvie, C. E., Moller, N., Weare, J. H., *Geochim. Cosmochim. Acta* **48**, 723 (1984).
- 89COX/WAG Cox, J. D., Wagman, D. D., Medvedev, V. A., *CODATA Key Values for Thermodynamics* (Hemisphere, Washington, DC, 1989).
- 91RAI/FEL Rai, D., Felmy, A. R., Moore, D. A., *J. Solution Chem.* **20**, 1169 (1991).
- 93STI/PAR Stipp, S. L. S., Parks, G. A., Nordstrom, D. K., Leckie, J. O., *Geochim. Cosmochim. Acta* **57**, 2699 (1993).
- 96ARC Archer, D. G., *J. Chem. Eng. Data* **41**, 852 (1996).

## 24. $\text{CdCO}_3^0(\text{aq})$

### A. Selected Values, NBS Tables

No value was given.

## E. More Recent Determinations of the Thermodynamic Properties of $\text{CdCO}_3^0(\text{cr})$

91RAI/FEL measured the solubility of cadmium in water as a function of pH,  $\text{pCO}_2$ , and varying concentrations of  $\text{Na}_2\text{CO}_3(\text{aq})$ . These measurements were regressed with a chemical equilibrium model that accounted for hydrolysis reactions and ion-pairing reactions. The statistical treatment of the measurements required assumption of knowledge of thermodynamic properties of other reactions, including but not limited to cadmium hydroxides. The Gibbs energy of formation for  $\text{CdCO}_3^0(\text{aq})$  and  $\text{Cd}(\text{CO}_3)_2^{2-}(\text{aq})$  were also obtained from the treatment of the measured solubilities. From these measurements and a combination with auxiliary values from the NBS Tables [ $\text{Cd}^{2+}(\text{aq})$ ] and from 84HAR/MOL [ $\text{CO}_3^{2-}(\text{aq})$ ] they obtained  $\Delta_f G^\circ [\text{CdCO}_3^0(\text{aq})]$  of  $-632.41 \text{ kJ} \cdot \text{mol}^{-1}$ .

74GAR gave a value of  $\text{pK} = -4.02 \pm 0.04$  for formation of  $\text{CdCO}_3^0(\text{aq})$ , obtained by means of potential measurements with an ion-selective electrode.

76BIL gave a value of  $\text{pK} = -3.5$  for formation of  $\text{CdCO}_3^0(\text{aq})$ , obtained by means of potential measurements made with stripping voltammetry. It has been said that 76BIL/HUS doubt the significance of  $\text{CdCO}_3^0(\text{aq})$ . More correctly, 76BIL/HUS indicated that carbonate complex formation was less significant for cadmium than for some other metals at metal concentrations representative of ground water concentrations, i.e., an order of magnitude  $10^{-6} \text{ M}$ .

Other similarly obtained values of  $\text{pK}$  fall within the range  $-3 - -5$ , see 93STI/PAR.

## F. Bibliography

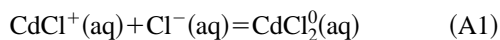
- 74GAR Gardiner, J., *Water Res.* **8**, 23 (1974).
- 76BIL/HUS Bilinski, H., Huston, R., Stumm, W., *Anal. Chim. Acta* **84**, 157 (1976).
- 84HAR/MOL Harvie, C. E., Moller, N., Weare, J. H., *Geochim. Cosmochim. Acta* **48**, 723 (1984).
- 91RAI/FEL Rai, D., Felmy, A. R., Moore, D. A., *J. Solution Chem.* **20**, 1169 (1991).
- 93STI/PAR Stipp, S. L. S., Parks, G. A., Nordstrom, D. K., Leckie, J. O., *Geochim. Cosmochim. Acta* **57**, 2699 (1993).

## 25. Appendix

This appendix addresses several matters raised by reviewers.

*Cancellation of errors.* A reviewer disagreed with an introductory statement in which it was noted that the nature of a sequential analysis is such that errors in the properties for some species can be carried into the properties for other species further in the sequence. The reviewer stated "This is misleading—in many cases the error cancels in the calculation of a process value and that (should) be pointed out." The reviewer also pointed to the specific case of the effect of a calculational error on the properties of the species  $\text{CdCl}_2^0(\text{aq})$  and  $\text{CdCl}_3^-(\text{aq})$ , and stated "If the error appears on both sides of the reaction, the process will be alright; a

statement to this effect should be made.’’ The reviewer’s point is true in a certain instance that is described here. It is not a useful claim for those attempting to calculate the speciations, or extents of reactions, in chemical systems; this is also described below. The reviewer is apparently implying that if one takes the reaction:

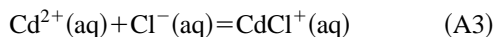


and calculates  $\Delta_{\text{rxn}}G^\circ$  that the correct value will be calculated because both  $\Delta_f G^\circ$  values for  $\text{CdCl}^+(\text{aq})$  and  $\text{CdCl}_2^0(\text{aq})$  possess the same value of error. This is true for calculation of the Gibbs energy of the reaction of Eq. (A1). However, and more importantly, the error does not ‘‘cancel’’ and, in fact, can have a large effect on the accuracy of calculated properties of the aqueous solution, or the calculated distribution of species, even if one of the processes is written as in Eq. (A1). This is shown next.

One is normally more interested in calculation of the amount of species found in the solution than in the value of a  $\Delta_r G^\circ$  *per se*. The reviewer’s pathway for calculation of the concentration of  $\text{CdCl}_2^0(\text{aq})$  in a solution containing chloride and cadmium ions is through the  $\Delta_r G^\circ$  value for Eq. (A1) and the corresponding equilibrium constant,  $K$ , for Eq. (A1):

$$K = (\text{CdCl}_2^0)/(\text{CdCl}^+)(\text{Cl}^-). \quad (\text{A2})$$

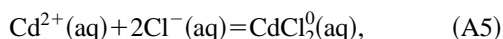
Therefore, calculation of  $(\text{CdCl}_2^0)$ , through the pathway of Eq. (A1), requires knowledge of the activity of  $\text{CdCl}^+(\text{aq})$ . The activity of  $\text{CdCl}^+(\text{aq})$  is calculated from the Gibbs energy of reaction for:



and its associated equilibrium constant expression. As discussed under the section for  $\text{CdCl}^+(\text{aq})$  the equilibrium constant for this reaction calculated from the Gibbs energies of formation would be about five times too large because of the apparent arithmetic error. Thus the value of  $(\text{CdCl}^+)$  calculated from:

$$K = (\text{CdCl}^+)/(\text{Cd}^{2+})(\text{Cl}^-) \quad (\text{A4})$$

is four to five times too large for a dilute solution of aqueous cadmium chloride ( $\sim 1 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1} \text{ CdCl}_2$ ). Incorporation of this too large value into Eq. (A2) results in a calculation of  $(\text{CdCl}_2^0)$  that would be too large also. Therefore, in the calculation of the solution behavior, the calculated activities of neither  $\text{CdCl}_2^0(\text{aq})$  nor  $\text{CdCl}^+(\text{aq})$  would be correct, even through the reviewer’s pathway, the error, does not ‘‘cancel.’’ Extension of the argument for  $\text{CdCl}_2^0(\text{aq})$  is straightforward. That these errors do not cancel when calculating a property of the solution should also be expected through the simple observation that the calculated Gibbs energy of reaction of:

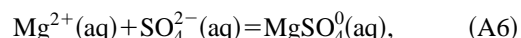


would have to be incorrect because the arithmetic error affects the Gibbs energy of formation of only one side of Eq. (A5). Of course, Eqs. (A2) and (A4) are coupled to each other and this coupling involves additional calculation; how-

ever, the coupling does not change the conclusion provided by this back-of-the-envelope heuristic demonstration, particularly so for very dilute solutions.

*Mixing of models and averages over models.* In descriptions of some of the species it was stated that values were chosen from different models and that, in some cases, an average of values over different models may have been performed. A reviewer questioned why these procedures would be noted by the author. This is discussed next.

When ion association is not strong, the values of equilibrium constants extracted from thermodynamic measurements depend strongly on the assumptions made regarding the non-ideality models used. Consider the example  $\text{MgSO}_4(\text{aq})$  and values given by 71ISO. In this system it is often hypothesized that the following ion-pairing reaction occurs:



and thermodynamic properties for it are determined from some sort of thermodynamic measurements. In 71ISO, measured freezing temperatures of aqueous solutions of magnesium sulfate were reported and from them were calculated osmotic coefficients. Equilibrium constants were then extracted from the calculated osmotic coefficients assuming different values of the ion size parameter in a Debye–Hückel equation:

$$\ln \gamma_{\pm} = (-Az^2I^{1/2})/(1 + BaI^{1/2}), \quad (\text{A7})$$

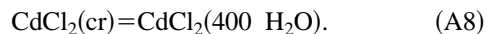
where  $\gamma_{\pm}$  is the activity coefficient of the solute ions,  $A$  is the Debye Hückel parameter for activity coefficient,  $z$  is the charge of the ions (2),  $I$  is the ionic strength of the solution, and  $B$  is a solvent-dependent constant. For each of the two values  $a = 0.4 \text{ nm}$  and  $a = 0.6 \text{ nm}$ , 71ISO reported an equilibrium constant for association,  $77 \pm 3$  and  $143 \pm 10$ , respectively, from the same set of examined values. Both models ( $a = 0.4 \text{ nm}$ ,  $K = 77$ ; and  $a = 0.6 \text{ nm}$ ,  $K = 143$ ) represent the measurements, but each equilibrium constant has meaning only when taken in conjunction with its assumed nonideality model. If one merely extracts the value  $K = 77$  from 71ISO, converts it into a Gibbs energy of reaction, and then tabulates a Gibbs energy of formation of  $\text{MgSO}_4^0(\text{aq})$  and does not also give the nonideality model, then it would be highly unlikely that somebody else could take that tabulated value and recalculate accurately the thermodynamic property of the solution, because that person would have to guess at which non-ideality model might have been used to obtain the tabulated value. This is an example of the general problem.

Now consider averaging the two values of the Gibbs energies of reactions, one from each of the two model-calculated equilibrium constants, obtained above. One would then be taking the average of  $-10.77 \text{ kJ} \cdot \text{mol}^{-1}$  ( $K = 77$ ) and  $-12.30 \text{ kJ} \cdot \text{mol}^{-1}$  ( $K = 143$ ) and calculating  $\Delta_r G^\circ = -11.54 \text{ kJ} \cdot \text{mol}^{-1}$ . But this value corresponds to neither of the nonideality models and could not be later combined with either of them to calculate accurately the properties of the solution. Statistically, one calculates an average of independent observations of a random variable. Averaging across different models, as was just done, is equivalent to averaging

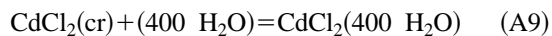


different random variables, not averaging different observations of the same random variable, and to the best of the author's knowledge does not have a valid statistical basis.

*Reaction stoichiometry.* A reviewer objected to the writing of chemical reaction equations corresponding to measurements of enthalpies of solution typified by:

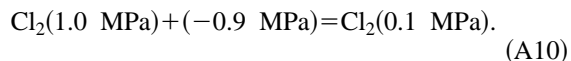


The reviewer stated that these written reactions are stoichiometrically unbalanced. Presumably, the reviewer believes such reactions should be written as:



similar to that given on page 2–27 of 82WAG/EVA. In both Eqs. (A8) and (A9), the information within parentheses refers to a *state* of the substance, not to the substance itself. Thus, in Eq. (A8),  $\text{CdCl}_2(\text{cr})$  denotes a substance, cadmium chloride, in a particular state, that of crystal. Similarly,  $\text{CdCl}_2(400 \text{ H}_2\text{O})$  refers to the same substance in a different state, an aqueous solution composed of 400 moles of water per mole of solute. The process measured is that of changing the state from one to the other. Thus, it necessarily follows that Eq. (A9) *adds a state* to a substance in a state to obtain the substance in the new state. But this is not the customary

way of writing chemical reactions. For example, consider writing in the same way the reaction corresponding to measurement of a Joule–Thomson enthalpy due to the expansion of chlorine gas from 1 to 0.1 MPa. Using a methodology analogous to that used to write Eq. (A9), the reaction would then be written as:



Equation (A10) is written in the same general way as Eq. (A9), namely, a state, or a change in state, has been added to a substance in one state to obtain the same substance in a new state. The only difference resides in the nature of the specific states. Since this is not the customary way of writing reactions, it has not been adopted in this article.

### References for the Appendix

- 71ISO Isono, T., *Sci. Rep. Inst. Phys. Chem. Res. (Jpn.)* **65**, 95 (1971).
- 82WAG/EVA Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L., *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).