An Overview of the Geochemical Code MINTEQ: Applications to Performance Assessment for Low-Level Wastes

**S. R. Peterson
B. E. Opitz
M. J. Graham
L. E. Eary**

March 1987

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SUMMARY

The MINTEQ geochemical computer code, developed at the Pacific Northwest Laboratory (PNL), integrates many of the capabilities of its two immediate predecessors, MINEQL and WATEQ3. The MINTEQ code will be used in the Special Waste Form Lysimeters-Arid program to perform the calculations necessary to simulate (model) the contact of low-level waste solutions with heterogeneous sediments or the interaction of ground water with solidified low-level wastes. The code can calculate ion speciation/solubility, adsorption, oxidation-reduction, gas phase equilibria, and precipitation/dissolution of solid phases.

Under the Special Waste Form Lysimeters-Arid program, the composition of effluents (leachates) from column and batch experiments, using laboratory-scale waste forms, will be used to develop a geochemical model of the interaction of ground water with commercial, solidified low-level wastes. The wastes being evaluated include power-reactor waste streams that have been solidified in cement, vinyl ester-styrene, and bitumen. The thermodynamic database for the code was upgraded preparatory to performing the geochemical modeling. Thermodynamic data for solid phases and aqueous species containing Sb, Ce, Cs, or Co were added to the MINTEQ database. The need to add these data was identified from the characterization of the waste streams. The geochemical model developed from the laboratory data will then be applied to predict the release from a field-lysimeter facility that contains full-scale waste samples. The contaminant concentrations migrating from the waste forms predicted using MINTEQ will be compared to the long-term lysimeter data. This comparison will constitute a partial field validation of the geochemical model.

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INTRODUCTION

The Special Waste Form Lysimeters-Arid program was initiated in 1983 under the Low-Level Waste Management Program, for the long-term field evaluation of commercial, solidified, low-level wastes intended for shallow land burial (Graham and Walter 1984; Walter et al. 1984). A similar task is being conducted at the Savannah River Laboratory for a humid climate. The primary objective of this program is to conduct waste-form leaching tests in a field facility to identify typical source terms generated by these wastes. The solidification agents being tested are cement, vinyl ester-styrene, and bitumen. The chemical reactions and physical processes that control the concentrations of radionuclides in the soil solution surrounding the waste in an arid climate are being identified.

In addition to the field monitoring, a series of laboratory testing and geochemical modeling exercises are under way. Standard leaching tests have been completed at Brookhaven National Laboratory. Column experiments are currently under way at Pacific Northwest Laboratory (PNL) to determine if the release of radionuclides from the waste is primarily controlled by diffusion through the waste form or by factors related to the adsorption of leachate onto the surrounding soil. The MINTEQ geochemical code will be used to develop an understanding of the contact of the low-level waste solutions with heterogeneous sediments and of the interaction of ground water with solidified, low-level wastes. MINTEQ will be used to model the waste stream, the waste form, and the column effluent from the field and laboratory experiments. Specifically, the goals of the laboratory and modeling work are to identify the mechanisms that control the release of radionuclides from the waste forms. Only reactions involving inorganic species will be considered in the modeling effort.

For the purposes of this report, a geochemical code is defined as the formulation in computer language of a mathematical model used to predict chemical behavior in geologic settings. One such code, MINTEQ, is being used on the Special Waste Form Lysimeters-Arid program to develop an understanding of the chemical interactions that occur when ground water contacts commercial, low-level wastes and when leachates from these wastes contact the surrounding

sediments in an arid environment. This report provides an overview of the MINTEQ geochemical code in the context of applications to performance assessments of shallow land burial of low-level wastes. Additionally, information on thermodynamic data for the solid and aqueous species of Sb, Ce, Cs, and Co is given. The background of the Special Waste Form Lysimeters-Arid program and the rationale for selecting MINTEQ are described, as is the geochemical modeling process, including examples of the application of MINTEQ to other problems.

FEATURES OF THE MINTEQ CODE

The MINTEQ geochemical computer code was constructed by Felmy, Girvin and Jenne (1984) of PNL, who combined the best features of its two immediate predecessors, MINEQL (Westall et al. 1976) and WATEQ3 (Ball et al. 1981). MINTEQ can calculate ion speciation/solubility, adsorption, oxidation-reduction, gas phase equilibria, and precipitation/dissolution of solid phases. Moreover, MINTEQ can accept a finite mass for any solid considered for dissolution. Therefore, MINTEQ will continue to calculate the dissolution of the specified solid phase only until its initial mass is exhausted. MINTEQ is the only member of the REDEQL family of computer codes known to have this capability. [Other members of this family of computer codes include REDEQL (Morel and Morgan 1972), REDEQL2 (McDuff and Morel 1973), GEOCHEM (Sposito and Mattigod 1980), and MINEQL (Westall et al. 1976).] This valuable feature enables MINTEQ to model flow-through systems. In such systems, the masses of solid phases that precipitate at earlier pore volumes can be dissolved at later pore volumes according to thermodynamic constraints imposed by the solution composition and solid phases present. It is imperative to have this feature incorporated into the computer code to perform the predictive geochemical modeling necessary to evaluate shallow land burial sites. For a discussion of other geochemical computer codes, see Jenne (1981).

SELECTION OF THE MINTEQ CODE

Kincaid et al. (1984a, 1984b), after an exhaustive study of the existing geochemical computer codes, recommended MINTEQ and EQ3/EQ6 as the best codes available for modeling solute migration. From about 25 geochemical codes, they selected six for further evaluation on the basis of documented capabilities (Kincaid et al. 1984a). Five of these six codes were evaluated on their abilities to simulate solid-waste scenarios associated with deposits of fly ash, bottom ash, and flue gas desulfurization sludge (Kincaid et al. 1984b). Although these codes were not evaluated for low-level waste problems, the key aspects of the codes considered in the analysis are applicable to modeling low-level wastes. For the Special Waste Form Lysimeters-Arid program, the MINTEQ computer code was chosen over EQ3/EQ6 because it is more "user friendly" and has the ability to model adsorption reactions, something the current version of EQ3/EQ6 (Wolery 1984) cannot do. Adsorption reactions are important in many natural systems and in predicting the concentrations of contaminants in plumes migrating from shallow land burial sites.

Other important capabilities were considered in selecting the MINTEQ computer code for potential application to evaluating the geochemistry of low-level waste in shallow land burial sites. For example, unlike certain codes [e.g., PHREEQE (Parkhurst et al. 1980)], MINTEQ has the ability to automatically select and equilibrate a solution with the solids that are thermodynamically most stable in response to changes in solution composition. PHREEQE, in contrast, will not automatically consider all solids in the database that could enter into the equilibrium calculations. The MINTEQ computer program can also recompute the pH and pe (negative log of electron activity) as the solution composition changes in response to aqueous speciation and precipitation and dissolution of solid phases. The pH is computed from a modified form of the electroneutrality condition commonly termed the "proton condition" (Morel and Morgan 1972). The pe is calculated by initializing the mass totals for each oxidation state of an element and including a redox reaction between the components of each oxidation state. Alternatively, the pH and pe can also be fixed at the analytically measured values. Further details of the computational methods are provided by Felmy et al. (1984) and Westall et al. (1976).

Finally, the completeness and credibility of the code's thermodynamic database were important factors in the geochemical code selection. The thermodynamic database in MINTEQ was taken from the database of WATEQ3 and is well documented. The WATEQ3 database was developed and documented over a period of years by members of the U.S. Geological Survey (Truesdell and Jones 1974; Ball et al. 1980; Ball et al. 1981). The MINTEQ database (Felmy et al. 1984) has recently been expanded using published critical reviews and studies of the aqueous species and solids of Cr (Schmidt 1984). In addition, preliminary compilations have been completed by S. R. Peterson and others at PNL for the aqueous species and solids of Mo, Ra, Se, Th, and V, and for reduced sulfur species.

Under the Special Waste Form Lysimeters-Arid program, thermodynamic data for the solid phases and aqueous species of Sb, Ce, Cs, and Co were added to the MINTEQ database. The need to add these data was identified from the characterization of the waste streams. Thermodynamic data for solid and aqueous species for Sb, Ce, Cs, and Co are tabulated in Tables 1 to 8. These tables list Gibb's free energies of formation ($\Delta G_f^0, 298$), enthalpies of formation ($\Delta H_f^0, 298$) and entropies (S_{298}^0) for the solid phases and the aqueous species. Table 9 contains auxiliary thermodynamic data for the basis species used in formulating the chemical reactions. The references used are also listed in Tables 1 to 9. The reactions for aqueous and solid species for Sb, Ce, Cs, and Co, as formulated for the MINTEQ database, are listed in Appendix A along with their associated values for $\log K_{298}$ and $\Delta H_r^0, 298$ values. Also included in the Appendix Tables are the designated identification (ID) numbers for each of the aqueous species and solid phases. The ID numbers are seven-digit numbers. For aqueous complexes, the first three digits represent the ID number of the cationic component and the next three digits represent the anionic component. The last digit is an arbitrary designation. The first two digits of the ID numbers for solids correspond to the mineral group and roughly follow the mineralogical classification in Dana's system (Dana and Ford 1957) and that described by Robie et al. (1978). The next three digits represent the leading cation in the chemical formula and the last two digits are arbitrary designations. The data listed here have been calculated and formatted for the database of the geochemical computer code via the data processing code MCRT (Wolery 1984).

TABLE 1. Thermochemical Data for the Aqueous Species of Antimony

Formula	$\Delta G_f^0, 298$ kJ/mol	$\Delta H_f^0, 298$ (a) kJ/mol	S_{298}^0 (a) J/K·mol	References
$\text{Sb}_2\text{S}_4^{2-}$	-99.500	-219.200	-52.300	Wagman et al. 1982
SbO^+	-177.110	NA	NA	Wagman et al. 1982
SbO_2^-	-340.190	NA	NA	Wagman et al. 1982
SbOF^0	-487.400	NA	NA	Wagman et al. 1982
$\text{Sb(OH)}_2\text{F}^0$	-724.600	NA	NA	Wagman et al. 1982
Sb(OH)_3^0	-644.700	-773.600	116.300	Wagman et al. 1982
Sb(OH)_6^-	-1188.709	NA	NA	Baes and Mesmer 1976

(a) Values unavailable for data listed as 'NA'. Species without available data for $\Delta G_f^0, 298$ could not be added to the database because the $\log K_{298}$ values could not be calculated.

The thermodynamic data selected in the compilations are primarily based on accepted tabulations provided by such sources as the U.S. National Bureau of Standards (Wagman et al. 1982), the committee on Data from Science and Technology of the International Council of Scientific Unions (CODATA Task Group 1978), and the U.S. Geological Survey (Robie et al. 1978). Some data, particularly for the cobalt sulfides, were taken from Vaughan and Craig (1978). Other sources of data include Cosovic et al. (1982) and Zhorov et al. (1976). Time constraints precluded a thorough review of the most recent journal literature on thermodynamic data for solids and aqueous species of Sb, Ce, Cs, and Co. In addition to the compilations, a limited number of journal articles were used to augment the thermodynamic data for these elements.

The data collected were not critically reviewed in the effort undertaken in the Special Waste Form Lysimeters-Arid program. Where values from sources differed, preference was given to data from compilations that had been critically reviewed and checked for internal consistency by the original authors. The following sources of data for the solid phases of Sb, Ce, Cs, and Co are listed in descending order of preference: 1) CODATA Task Group (1976, 1978), 2) Robie et al. (1978), 3) Wagman et al. (1982), and 4) Stull and Prophet (1971). Data from other sources were used only if data from these sources were

TABLE 2. Thermochemical Data for the Solid Phases of Antimony

Formula	$\Delta G_f^0, 298$ kJ/mol	$\Delta H_f^0, 298$ (a) kJ/mol	S_{298}^0 (a) J/K·mol	References
Sb	0	0	45.69	Wagman et al. 1982
Sb ₂ O ₃	-626.345	-708.560	123.010	Robie et al. 1978
Sb ₂ O ₄	-795.700	-907.500	127.200	Wagman et al. 1982
Sb ₂ O ₅	-829.200	-971.900	125.100	Wagman et al. 1982
Sb ₂ S ₃	-173.600	-174.900	182.000	Robie et al. 1978
Sb ₄ O ₆ Cubic	-1268.100	-1440.600	220.900	Wagman et al. 1982
Sb ₄ O ₆ Orthorhombic	-1253.000	-1417.100	246.000	Wagman et al. 1982
SbCl ₃	-323.670	-382.170	184.100	Wagman et al. 1982
Sb(OH) ₃	-685.200	NA	NA	Wagman et al. 1982
SbBr ₃	-239.3	-259.4	207.1	Wagman et al. 1982

(a) Values unavailable for data listed as 'NA'. Species without available data for $\Delta G_f^0, 298$ could not be added to the database because the $\log K_{298}$ values could not be calculated.

not available. For aqueous data, the following primary sources are listed in descending order of preference: 1) CODATA Task Group (1976, 1978), 2) Wagman et al. (1982), 3) Baes and Mesmer (1976), and 4) Smith and Martell (1976). Data were selected from other sources if information could not be found for a particular species in any of these sources.

The above sources list data for standard state pressures of either 1 bar or 1 atmosphere. Wagman et al. (1982) have pointed out that the effect of this small difference in standard state pressures on thermochemical data for the condensed phases is negligible, and hence the difference is ignored here.

In cases where sources, such as Smith and Martell (1976), give data as $\log K$ values for a specific reaction, $\Delta G_f^0, 298$ for a particular aqueous species or solid phase is calculated from

$$\Delta G_r^0, 298 = - [2.303 R(298)](\log K_{298})$$

where $R = 1.987 \times 10^{-3}$ kcal/K·mol

TABLE 3. Thermochemical Data for the Aqueous Species of Cerium

Formula	$\Delta G_{f,298}^0$ kJ/mol	$\Delta H_{f,298}^0$ (a) kJ/mol	S_{298}^0 (a) J/K·mol	References
CeBr^{2+}	-779.500	NA	NA	Wagman et al. 1982
Ce^{4+}	-503.800	-537.200	-301.000	Wagman et al. 1982
CeClO_4^{2+}	-691.100	-874.900	-155.000	Wagman et al. 1982
CeF^{2+}	-973.600	NA	NA	Wagman et al. 1982
CeNO_3^{2+}	-789.500	NA	NA	Wagman et al. 1982
CeSO_4^+	-1436.300	-1590.800	-71.000	Wagman et al. 1982
$\text{Ce}(\text{SO}_4)_2^-$	-2190.600	-2493.200	8.000	Wagman et al. 1982
CeCl^{2+}	-798.7	-840.6	-88.3	Wagman et al. 1982
Ce^{3+}	-672.0	-696.2	-205.	Wagman et al. 1982

(a) Values unavailable for data listed as 'NA'.

The relationship

$$\Delta G_{r,298}^0 = \Delta G_{f,298}^0(\text{products}) - \Delta G_{f,298}^0(\text{reactants})$$

was then used to calculate $\Delta G_{f,298}^0$ for the unknown solid phase or aqueous species in the specific reactions. A consistent set of auxiliary data (Table 9) were used in such calculations. Gibb's free energies of formation taken from Naumov et al. (1974) were recalculated, when the $\log K_{298}$ for the associated reaction was given, by using the auxiliary data listed in Table 9.

Equilibrium constants are reported in compilations for solutions with particular ionic strengths. In the above calculations, where Gibb's free energies of formation for a particular solid phase or aqueous species were calculated from $\log K_{298}$, no attempt was made to correct the calculated values for ionic strength effects. Instead, ionic strengths are listed for the particular $\Delta G_{f,298}^0$ values, and the data should be viewed with this fact in mind.

It should be noted that the thermodynamic data assume that all reactions are written as formation reactions with either the solid or aqueous products on the right side. This convention is consistent with that used in MINTEQ. In

TABLE 4. Thermochemical Data for the Solid Phases of Cerium

Formula	$\Delta G_{f,298}^0$ kJ/mol	$\Delta H_{f,298}^0$ (a) kJ/mol	S_{298}^0 (a) J/K·mol	References
Ce	0	0	72.0	Wagman et al. 1982
Ce ₂ O ₃	-1706.2	-1796.200	150.600	Wagman et al. 1982
Ce ₂ (SO ₄) ₃ ·8H ₂ O	-5524.800	NA	NA	Wagman et al. 1982
CeCl ₃	-977.800	-1053.500	151.000	Wagman et al. 1982
Ce(IO ₃) ₃ ·2H ₂ O	-1582.600	NA	NA	Wagman et al. 1982
CeO ₂	-1024.6	-1088.7	62.300	Wagman et al. 1982
CeS	-451.500	-459.400	78.200	Wagman et al. 1982
CeCrO ₃	-1452.0	-1540.0	105.0	Wagman et al. 1982

(a) Values unavailable for data listed as 'NA'. Species without available data for $\Delta G_{f,298}^0$ could not be added to the database because the $\log K_{298}$ values could not be calculated.

addition, reactions are written in terms of the basis species used in the MINTEQA code. For example, the formation of the aqueous complex CoOH^+ is written as

A version of the data processing code MCRT (Wolery 1984) was used to check hand calculations of equilibrium constants for the formation reactions. MCRT calculates $\log K_{298}$ as $-\Delta G_{r,298}^0/[2.303R(298)]$.

MCRT provides a check of reaction stoichiometries, charge balance, and internal consistency of the thermochemical data. The internal consistency was checked where possible with the following expression:

$$\Delta G_{f,298}^0 = \Delta H_{f,298}^0 - T \Delta S_{298}^0$$

In a few cases, data were determined to be inconsistent with respect to this equation. The authors of the compilations listing such data generally indicated that the free energy and enthalpy values were based on experimental

TABLE 5. Thermochemical Data for the Aqueous Species of Cesium

Formula	$\Delta G_{f,298}^0$ kJ/mol	$\Delta H_{f,298}^0$ (a) kJ/mol	S_{298}^0 (a) J/K·mol	References
Cs^+	-291.72	-258.04	132.84	COOATA Task Group 1978
CsCl^0	-421.08	NA	NA	Smith and Martell 1976

(a) Values unavailable for data listed as 'NA'.

measurements, whereas the entropies were estimated. In such cases, MCRT was used to calculate entropy values given the measured values for free energies and enthalpies of formation. It is these calculated values that are reported here for such cases.

MCRT also generates a set of correctly formatted files containing the assigned MINTEQ identification numbers and pertinent thermodynamic data for inclusion into the MINTEQ database.

The thermodynamic data for the solids and aqueous species of Sb, Ce, Cs, and Co were added to the database because they are potentially important as migrating contaminants and, additionally, because it is important to have a thermodynamic database that is as complete as possible. All components in the MINTEQ thermodynamic database are potentially important to low-level waste, even though a particular component (element or species) may not be a constituent of the initial waste. This is the case because the waste may react with surrounding sediments, indigenous migrating solutions, or solidification agents that do contain the specified component. This external component could then be important in the adsorption/ desorption and precipitation/dissolution reactions that affect the concentrations of components found in the unreacted low-level waste.

TABLE 6. Thermochemical Data for the Solid Phases of Cesium

Formula	$\Delta G_f^0, 298$ kJ/mol	$\Delta H_f^0, 298$ (a) kJ/mol	S_{298}^0 (a) J/K·mol	References
Cs	0	0	85.23	Wagman et al. 1982
CsOH	-370.702	-415.722	98.742	Robie et al. 1978
Cs ₂ CO ₃	-1054.368	-1139.722	204.472	Wagman et al. 1981
Cs ₂ Cr ₂ O ₇	-1908.281	-2088.820	330.076	Wagman et al. 1981
Cs ₂ O	-308.361	-346.812	146.858	Robie et al. 1978
Cs ₂ SO ₄	-1323.818	-1443.020	211.920	Wagman et al. 1981
Cs ₂ UO ₄	-1797.279	-1919.996	219.660	Robie et al. 1978
CsAl(SO ₄) ₂ (H ₂ O) ₁₂	-5168.077	-6094.833	686.092	Wagman et al. 1981
CsBr	-391.413	-405.806	113.052	Wagman et al. 1981
CsBr ₃	-405.011	-432.626	221.752	Wagman et al. 1981
CsBrO ₃	-284.972	-375.807	163.594	Wagman et al. 1981
CsCl	-414.551	-443.044	101.169	Wagman et al. 1981
CsClO ₃	-307.942	-411.706	156.063	Wagman et al. 1981
CsClO ₄	-314.344	-443.086	175.059	Wagman et al. 1981
CsCuCl ₃	-627.182	-698.728	213.384	Wagman et al. 1981
CsF	-525.510	-553.543	92.801	Wagman et al. 1981
CsHF ₂	-858.975	-923.827	135.185	Wagman et al. 1981
CsI	-340.578	-346.603	123.051	Wagman et al. 1981
CsI ₂ Br	-385.346	-397.062	238.488	Wagman et al. 1981
CsI ₃	-354.803	-361.916	235.141	Wagman et al. 1981
CsI ₄	-357.732	-365.682	290.788	Wagman et al. 1981
CsIBr ₂	-422.584	NA	NA	Wagman et al. 1981
CsIBrCl	-443.504	NA	NA	Wagman et al. 1981
CsIBrF	-546.012	NA	NA	Wagman et al. 1981
CsIO ₃	-433.881	NA	NA	Wagman et al. 1981

(a) Values unavailable for data listed as 'NA'. Species without available data for $\Delta G_f^0, 298$ could not be added to the database because the log K_{298} values could not be calculated.

TABLE 6. (contd)

Formula	$\Delta G_{f,298}^0$ kJ/mol	$\Delta H_{f,298}^0$ (a) kJ/mol	S_{298}^0 (a) J/K·mol	References
CsIO ₄	-380.744	NA	NA	Wagman et al. 1981
CsNO ₃	-406.601	-505.971	155.226	Wagman et al. 1981
CsBO ₂	-915.1	-972.4	104.35	Wagman et al. 1982
CsBCl ₄	-826.7	-941.8	151.0	Wagman et al. 1982

(a) Values unavailable for data listed as 'NA'. Species without available data for $\Delta G_{f,298}^0$ could not be added to the database because the log K_{298} values could not be calculated.

TABLE 7. Thermochemical Data for the Aqueous Species of Cobalt

Formula	$\Delta G_f^0, 298$ kJ/mol	$\Delta H_f^0, 298$ ^(a) kJ/mol	S_{298}^0 ^(a) J/K·mol	References
Co^{2+}	-54.392	-58.199	-112.968	Robie et al. 1978
$\text{Co}_2\text{OH}^{3+}$	-281.583	NA	NA	Smith and Martell 1976
Co^{3+}	134.014	92.006	-305.892 ^(b)	Robie et al. 1978
$\text{Co}_4(\text{OH})_4^{4+}$	-993.282	NA	NA	Smith and Martell 1976
CoCO_3^0	-600.404	NA	NA	Cosovic et al. 1982, I = 0.56
CoF^+	-338.486	NA	NA	Smith and Martell 1976
CoHCO_3^+	-649.189	NA	NA	Zhorov et al. 1976, I = 0.7
CoHPO_4^0	-1156.123	NA	NA	Smith and Martell 1976, I = 0.5
CoHS^+	-79.496	NA	NA	Smith and Martell 1976
$\text{Co}(\text{HS})_2^0$	-80.333	NA	NA	Naumov et al. 1974
$\text{Co}(\text{NH}_3)^{2+}$	-92.466	-145.185	12.552	Wagman et al. 1982
$\text{Co}(\text{NH}_3)_2^{2+}$	-127.612	NA	NA	Wagman et al. 1982
$\text{Co}(\text{NH}_3)_3^{2+}$	-158.992	NA	NA	Wagman et al. 1982
$\text{Co}(\text{NH}_3)_4^{2+}$	-189.117	NA	NA	Wagman et al. 1982
$\text{Co}(\text{NH}_3)_5^{2+}$	-216.313	NA	NA	Smith and Martell 1976, T = 293 K
$[\text{Co}(\text{NH}_3)_5]\text{Cl}^{2+}$	-291.625	-628.018	341.414	Wagman et al. 1982
$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$	-167.360	-613.374	163.176	Wagman et al. 1982
$\text{Co}(\text{NH}_3)_6^{3+}$	-156.900	-584.923	146.022	Wagman et al. 1982
$[\text{Co}(\text{NH}_3)_6]\text{Br}^{2+}$	-252.714	-718.393	163.176	Wagman et al. 1982
$[\text{Co}(\text{NH}_3)_6]\text{Cl}^{2+}$	-279.910	-770.274	117.152	Wagman et al. 1982
$[\text{Co}(\text{NH}_3)_6]\text{I}^{2+}$	-202.924	-648.938	213.384	Wagman et al. 1982
$[\text{Co}(\text{NH}_3)_6]\text{OH}^{2+}$	-330.536	NA	NA	Wagman et al. 1982
$[\text{Co}(\text{NH}_3)_6]\text{SO}_4^+$	-920.898	-1492.433	238.070	Wagman et al. 1982
CoOH^+	-236.396	NA	NA	Smith and Martell 1976
$\text{Co}(\text{OH})_2^0$	-421.705	NA	NA	Wagman et al. 1982
$\text{Co}(\text{OH})_3^0$	-581.994	NA	NA	Smith and Martell 1976
$\text{Co}(\text{OH})_4^{2-}$	-741.823	NA	NA	Smith and Martell 1976
$\text{CoP}_2\text{O}_7^{2-}$	-2008.320	NA	NA	Smith and Martell 1976
CoS_2O_3^0	-471.955	NA	NA	Smith and Martell 1976, I = 0.1
HCoO_2^-	-407.522	NA	NA	Wagman et al. 1982

(a) Values unavailable for data listed as 'NA'.

(b) Calculated by MCRT.

TABLE 8. Thermochemical Data for the Solid Phases of Cobalt

Formula	$\Delta G_{f,298}^0$ kJ/mol	$\Delta H_{f,298}^0$ ^(a) kJ/mol	S_{298}^0 ^(a) J/K·mol	References
Co, α hexagonal	0.000	0.000	30.041	Robie et al. 1978
CoSO ₄ ·7H ₂ O	-2473.42	-2979.93	406.06	Wagman et al. 1982
Co ₃ (AsO ₄) ₂	-1620.8	NA	NA	Wagman et al. 1982
Co ₃ (PO ₄) ₂	-2398.6	NA	NA	Wagman et al. 1982
Co ₃ O ₄	-772.868	-891.192	102.508	Robie et al. 1978
CoCl ₂	-269.8	-312.5	109.16	Wagman et al. 1982
CoCl ₂ ·2H ₂ O	-764.835	-922.990	188.280	Wagman et al. 1982
CoCl ₂ ·6H ₂ O	-1725.482	-2115.430	343.088	Wagman et al. 1982
CoCl ₂ ·H ₂ O	-527.184	-615.048	191.209	Wagman et al. 1982
CoF ₂	-647.265	-692.034	81.965	Wagman et al. 1982
CoHPO ₄	-1181.9	NA	NA	Wagman et al. 1982
[Co(NH ₃) ₅ Cl]Cl ₂	-582.5	-1017.1	366.100	Wagman et al. 1982
[Co(NH ₃) ₅ H ₂ O]Cl ₃	-777.8	-1288.0	346.0	Wagman et al. 1982
Co(NH ₃) ₅ NO ₂ (NO ₃) ₂	-412.9	-1088.7	331.0	Wagman et al. 1982
Co(NH ₃) ₆ Br ₃	-500.9	-1002.90	325.1	Wagman et al. 1982
Co(NH ₃) ₆ (ClO ₄) ₃	-221.1	-1034.7	615.0	Wagman et al. 1982
Co(NH ₃) ₆ (NO ₃) ₃	-524.5	-1282.0	448.0	Wagman et al. 1982
CoO	-214.179	-237.944	52.969	Robie et al. 1978
Co(OH) ₂ ^(b)	-450.198	NA	NA	Wagman et al. 1982
Co(OH) ₂ ^(c)	-454.382	-539.736	79.496	Wagman et al. 1982
Co(OH) ₂ ^(d)	-458.148	NA	NA	Wagman et al. 1982
Co(OH) ₂ ^(e)	-459.82	NA	NA	Naumov et al. 1974
Co(OH) ₃	-596.638	-730.526	83.680	Latimer 1952
CoSO ₄	-782.3	-888.3	118.0	Wagman et al. 1982
CoSO ₄ ·6H ₂ O	-2235.36	-2683.6	367.61	Wagman et al. 1982

(a) Values unavailable for data listed as 'NA'.

(b) Blue precipitate.

(c) Pink precipitate.

(d) Pink precipitate, aged.

(e) Transvaalite.

TABLE 8. (contd)

Formula	$\Delta G_{f,298}^0$ kJ/mol	$\Delta H_{f,298}^0$ (a) kJ/mol	S_{298}^0 (a) J/K·mol	References
$\text{CoSO}_4 \cdot \text{H}_2\text{O}$	-1042.946	-1200.724	175.728	Naumov et al. 1974
CoS_2	-145.603	-153.134	69.036	Vaughan and Craig 1978
Co_9S_8	-834.708	-851.026	471.955 (b)	Vaughan and Craig 1978
$\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	-3518.744	NA	NA	Naumov et al. 1974
CoOOH	-398.735	NA	NA	Sillen and Martell 1964
CoS	-95.395	-96.232	58.576	Vaughan and Craig 1978
Co_3S_4	-348.946	-358.987	184.514	Vaughan and Craig 1978
CoAs	-49.371	-51.045	59.413	Naumov et al. 1974
CoAs_2	-96.650	-83.262	146.440	Naumov et al. 1974
CoCO_3	-640.152	-716.092	88.617	Naumov et al. 1974

(a) Values unavailable for data listed as 'NA'.

(b) Calculated by MCRT.

TABLE 9. Thermochemical Data for Auxiliary Species

Formula	$\Delta G_f^0, 298$ kcal/mol	$\Delta H_f^0, 298$ kcal/mol	S_{298}^0 cal/K·mol	References
H ₂ O	-56.69	-68.32	16.72	Robie et al. 1978
F ⁻	-67.34	-80.15	-3.15	Robie et al. 1978
Cl ⁻	-31.38	-39.93	13.56	Robie et al. 1978
Br ⁻	-24.87	-29.04	19.80	Robie et al. 1978
ClO ₄ ⁻	-2.06	-30.91	43.50	Wagman et al. 1982
HS ⁻	2.88	4.20	15.00	Robie et al. 1978
S ₂ O ₃ ²⁻	-122.80	-155.90	8.90	Naumov et al. 1974
SO ₄ ²⁻	-177.97	-217.32	4.80	Robie et al. 1978
CO ₃ ²⁻	-126.17	-161.84	-13.60	Robie et al. 1978
PO ₄ ³⁻	-243.50	-305.30	-53.00	Robie et al. 1978
H ₃ AsO ₄ ⁰	-183.10	-215.70	44.00	Wagman et al. 1982
NO ₂ ⁻	-8.9	-25.0	33.5	Robie et al. 1978
NO ₃ ⁻	-26.61	-49.57	35.00	Robie et al. 1978
NH ₄ ⁺	-18.99	-31.85	26.57	Wagman et al. 1982
H ⁺	0.000	0.000	0.000	By Definition
I ⁻	-12.412	-13.599	25.500	CODATA 1976
Al ³⁺	-116.900	-126.910	-73.610	Robie et al. 1978
Cu ²⁺	15.720	15.700	-23.200	Cowan 1986
UO ₂ ²⁺	-227.700	-243.500	-23.200	Langmuir 1978
CrO ₄ ²⁻	-174.810	-210.930	13.780	Schmidt 1984
H ₃ BO ₃ ⁰	-231.560	-256.290	38.800	Wagman et al. 1968
Mn ²⁺	-19.600	-27.000	-63.980	Plummer et al. 1976
MoO ₄ ²⁻	-199.900	-238.500	6.500	Wagman et al. 1969
VO ₂ ⁺	-140.300	-155.300	-10.100	Wagman et al. 1971
VO ²⁺	-106.700	-116.300	-32.00	Wagman et al. 1968
Mg ²⁺	-108.700	-111.580	-33.000	Parker et al. 1971
Cr(OH) ₂ ⁺	-153.350	-177.290	-10.030	Schmidt 1984
e ⁻	0.000	0.000	15.604	CODATA 1976

APPLICATIONS TO SPECIAL WASTE FORM LYSIMETERS-ARID PROGRAM

For the modeling associated with the Special Waste Form Lysimeters-Arid program, the MINTEQ computer code can be considered to have four parts: 1) a speciation submodel, 2) a solubility submodel, 3) a mass transfer submodel, and 4) an adsorption submodel. The calculations completed by each submodel are dependent on the thermodynamic data stored in the MINTEQ database. Based on a need identified from thorough characterization of the wastes being evaluated in the program, thermodynamic data for Sb, Ce, Cs, and Co were added to the database. Because of their interrelationship, the ion speciation and solubility submodels will be discussed together.

SPECIATION AND SOLUBILITY

In the speciation submodel, MINTEQ computes the activities of complexed and uncomplexed cationic and anionic species, neutral ion pairs, and the activities of cationic and anionic redox species. These activities are then used in the solubility submodel, which performs solubility calculations in which ion activity products for solids and minerals are calculated. The calculated activity products (AP) are compared to the solubility products (K) of minerals and solids stored in the thermodynamic database of MINTEQ to develop a saturation index [$\log (AP/K)$]. This saturation index indicates the degree of undersaturation or oversaturation of a solution relative to solids and minerals of interest. If a solution is oversaturated with respect to a particular solid phase, the value of the saturation index [$\log (AP/K)$] is greater than 0. Oversaturation conditions are usually explained by precipitation kinetics and/or mineralogical factors that prevent the solid from precipitating at a rate sufficient to control the concentrations of its dissolved components. If the saturation index reflects undersaturation [$\log (AP/K)$ is less than 0], it is concluded that either 1) a less soluble (thermodynamically more stable) solid is controlling the dissolved constituents' concentrations, 2) another mechanism, such as adsorption, is controlling the concentrations of the component species below their solubility products, or 3) the constituents' concentrations in the source are low. A consideration of the saturation indices of the solutions resulting from the interactions of low-level waste with aqueous solutions

will provide useful information as to solids, minerals, and mechanisms that control or affect the concentrations of specified constituents of the system. It will then be possible, using this information, to make predictions about future environmental concentrations of the constituents.

MASS TRANSFER

The results from the solubility submodel of MINTEQ are used by the mass transfer submodel to calculate the mass of solid that precipitates or dissolves. MINTEQ keeps track of the mass of solid that precipitates from solution or dissolves from the sediment. The solids that represent the solution are those considered likely to precipitate from solution because of changes that occur in specific solution parameters (e.g., pH and pe) when the solution comes into contact with the assemblage of solid phases (chemical model) that represent the waste forms. If the solubility submodel indicates that a given solution is oversaturated with respect to a solid phase considered in the chemical model of the system, the mass transfer submodel will precipitate that solid until the solution is at equilibrium [i.e., $\log (\log AP/K) = 0$] with the solid. If the solubility submodel indicates that a solution is undersaturated with regard to a particular solid in the chemical model of the system, the MINTEQ mass transfer submodel will dissolve that solid until solution equilibrium is achieved with respect to the solid, or until the finite mass of the solid is completely dissolved.

ADSORPTION

Adsorption of a solute molecule on the surface of a solid can involve removing the solute molecule from the solution, removing solvent from the solid surface, and attaching the solute to the surface of the solid (Stumm and Morgan 1981). The MINTEQ computer code can model adsorption onto solid surfaces via several mechanisms: 1) a distribution coefficient, K_d , 2) a Langmuir isotherm, 3) a Freundlich isotherm, 4) an ion exchange model, 5) a constant-capacitance surface complexation model, and 6) a triple-layer surface complexation model.

The K_d is defined as the ratio of the mass of adsorbed species to the concentration of the species remaining in solution. Adsorption models conveniently describe the adsorption of solutes by solids at constant temperature (thus the label "isotherm") in quantitative terms (Bohn et al. 1979). The Langmuir isotherm has the advantage over the K_d (linear isotherm) in considering a mass balance on surface adsorption sites (Felmy et al. 1984). The Freundlich isotherm was derived empirically from adsorption data for dilute solutions. The Freundlich isotherm implies that the energy of adsorption decreases logarithmically as the fraction of surface covered increases (Bohn et al. 1979). In the MINTEQ code, the activities of the aqueous species that dominate the adsorption reaction with the surface sites are used instead of the total concentrations of the adsorbate. The use of the activities instead of concentrations allows consideration of the "effective" concentration of each adsorbate. Consequently, the K_d 's and Langmuir and Freundlich isotherms are referred to as "activity" K_d 's and "activity" Langmuir and Freundlich isotherms. Ion exchange reactions involve the exchange of ions with like charge on the solid surface. The two surface complexation models include treatment of electrostatic effects due to surface charge and the effect of solution chemistry on the solid. A general description of each algorithm is given by Felmy et al. (1984). Additional details on the mathematical formulation and nuances of the algorithms can be obtained from references cited by Felmy et al. (1984).

GEOCHEMICAL MODELING PROCESS

A chemical model of the interaction of low-level wastes with sediments and solutions indigenous to the shallow land burial site can be developed through many different methods and thought processes. Plummer (1984) has conveniently classified the modeling approach into "inverse" and "forward" methods. The inverse method, as described by Plummer, is similar to the inverse problem in hydrology (Freeze and Cherry 1979). The goal of both the inverse and forward methods is to identify the dominant mechanisms that account for concentration distributions of aqueous and solid phases along a flow path. These mechanisms involve such things as precipitation/dissolution of solids, adsorption/desorption, ion exchange, and advection-dispersion. Once the dominant mechanisms are identified and incorporated into a chemical model of the system, the chemical model can be used in the forward mode to predict aqueous concentrations and mass transfers in as yet unstudied systems. In this report, the term "inverse method" is used narrowly to mean a method that considers only mass transfers between two points such that the analytical data at the final point are replicated exactly. Any other method is considered to be a forward method.

The inverse method of modeling is more quantitative than the forward method. However, it can be employed only when appropriate hydrogeochemical data along the evolution-path (i.e., the flow path along which mass transfer mechanisms operate) are available. With the inverse method, one works from observed data at two points separated in space along a single flow path. The objective is to find a reaction model that produces mass transfers along the flow path that are consistent with the data at the two observed points. The inverse method is not constrained by thermodynamics; however, the results should be checked by the forward method using thermodynamic constraints on the plausible phases selected for the conceptual chemical model of the system. Minimally, ion speciation and solubility calculations should be performed on the initial and final points in the system to check thermodynamic feasibility. In other words, the inverse method predicts the mass transfers that are consistent with the geochemistry of the initial and final observation points. These mass transfers are unconstrained by thermodynamic considerations.

A simple mass balance computer code, such as BALANCE (Parkhurst et al. 1982) is sufficient to develop a model using the inverse method. The column experiments conducted at PNL will provide the data necessary to perform the inverse modeling. The two points to be modeled are the chemistry of the batch leachate entering the soil column and the chemistry of the leachate after it passes through the column.

The forward method uses a developed conceptual chemical model of the system to predict the aqueous compositions and mass transfers resulting from the sediment/solution interaction. This is the only practical approach in the absence of analytical data sufficient for inverse modeling. The conceptual chemical model of the system may or may not be constrained thermodynamically. Even if it is not constrained thermodynamically, the forward method differs from the inverse method by being used in a predictive mode. One may develop a chemical model using the inverse method and subsequently use the chemical model in a forward mode to predict water quality data and mass transfers in the future or at another site. To use thermodynamic constraints in making predictions regarding a site, the forward method is implied. This use of thermodynamic constraints is both an advantage and liability of the forward method. We gain a better thermodynamic understanding of the system, but it is difficult to consider the rate-dependent or kinetic effects. The inverse method leads to field-derived kinetic data. The kinetic data are field derived in the sense that any reactions that might occur are merged in the postulated mass transfer reactions that produce the measured aqueous phase compositions at the final point in the evolution-path.

Using either the forward or the inverse method, one tries to develop a conceptual chemical model of the system, hereafter referred to as a chemical model. Depending on the method selected, the chemical model is used to replicate exactly or predict as closely as possible the observed or future analytical data at a point. Using the forward method, one could develop a generic chemical model of the interactions of low-level wastes with geologic sediments that could be used in a predictive mode at other sites; this would preclude the necessity of developing an individual chemical model for each site. The forward method is the only alternative at sites where sufficient and appropriate

data are unavailable. Use of the forward method would enable a regulatory agency to evaluate a potential site for suitability as a low-level waste burial site. The inverse method can only be used at existing sites to develop a reaction model to account for what has been observed at the site. However, this reaction model could then be used in a forward mode to predict future conditions at the site.

For the Special Waste Form Lysimeters-Arid program, the geochemical model will be developed using the laboratory data and employing both the inverse and forward methods. Once developed, the model will be used in the forward mode to predict the release from the field-lysimeter facility containing full-scale waste samples. The contaminant concentrations migrating from the wastes will be predicted and compared to the long-term lysimeter data. This will constitute a partial field validation of the geochemical model.

APPLICATION OF THE MODEL

Peterson et al. (1983) were among the first to use a hypothesized solid-phase assemblage to predict the aqueous compositions resulting from a solution contacting heterogeneous sediments in a flow-through system. The solids and minerals in this solid-phase assemblage were allowed to precipitate and dissolve as the solution composition changed. The solid-phase assemblage, in conjunction with the MINTEQ geochemical computer code, was used to simulate the contact of acid uranium mill tailings solutions from Wyoming with indigenous geologic sediments containing calcium carbonate. The compositions of the aqueous phase and the change in mass of each solid phase in the assemblage were calculated as successive pore volumes of solution interacted with the solid-phase assemblage. This generic approach has been successful in predicting contaminant concentrations in plumes migrating from uranium mill tailings waste impoundments, and it is currently being used to evaluate migration from coal combustion by-products. The MINTEQ computer code will be a useful tool for better understanding the interaction of low-level wastes with the surrounding environments, and in developing a chemical model of these interactions. This

chemical model, partially validated under the Special Waste Form Lysimeters-Arid program, will be valuable in helping evaluate the migration of radionuclides from solidified low-level waste at shallow land burial sites.

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APPENDIX A

REACTIONS INVOLVING AQUEOUS SPECIES AND
SOLID PHASES OF ANTIMONY, CERIUM, CESIUM, AND COBALT

TABLE A.1. Reactions Involving Antimony Aqueous Species

ID Number	Reaction	$\Delta H_r^0, 298$ kJ/mol	Log K ₂₉₈
7403300	$H^+ + Sb(OH)_3^0 \rightleftharpoons SbO^+ + 2H_2O$	NA	+1.180
7403301	$Sb(OH)_3^0 \rightleftharpoons SbO_2^- + H_2O + H^+$	NA	-11.803
7402700	$Sb(OH)_3^0 + H^+ + F^- \rightleftharpoons SbOF^0 + 2H_2O$	NA	+6.180
7402702	$Sb(OH)_3^0 + F^- + H^+ \rightleftharpoons Sb(OH)_2F^0 + H_2O$	NA	+6.182
7407300	$2Sb(OH)_3^0 + 4HS^- + 2H^+ \rightleftharpoons Sb_2S_4^{2-} + 6H_2O$	-316.64	+49.287
7407410	$Sb(OH)_3^0 + 3H_2O \rightleftharpoons Sb(OH)_6^- + 3H^+ + 2e^-$	NA	-29.37

TABLE A.2. Reactions Involving Antimony Solid Phases

ID Number	Reaction	$\Delta H_r^0, 298$ kJ/mol	Log K ₂₉₈
1074000	$2Sb(OH)_3^0 + 3HS^- + 3H^+ \rightleftharpoons Sb_2S_3 + 6H_2O$	-289.91	+60.134
2074000	$2Sb(OH)_3^0 \rightleftharpoons Sb_2O_3 + 3H_2O$	-18.79	+8.481
2074001	$2Sb(OH)_3^0 \rightleftharpoons Sb_2O_4 + 2H_2O + 2H^+ + 2e^-$	+68.07	-3.403
2074100	$2Sb(OH)_6^- + 2H^+ \rightleftharpoons Sb_2O_5 + 7H_2O$	NA	+19.654
2074002	$4Sb(OH)_3^0 \rightleftharpoons Sb_4O_6 + 6H_2O$ (cubic)	-61.09	+19.661
2074003	$4Sb(OH)_3^0 \rightleftharpoons Sb_4O_6 + 6H_2O$ (orthorhombic)	-37.59	+17.016
2074004	$Sb(OH)_3^0 \rightleftharpoons Sb(OH)_3$ (solid)	NA	+2.355
4174000	$Sb(OH)_3^0 + 3Cl^- + 3H^+ \rightleftharpoons SbCl_3 + 3H_2O$	+35.20	-0.592
4074000	$Sb(OH)_3^0 + 3Br^- + 3H^+ \rightleftharpoons SbBr_3 + 3H_2O$	+21.23	-1.053

TABLE A.3. Reactions Involving Cerium Aqueous Species

ID Number	Reaction	$\Delta H_r^0, 298$ kJ/mol	Log K ₂₉₈
1701710	$Ce^{3+} \rightleftharpoons Ce^{4+} + e^-$	+159.00	-29.467
1702700	$Ce^{3+} + F^+ \rightleftharpoons CeF^{2+}$	NA	+3.477
1701800	$Ce^{3+} + Cl^- \rightleftharpoons CeCl^{2+}$	+22.68	-0.804
1701802	$Ce^{3+} + Cl^- + 4H_2O \rightleftharpoons CeClO_4^{2+} + 8H^+ + 8e^-$	+1131.70	-185.866
1701300	$Ce^{3+} + Br^- \rightleftharpoons CeBr^{2+}$	NA	+0.605
1707320	$Ce^{3+} + SO_4^{2-} \rightleftharpoons CeSO_4^+$	+14.67	+3.446
1707321	$Ce^{3+} + 2SO_4^{2-} \rightleftharpoons Ce(SO_4)_2^-$	+21.53	+5.071
1704920	$Ce^{3+} + NO_3^- \rightleftharpoons CeNO_3^{2+}$	NA	+1.080

TABLE A.4. Reactions Involving Cerium Solid Phases

ID Number	Reaction	$\Delta H_r^0, 298$ kJ/mol	Log K_{298}
2017000	$\text{Ce}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{CeO}_2 \text{ (cerianite)} + 4\text{H}^+ + \text{e}^-$	+179.18	-21.198
2017001	$2\text{Ce}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Ce}_2\text{O}_3 + 6\text{H}^+$	+453.69	-60.901
4117000	$\text{Ce}^{3+} + 3\text{Cl}^- \rightleftharpoons \text{CeCl}_3$	+143.94	-15.429
4317002	$\text{Ce}^{3+} + 3\text{I}^- + 11\text{H}_2\text{O} \rightleftharpoons \text{Ce}(\text{IO}_3)_3 \cdot 2\text{H}_2\text{O} + 18\text{H}^+ + 18\text{e}^-$	NA	-324.850
1017000	$\text{Ce}^{3+} + \text{HS}^- + \text{e}^- \rightleftharpoons \text{CeS} + \text{H}^+$	+254.37	-36.518
5417001	$\text{Ce}^{3+} + \text{Cr}(\text{OH})_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{CeCrO}_3 + 4\text{H}^+$	+183.81	-17.310
6017001	$2\text{Ce}^{3+} + 3\text{SO}_4^{2-} + 8\text{H}_2\text{O} \rightleftharpoons \text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	NA	+8.653

TABLE A.5. Reactions Involving Cesium Aqueous Species

ID Number	Reaction	$\Delta H_r^0, 298$ kJ/mol	Log K_{298}
2201800	$\text{Cs}^+ + \text{Cl}^- \rightleftharpoons \text{CsCl}^0$	NA	-0.34

TABLE A.6. Reactions Involving Cesium Solid Phases

ID Number	Reaction	$\Delta H_r^0, 298$ kJ/mol	Log K_{298}
2022001	$2\text{Cs}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Cs}_2\text{O} + 2\text{H}^+$	+455.10	-89.742
2022002	$\text{Cs}^+ + \text{H}_2\text{O} \rightleftharpoons \text{CsOH} + \text{H}^+$	+127.14	-27.715
4222000	$\text{Cs}^+ + \text{F}^- \rightleftharpoons \text{CsF}$	+39.85	-8.401
4222001	$\text{Cs}^+ + \text{H}^+ + 2\text{F}^- \rightleftharpoons \text{CsHF}_2$	+4.916	+0.658
4122001	$\text{Cs}^+ + \text{Cl}^- \rightleftharpoons \text{CsCl}$	-17.92	-1.481
4122003	$\text{Cs}^+ + \text{Cl}^- + 3\text{H}_2\text{O} \rightleftharpoons \text{CsClO}_3 + 6\text{H}^+ + 6\text{e}^-$	+870.90	-144.816
4122004	$\text{Cs}^+ + \text{Cl}^- + 4\text{H}_2\text{O} \rightleftharpoons \text{CsClO}_4 + 8\text{H}^+ + 8\text{e}^-$	+1125.35	-185.248
4022001	$\text{Cs}^+ + \text{Br}^- \rightleftharpoons \text{CsBr}$	-26.27	-0.762
4022003	$\text{Cs}^+ + 3\text{Br}^- \rightleftharpoons \text{CsBr}_3 + 2\text{e}^-$	+189.91	-34.834
4022004	$\text{Cs}^+ + \text{Br}^- + 3\text{H}_2\text{O} \rightleftharpoons \text{CsBrO}_3 + 6\text{H}^+ + 6\text{e}^-$	+861.22	-144.067
4322001	$\text{Cs}^+ + \text{I}^- \rightleftharpoons \text{CsI}$	-31.66	-0.538
4322003	$\text{Cs}^+ + 3\text{I}^- \rightleftharpoons \text{CsI}_3 + 2\text{e}^-$	+66.82	-16.241
4322004	$\text{Cs}^+ + 4\text{I}^- \rightleftharpoons \text{CsI}_4 + 3\text{e}^-$	+119.95	-24.826
4322005	$\text{Cs}^+ + \text{I}^- + 3\text{H}_2\text{O} \rightleftharpoons \text{CsIO}_3 + 6\text{H}^+ + 6\text{e}^-$	NA	-108.851
4322006	$\text{Cs}^+ + \text{I}^- + 4\text{H}_2\text{O} \rightleftharpoons \text{CsIO}_4 + 8\text{H}^+ + 8\text{e}^-$	NA	-159.713
4022005	$\text{Cs}^+ + \text{I}^- + 2\text{Br}^- \rightleftharpoons \text{CsIBr}_2 + 2\text{e}^-$	NA	-22.626
4322007	$\text{Cs}^+ + 2\text{I}^- + \text{Br}^- \rightleftharpoons \text{CsI}_2\text{Br} + 2\text{e}^-$	+96.27	-20.020
4322008	$\text{Cs}^+ + \text{I}^- + \text{Br}^- + \text{F}^- \rightleftharpoons \text{CsIBrF} + 2\text{e}^-$	NA	-32.135
4322009	$\text{Cs}^+ + \text{I}^- + \text{Br}^- + \text{Cl}^- \rightleftharpoons \text{CsIBrCl} + 2\text{e}^-$	NA	-23.734
6022001	$2\text{Cs}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{Cs}_2\text{SO}_4$	-17.67	-0.743
5122001	$\text{Cs}^+ + \text{NO}_3^- \rightleftharpoons \text{CsNO}_3$	-40.57	+0.622
5022001	$2\text{Cs}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{Cs}_2\text{CO}_3$	+53.50	-9.979
6022002	$\text{Cs}^+ + \text{Al}^{3+} + 2\text{SO}_4^{2-} + 12\text{H}_2\text{O} \rightleftharpoons \text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	-57.31	+9.058
4122005	$\text{Cs}^+ + \text{Cu}^{2+} + 3\text{Cl}^- \rightleftharpoons \text{CsCuCl}_3$	-5.14	+1.291
7522000	$2\text{Cs}^+ + \text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cs}_2\text{UO}_4 + 4\text{H}^+$	+186.55	-37.356
3022003	$2\text{Cs}^+ + 2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cs}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$	-93.51	+17.383
5222000	$\text{Cs}^+ + \text{H}_3\text{BO}_3 \rightleftharpoons \text{CsBO}_2 + \text{H}_2\text{O} + \text{H}^+$	+72.13	-18.968
5222001	$\text{Cs}^+ + \text{H}_3\text{BO}_3 + 4\text{Cl}^- + 3\text{H}^+ \rightleftharpoons \text{CsBCl}_4 + 3\text{H}_2\text{O}$	+199.39	-43.350

TABLE A.7. Reactions Involving Cobalt Aqueous Species

ID Number	Reaction	$\Delta H_r^0, 298$ kJ/mol	Log K ₂₉₈
2012000	$\text{Co}^{3+} + \text{e}^- \rightleftharpoons \text{Co}^{2+}$	NA	+33.01
2003300	$\text{Co}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CoOH}^+ + \text{H}^+$	NA	-9.67
2003301	$\text{Co}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Co(OH)}_2^0 + 2\text{H}^+$	NA	-18.76
2003302	$\text{Co}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Co(OH)}_3^- + 3\text{H}^+$	NA	-32.23
2003303	$\text{Co}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Co(OH)}_4^{2-} + 4\text{H}^+$	NA	-45.78
2003304	$2\text{Co}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Co}_2\text{OH}^{3+} + \text{H}^+$	NA	-11.28
2003305	$\text{Co}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{HCoO}_2^- + 3\text{H}^+$	NA	-21.24
2003306	$4\text{Co}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Co}_4(\text{OH})_4^{4+} + 4\text{H}^+$	NA	-30.32
2002700	$\text{Co}^{2+} + \text{F}^- \rightleftharpoons \text{CoF}^+$	NA	+0.41
2001400	$\text{Co}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CoCO}_3^0$	NA	+3.17
2001401	$\text{Co}^{2+} + \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{CoHCO}_3^+$	NA	+11.72
2007300	$\text{Co}^{2+} + \text{HS}^- \rightleftharpoons \text{CoHS}^+$	NA	+6.51
2007301	$\text{Co}^{2+} + 2\text{HS}^- \rightleftharpoons \text{Co(HS)}_2^0$	NA	+8.77
2007350	$\text{Co}^{2+} + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{CoS}_2\text{O}_3^0$	NA	-16.86
2005800	$\text{Co}^{2+} + \text{PO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{CoHPO}_4^0$	NA	+14.53
2005801	$\text{Co}^{2+} + 2\text{PO}_4^{3-} + 2\text{H}^+ \rightleftharpoons \text{CoP}_2\text{O}_7^{2-} + \text{H}_2\text{O}$	NA	+26.89
2004900	$\text{Co}^{2+} + \text{NH}_4^+ \rightleftharpoons \text{CoNH}_3^{2+} + \text{H}^+$	+46.27	-7.25
2004901	$\text{Co}^{2+} + 2\text{NH}_4^+ \rightleftharpoons \text{Co(NH}_3)_2^{2+} + 2\text{H}^+$	NA	-15.01
2004902	$\text{Co}^{2+} + 3\text{NH}_4^+ \rightleftharpoons \text{Co(NH}_3)_3^{2+} + 3\text{H}^+$	NA	-23.44
2004903	$\text{Co}^{2+} + 4\text{NH}_4^+ \rightleftharpoons \text{Co(NH}_3)_4^{2+} + 4\text{H}^+$	NA	-32.08
2004904	$\text{Co}^{2+} + 5\text{NH}_4^+ \rightleftharpoons \text{Co(NH}_3)_5^{2+} + 5\text{H}^+$	NA	-41.23
2014907	$\text{Co}^{3+} + 6\text{NH}_4^+ \rightleftharpoons \text{Co(NH}_3)_6^{3+} + 6\text{H}^+$	+122.63	-32.56
2014900	$\text{Co}^{3+} + 5\text{NH}_4^+ + \text{NO}_2^- \rightleftharpoons [\text{Co(NH}_3)_5\text{NO}_2]^{2+} + 5\text{H}^+$	+65.52	-23.33
2014901	$\text{Co}^{3+} + 6\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons [\text{Co(NH}_3)_6\text{OH}]^{2+} + 7\text{H}^+$	NA	-43.69
2014902	$\text{Co}^{3+} + 5\text{NH}_4^+ + \text{Cl}^- \rightleftharpoons [\text{Co(NH}_3)_5\text{Cl}]^{2+} + 5\text{H}^+$	+113.36	-18.03
2014903	$\text{Co}^{3+} + 6\text{NH}_4^+ + \text{Cl}^- \rightleftharpoons [\text{Co(NH}_3)_6\text{Cl}]^{2+} + 6\text{H}^+$	+104.36	-34.01
2014904	$\text{Co}^{3+} + 6\text{NH}_4^+ + \text{Br}^- \rightleftharpoons [\text{Co(NH}_3)_6\text{Br}]^{2+} + 6\text{H}^+$	+110.66	-39.99
2014905	$\text{Co}^{3+} + 6\text{NH}_4^+ + \text{I}^- \rightleftharpoons [\text{Co(NH}_3)_6\text{I}]^{2+} + 6\text{H}^+$	+115.52	-33.59
2014906	$\text{Co}^{3+} + 6\text{NH}_4^+ + \text{SO}_4^{2-} \rightleftharpoons [\text{Co(NH}_3)_6\text{SO}_4]^{2+} + 6\text{H}^+$	+124.39	-29.16

TABLE A.8. Reactions Involving Cobalt Solid Phases

ID Number	Reaction	$\Delta H_r^0, 298$ kJ/mol	Log K_{29}
0020000	$\text{Co}^{2+} + 2\text{e}^- \rightleftharpoons \text{Co}(\text{alpha, hexagonal})$	+58.20	-9.53
2020001	$\text{Co}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CoO} + 2\text{H}^+$	+106.08	-13.56
2020002	$\text{Co}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{OH})_2(\text{blue ppt.}) + 2\text{H}^+$	NA	-13.77
2020003	$\text{Co}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{OH})_2(\text{pink ppt.}) + 2\text{H}^+$	+90.12	-13.03
2020004	$\text{Co}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{OH})_2(\text{pink ppt., aged}) + 2\text{H}^+$	NA	-12.37
2020005	$\text{Co}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{OH})_2(\text{transvaalite}) + 2\text{H}^+$	NA	-12.08
2020100	$\text{Co}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{OH})_3 + 3\text{H}^+$	+34.96	+3.34
3020100	$3\text{Co}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Co}_3\text{O}_4(\text{cobalt spinel}) + 8\text{H}^+ + 2\text{e}^-$	+426.73	-59.40
2020101	$\text{Co}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{CoOOH}(\text{heterogenite}) + 3\text{H}^+$	NA	+10.23
4220000	$\text{Co}^{2+} + 2\text{F}^- \rightleftharpoons \text{CoF}_2$	+36.86	+5.15
4120000	$\text{Co}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CoCl}_2$	+79.81	-8.25
4120001	$\text{Co}^{2+} + 2\text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{CoCl}_2 \cdot \text{H}_2\text{O}$	+63.14	-4.73
4120002	$\text{Co}^{2+} + 2\text{Cl}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$	+41.03	-4.65
4120003	$\text{Co}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O} \rightleftharpoons \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	-8.09	-2.56
7020000	$\text{Co}^{2+} + \text{PO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{CoHPO}_4$	NA	+19.06
7020001	$3\text{Co}^{2+} + 2\text{PO}_4^{3-} \rightleftharpoons \text{Co}_3(\text{PO}_4)_2$	NA	+34.67
5020000	$\text{Co}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CoCO}_3(\text{sphero-cobaltite})$	+19.25	+10.14
1020000	$\text{Co}^{2+} + \text{HS}^- \rightleftharpoons \text{CoS}(\text{jaipurite}) + \text{H}^+$	-20.46	+9.29
1020001	$\text{Co}^{2+} + 2\text{HS}^- \rightleftharpoons \text{CoS}_2(\text{cattierite}) + 2\text{H}^+ + 2\text{e}^-$	-59.79	+20.20
1020002	$3\text{Co}^{2+} + 4\text{HS}^- \rightleftharpoons \text{Co}_3\text{S}_4(\text{linnaeite}) + 4\text{H}^+ + 2\text{e}^-$	-114.10	+40.99
1020003	$9\text{Co}^{2+} + 8\text{HS}^- + 2\text{e}^- \rightleftharpoons \text{Co}_9\text{S}_8(\text{cobalt pentlandite}) + 8\text{H}^+$	-186.65	+77.36
6020000	$\text{Co}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CoSO}_4$	+79.20	-2.91
6020001	$\text{Co}^{2+} + \text{SO}_4^{2-} + 7\text{H}_2\text{O} \rightleftharpoons \text{CoSO}_4 \cdot 7\text{H}_2\text{O}(\text{bieberite})$	-11.65	+2.46
6020002	$\text{Co}^{2+} + \text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightleftharpoons \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	-1.17	+2.31
6020003	$\text{Co}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{CoSO}_4 \cdot \text{H}_2\text{O}$	+52.57	+1.18
7220002	$\text{Co}^{2+} + \text{H}_3\text{AsO}_4^0 + 5\text{H}^+ + 7\text{e}^- \rightleftharpoons \text{CoAs}(\text{modderite}) + 4\text{H}_2\text{O}$	-233.68	+31.12
7220003	$\text{Co}^{2+} + 2\text{H}_3\text{AsO}_4^0 + 10\text{H}^+ + 12\text{e}^- \rightleftharpoons \text{CoAs}_2(\text{safflorite}) + 8\text{H}_2\text{O}$	-506.72	+71.41
7220000	$3\text{Co}^{2+} + 2\text{H}_3\text{AsO}_4^0 \rightleftharpoons \text{Co}_3(\text{AsO}_4)_2 + 6\text{H}^+$	NA	-13.05
7220001	$3\text{Co}^{2+} + 2\text{H}_3\text{AsO}_4^0 + 8\text{H}_2\text{O} \rightleftharpoons \text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{erythrite}) + 6\text{H}^+$	NA	-12.99
5120100	$\text{Co}^{3+} + 5\text{NH}_4^+ + \text{NO}_2^- + 2\text{NO}_3^- \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2 + 5\text{H}^+$	+4.94	-19.31
4120100	$\text{Co}^{3+} + 5\text{NH}_4^+ + 3\text{Cl}^- \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + 5\text{H}^+$	+58.40	-13.09
4120101	$\text{Co}^{3+} + 5\text{NH}_4^+ + \text{H}_2\text{O} + 3\text{Cl}^- \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3 + 5\text{H}^+$	+73.53	-20.42
4120102	$\text{Co}^{3+} + 6\text{NH}_4^+ + 3\text{ClO}_4^- \rightleftharpoons [\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3 + 6\text{H}^+$	+60.83	-25.87
4020100	$\text{Co}^{3+} + 6\text{NH}_4^+ + 3\text{Br}^- \rightleftharpoons [\text{Co}(\text{NH}_3)_6]\text{Br}_3 + 6\text{H}^+$	+69.15	-26.99
5120101	$\text{Co}^{3+} + 6\text{NH}_4^+ + 3\text{NO}_3^- \rightleftharpoons [\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3 + 6\text{H}^+$	+47.66	-26.64

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