

RECEIVED BY DTIE JUN 18 1970

FINAL REPORT
 TO THE UNITED STATES ATOMIC ENERGY
 COMMISSION ON CONTRACT NO. AT(11-1)-1782,
 FORMERLY NO. AT(04-3)-299

MASTER

For the Period 1 May 1959 to 28 February 1970

"Thermodynamics of Metal-Ligand Interaction
 In Aqueous Solution"

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

by

Reed M. Izatt
 Professor, Department of Chemistry

and

James J. Christensen
 Professor, Department of Chemical Engineering

Brigham Young University
 Provo, Utah

fag

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FINAL REPORT TO THE UNITED STATES ATOMIC
ENERGY COMMISSION ON CONTRACT NO. AT(11-1)-1782,
FORMERLY AT(04-3)-299

Covering the Period 1 May 1959 - 28 February 1970

I. General

The work supported during the period of this contract has made a significant contribution to scientific research in the following areas: increased knowledge of metal-ligand reactions, development of precision calorimetric equipment and training of undergraduate and graduate students. The work completed during the contract period is summarized under the following headings: Metal-Ligand Systems, Calorimeter Development, Other Studies, Presentation of Scientific Papers and Achievement of Student Training. Under the first three headings the report consists of listing the titles and references to published manuscripts. Six copies of each listed manuscript either have been submitted with previous reports or are included with this report. If manuscript copies are included, this fact is so indicated. Thirty two published papers have resulted from this research.

II. Metal-Ligand Systems

A. Metal-Cyanide Systems

1. R. M. Izatt, J. J. Christensen, R. T. Pack, and R. Bench, "Thermodynamics of Metal-Cyanide Coordination. I. pK , ΔH° , and ΔS° Values as a Function of Temperature for Hydrocyanic Acid Dissociation in Aqueous Solution," Inorg. Chem., 1, 828 (1962).

2. J. J. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack, and G. D. Watt, "Thermodynamics of Metal Cyanide Coordination. II. ΔG° , ΔH° , and ΔS° Values for Tetracyanonickolate (II) Ion Formation in Aqueous Solution at 25°," Inorg. Chem., 2, 337 (1963)

3. G. D. Watt, J. J. Christensen, and R. M. Izatt, "Thermodynamics of Metal Cyanide Coordination, III. ΔG° , ΔH° , and ΔS° Values for Ferrocyanide and Ferricyanide Ion Formation in Aqueous Solution at 25°," Inorg. Chem., 4, 220 (1965).

4. R. M. Izatt, J. J. Christensen, J. W. Hansen, and G. D. Watt, "Thermodynamics of Metal Cyanide Coordination. IV. $\log \beta^\circ_1$, ΔH°_1 , and ΔS°_1 Values for the Zinc (II)-Cyanide System at 25°," Inorg. Chem., 4, 718 (1965).

5. J. J. Christensen, R. M. Izatt, and D. Eatough, "Thermodynamics of Metal Cyanide Coordination. V. $\log K$, ΔH° , and ΔS° Values for the Hg^{2+} - CN^- System," Inorg. Chem., 4, 1278 (1965).

6. R. M. Izatt, H. D. Johnston, G. D. Watt, and J. J. Christensen, "Thermodynamics of Metal Cyanide Coordination. VI. Copper (I) and Silver (I) Cyanide Systems," Inorg. Chem., 6, 132 (1967).

7. R. M. Izatt, J. J. Christensen, D. Eatough, and G. D. Watt, "Thermodynamics of Metal Cyanide Coordination. VII. $\log K$, ΔH° , and ΔS° Values for the Interaction of CN^- with Pd^{2+} . ΔH° Values for the Interaction of Cl^- and Br^- with Pd^{2+} ," J. Chem. Soc. (London) (A), 1967, 1304.

8. R. M. Izatt, G. D. Watt, C. H. Bartholomew, and J. J. Christensen, "Thermodynamics of Metal Cyanide Coordination. VIII. A Calorimetric Study of Co^{2+} - CN^- Interaction," Inorg. Chem., 7, 2236 (1968).

9. R. M. Izatt, H. D. Johnston, D. J. Eatough, J. J. Christensen, and J. W. Hansen, "Thermodynamics of Metal Cyanide Coordination. IX. $\log \beta^\circ_i$, ΔH°_i and ΔS°_i Values for the Ni^{2+} -, Zn^{2+} -, Cd^{2+} - and Hg^{2+} - CN^- Systems at 10, 25 and 40°, Thermochimica Acta, submitted for publication. Six copies are enclosed.

10. R. M. Izatt, G. D. Watt, C. H. Bartholomew and J. J. Christensen, "A Calorimetric Study of Prussian Blue and Turnbull's Blue Formation," Inorg. Chem., In Press. Six copies are enclosed.

B. Metal-Halide Systems

1. L. D. Hansen, R. M. Izatt, and J. J. Christensen, "Thermodynamics of Metal-Halide Coordination in Aqueous Solution, I. Equilibrium Constants for Several Mercury (I)- and Mercury (II)-Halide Systems as a Function of Temperature," Inorg. Chem., 2, 1243 (1963).

2. J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. D. Hale, "Thermodynamics of Metal-Halide Coordination. II. ΔH° and ΔS° Values for Stepwise Formation of HgX_2 (X = Cl, Br, I) in Aqueous Solution at 8, 25, and 40°C," Inorg. Chem., 3, 130 (1964).

3. J. A. Partridge, R. M. Izatt, and J. J. Christensen, "Values of Log K, ΔH° , and ΔS° at 25° for Stepwise Replacement of Cl^- by OH^- in Mercuric Chloride, $HgCl_2(aq)$," J. Chem. Soc., 4231 (1965).

4. J. A. Partridge, J. J. Christensen, and R. M. Izatt, "Log K, ΔH° , and ΔS° Values for Stepwise Replacement of Cl^- in $HgCl_2(aq)$ by Ethylenediamine, Glycinate Ion, and Methylamine at 25°," J. Amer. Chem. Soc., 88, 1649 (1966).

C. Reactions in Non-Aqueous Solvents

1. R. M. Izatt, D. Eatough, and J. J. Christensen, "Calorimetric Determination of Log K_i , ΔH°_i , and ΔS°_i Values for the Interaction at 25° of $Hg(CN)_2$ with Thiourea in Water-Ethanol Solvents," J. Phys. Chem., 72, 2720 (1968).

2. R. M. Izatt, C. H. Bartholomew, C. E. Morgan, D. J. Eatough and J. J. Christensen, "Calorimetric Determination of Log K_i , ΔH°_i and ΔS°_i Values for the Interaction of Thiourea with $Hg(CN)_2$ in Water-Formamide Solvents

at 25°, " Thermo. Acta, submitted for publication. Six copies are enclosed.

D. Metal-Sulfate Systems

1. R. M. Izatt, D. Eatough, J. J. Christensen, and C. H. Bartholomew, "Calorimetrically Determined Log K, ΔH° , and ΔS° Values for the Interaction of SO_4^{2-} with H^+ , Na^+ , and K^+ in the Presence of n-Tetraalkylammonium Ion," J. Chem. Soc. (London), (A), 45, 1969.

2. R. M. Izatt, D. Eatough, J. J. Christensen, and C. H. Bartholomew, "Calorimetrically Determined Log K, ΔH° , and ΔS° Values for the Interaction of SO_4^{2-} with Several Bi- and Tri-Valent Metal Ions," J. Chem. Soc. (London), (A), 47, 1969.

E. Metal-Glycinate Systems

1. R. M. Izatt, H. D. Johnston and J. J. Christensen, "Log K_i , ΔH°_i and ΔS°_i Values for the Interaction of Glycinate Ion with Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} at 10, 25, and 40°," Thermochimica Acta, submitted for publication. Six copies are enclosed.

F. Pd^{2+} -OH⁻ System

1. R. M. Izatt, D. Eatough, and J. J. Christensen, "A Study of Pd^{2+} (aq) Hydrolysis, Hydrolysis Constants and the Standard Potential for the Pd, Pd^{2+} Couple," J. Chem. Soc. (London) (A), 1967, 1301.

III. Calorimeter Development

1. J. J. Christensen and R. M. Izatt, "Thermodynamics of Proton Dissociation in Dilute Aqueous Solution. II. Heats of Proton Dissociation from Ribonucleotides and Related Compounds Determined by a Thermometric Titration Procedure," J. Phys. Chem., 66, 1030 (1962).

2. J. J. Christensen, R. M. Izatt, and L. D. Hansen, "New Precision Thermometric Titration Calorimeter," Rev. Sci. Instr., 36, 779 (1965).

3. J. J. Christensen, L. D. Hansen, R. M. Izatt, and J. A. Partridge, "Application of High Precision Thermometric Titration Calorimetry to Several Chemical Systems," in *Microcalorimetrie et Thermogenese*, "Publication No. 156 from Centre National de la Recherche Scientifique, Paris, France (1967), p. 207.

4. J. J. Christensen, J. D. Johnston, and R. M. Izatt, "An Isothermal Titration Calorimeter," *Rev. Sci. Instr.*, **39**, 1356 (1968).

IV. Other Studies

1. J. D. Hale, R. M. Izatt, and J. J. Christensen, "Heat of Ionization of Water," *Proc. of Chem Soc.*, August, 240 (1963).

2. J. D. Hale, R. M. Izatt, and J. J. Christensen, "A Calorimetric Study of Heat of Ionization of Water at 25°," *J. Phys. Chem.*, **67**, 2605 (1963).

3. L. D. Hansen, J. J. Christensen, and R. M. Izatt, "Entropy Titration, A Calorimetric Method for the Determination of $\Delta G^\circ(K)$, ΔH° , and ΔS° ," *Chem. Comm.*, **3**, 36 (1965).

4. J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, "Entropy Titration. A Calorimetric Method for the Determination of ΔG° , ΔH° , and ΔS° from a Single Thermometric Titration," *J. Phys. Chem.*, **70**, 2003 (1966).

5. R. M. Izatt, D. Eatough, J. J. Christensen, and R. L. Snow, "Computer Evaluation of Entropy Titration Data. Calorimetric Determination of $\log \beta_i$, ΔH°_i , and ΔS°_i Values for the Silver (I)-and Copper (II)-Pyridine System," *J. Phys. Chem.*, **72**, 1208 (1968).

6. J. J. Christensen and R. M. Izatt, "Thermochemistry in Inorganic Solution Chemistry," Chapter in "Techniques in Advanced Inorganic Chemistry," ed. P. Day and A. Hill, John Wiley and Sons, New York, 1968.

7. J. J. Christensen, H. D. Johnston and R. M. Izatt, "Thermodynamics of Proton Ionization in Aqueous Solution. XII. pK , ΔH° , ΔS° and ΔC_p Values for HCN Dissociation at 10, 25, and 40°," J. Chem. Soc., (A), 454 (1970). Six reprints are enclosed.

8. R. M. Izatt, D. J. Eatough, C. E. Morgan and J. J. Christensen, "Half Cell Potential of the Pd, Pd^{2+} couple in 3.94M $HClO_4$ and the Entropy of $Pd(aq)^{2+}$," J. Chem. Soc., In Press. Six copies are enclosed

V. Presentation of Scientific Papers

The work described under II, III and IV was presented at various local, regional and national American Chemical Society meetings; Calorimetry Conferences and International Coordination Chemistry Conferences. More than fifty papers have been presented at regional, national and international meetings during the Contract period.

VI. Achievement of Student Training

The research program has made a significant contribution to the training and support of undergraduate and graduate students. Nine doctoral students, eleven M.S. students and more than twenty undergraduate students received partial or full support (salary, equipment and/or supplies) during the Contract period.

Opportunity has been provided the graduate students to attend and present papers at regional and national American Chemical Society meetings and at the Calorimetry Conferences.

Ten M.S. and six Ph.D. Theses have been completed by students who received partial or full support from Contract funds. On additional M.S. thesis and three Ph.D. theses will be completed by August 1970.