APPLICATION OF GEOCHEMICAL MODELS TO OIL SHALE SOLID WASTE

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SUMMARY

Several geochemical codes are available in the literature to model chemical processes such as oxidation-reduction, precipitationdissolution, formation of solution complexes, adsorption, and ion exchange. However, these models differ in the environments to which The objective of this research was to evaluate the they apply. applicability of existing geochemical codes to predict water quality from an oil shale solid waste environment. We selected EQ3/EQ6, GEOCHEM, MINTEQ, PHREEQE, SOLMNEQ, and WATEQFC geochemical models for further evaluation. We conclude that all these models lack thermodynamic data for minerals and solution complexes that are important for oil shale solid waste studies. Selection of any one of the models requires the development of a more reliable thermodynamic data base. Critical evaluation of thermodynamic data has been completed for cations and anions that are important for oil shale solid wastes. Equilibrium solubility studies suggest that akermanite and periclase are too soluble to control the solubility of calcium and magnesium. However, diopside does appear to control the solubility of calcium and magnesium in oil shale solid waste waters.

PART I - GEOCHEMICAL MODELING

Introduction

The major environmental issue associated with processed oil shale solid waste is the ability to understand and predict all types of emissions from the surface disposal of material. The different types of released emissions include surface runoff, leachate, gas, dust, etc., that will affect surface water, groundwater, and air quality within the region. The influence of hydrologic processes on pollutant transport, groundwater chemistry, and initial long-term properties of raw and retorted shale will determine the quantity of emissions from a site. Thus, an ultimate goal in environmental research, pertaining to potentially hazardous organic and inorganic chemicals found in oil shale solid waste, is the prediction of their behavior and fate in any number of physiochemical environments.

The behavior of potentially hazardous organic and inorganic chemicals in oil shale solid waste disposal environments is controlled by a number of chemical processes including precipitation-dissolution, formation of organic and inorganic complexes, adsorption, and ion exchange. Thus, it is important to understand these combined processes to adequately predict the quality of water from oil shale solid waste disposal environments. Several geochemical codes are available in the literature to model these chemical processes. However, these models differ in the environments to which they apply and in their numerical analysis techniques.

The objective of this study was to evaluate how well the existing geochemical models predict the quality of water from oil shale solid waste disposal environments.

Materials and Methods

To evaluate the applicability of existing geochemical codes for oil shale solid waste, the following criteria were established for preliminary screening of codes:

1. Is the code in the public domain?

- 2. Is the code well documented?
- 3. Is the code in use and being updated?
- 4. Is the code able to model processes of interest or could it be readily modified to include such processes?

Having met these criteria, the following six geochemical codes were obtained for further evaluation:

1. EQ3/6 (Worley 1979)

- 2. GEOCHEM (Sposito and Mattigod 1980)
- 3. MINTEQ (Felmy et al. 1984)
- 4. PHREEQE (Parkhurst et al. 1980)
- 5. SOLMNEQ (Kharaka and Barnes 1973)
- 6. WATEQFC (Runnells and Lindberg 1981)

Table 1 lists the capabilities of these selected geochemical codes. Of these, GEOCHEM and WATEQFC are examined in this study.

To examine the applicability of geochemical codes to western oil shale solid wastes, laboratory experiments were conducted to generate equilibrium solubility data. Western reference Green River Formation oil shale from the Piceance Creek Basin in Colorado was retorted under conditions typical of the Paraho process to produce indirectly retorted (PPP3) and directly retorted (PPP6) solid wastes. The retorting conditions used to generate three different solid wastes are summarized by Merriam et al. (1987).

Raw and retorted oil shale samples were ground to pass through a no. 60 sieve. Ground samples were used for X-ray diffraction (XRD) analysis and equilibrium solubility studies. The XRD analysis was performed on randomly oriented samples with a Scintag PAD V powder

				CODE		
CAPABILITY	1	2	3	4	5	6
Number of elements	18	44	32	35	24	34
Number of species	140	2000	373	296	181	500
Number of minerals	250	500	238	374	158	375
Speciation/saturation	Yes	Yes	Yes	Yes	Yes	Yes
Adsorption	No	Yes	Yes	No	No	No
Ion exchange	No	Yes	No	No	No	No
Organic complexation	No	Yes	No	No	No	No
Mass transfer	Yes	No	No	Yes	No	No
Temperature range, C	0-300	25	0-300	-	0-350	0-100
Pressure range, bars	1-500	1	-	-	1-1000	1
Data base						
easily modified	Yes	Yes	Yes	Yes	No	Yes

1.000

Table 1. Capabilities of Selected Geochemical Codes

Codes: (1) EQ3/EQ6 (Worley 1979); (2) GEOCHEM (Sposito and Mattigod 1980); (3) MINTEQ (Felmy et al. 1984); (4) PHREEQE (Parkhurst et al. 1980); (5) SOLMNEQ (Kharaka and Barnes 1973); (6) WATEQFC (Runnells and Lindberg 1981)

diffractometer using Ni-filtered CuK α radiation. The XRD profiles of raw and retorted oil shale samples were analyzed by manual interaction with Scintag Software containing JCPDS (Joint Committee on Powder Diffraction Standards) files to identify major minerals. For equilibrium studies, duplicate 25-gram samples were placed into 250-mL Nalgene bottles. Distilled H₂O (100 mL) was added to each bottle, and, to suppress microbial activity, three drops of toluene was added to each bottle. Each sample bottle was tightly capped, placed on a mechanical shaker, and equilibriated at 200 rpm in an incubator at constant 25°C (298.15 K). After 1-, 3-, 7-, and 14-day equilibration times, samples were filtered through a 0.45- μ m millipore filter. Filtrates were analyzed for pH and total concentrations of different elements.

The pH was measured with a combination pH electrode. Calcium, magnesium, sodium, potassium, barium, aluminum, strontium, molybdenum, boron, and zinc were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES). Carbonate and bicarbonate were measured by titration with 0.02 N standard HCl. Fluoride, chloride, and nitrate were measured with specific ion electrodes. Sulfate was measured by the BaCl₂ precipitation method. Total elemental concentrations, pH,

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and temperature of the extracts were used as input parameters to the GEOCHEM and WATEQFC geochemical codes to compute activities of free ions.

Results and Discussion

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One approach to examine the applicability of geochemical codes to spent oil shales is to examine the thermodynamic data base and compare ion activities in retorted shale-distilled H_20 extracts predicted by the codes. Table 2 summarizes the general features of the program, such as total number of elements, aqueous species, and solid phases; and the pressure and temperature ranges over which calculations can be made. The GEOCHEM, MINTEQ, SOLMNEQ, and WATEQFC are speciation and saturation codes. The EQ3/6 and PHREEQE are mass transfer as well as speciation and saturation codes.

Large differences were found in the equilibrium constants used by the models to make similar calculations (Table 2). All of the models lacked data for certain relevant minerals (e.g., akermanite, monticellite, and rankinite) and solution species (e.g., $HSiO_4^3$, SiO_4^4 , $CaH_3SiO_4^+$, $MgH_3SiO_4^+$, $NaH_3SiO_4^0$, $KH_3SiO_4^0$, and $Ca(H_3SiO_4)_2^0$). Selection of any one of these models requires the development of a reliable thermodynamic database.

The establishment of a reliable thermodynamic database requires critical evaluation and compilaton of the thermodynamic data. This involves reviewing available literature and selecting the most reliable thermodynamic data for minerals and solution complexes that are important for oil shale solid waste studies. Reddy and Drever (1987) critically evaluated the thermodynamic data for F, Mo, Sr, and Se. This year, critical evaluation of thermodynamic data has been completed for Ca, Mg, Na, and K. These evaluations are given in Part II of this report.

A comparison of ion activities, computed by GEOCHEM and WATEQFC codes using analytical data from 1-day contact of water with raw and retorted oil shale samples, is shown in Table 3. These data show good agreement between ion activities, except for $H_4SiO_4^0$ values, which are ower in GEOCHEM than they are in WATEQFC. This discrepancy occurs

			Log Equilibrium Constant					Recently
Reaction			WATEQFC	GEOCHEM	MINTEQ	EQ3/EQ6	PHREEQE	Value
SrCO 3(c)	=	$Sr^{2+} + CO_{3}^{2-}$	-11.41	-9.00	-9.25	-11.70	-9.25	-9.27 ¹
BaCO ₃ (c)	=	Ba ²⁺ + CO ₃ ²⁻	-13.22		-8.58	-13.90	****	-8.56 ²
CaF ₂ (c)	=	Ca ²⁺ + 2F ⁻	-10,96	-9.00	-10,96	-10.96	-10.96	-10,41 ³

Table 2. Comparison of Equilibrium Constants of $SrCO_{3}$ (c), $BaCO_{3}$ (c), and CaF_{2} (c) Used by Different Geochemical Models Along with Recently Reported Values

- ¹ Busenberg et al. (1984)
- 2 Busenberg et al. (1986)
- ³ Elrashidi and Lindsay (1986)

	R	aw	PP	P3	P	PPP6
Species	1	2	1	2	1	2
			-(-log ac	tivity)		
Ca² ⁺	2.74	2.80	5.86	5.75	3.20	3.01
Mg ² ⁺	2.99	3.07	6.68	6.68	5.90	5.80
Na ⁺	2.58	2.59	1.63	1.65	1.60	1.60
к+	3.65	3.67	3.25	3.24	2.38	2.38
F	3.85	3.87	3.36	3.37	4.16	4.17
CO ₃ ²	4.10	4.09	2.13	2.24	2.30	2.55
SO ²	3.08	3.10	2.82	2.77	2.50	2.48
MoO ²	5.40	5.43	5.28	5.28	4.93	4.91
H ₄ SiO ⁰	3.71	3.46	6.14	5.88	7.54	5.95

Table 3. Ion Activities Computed by Geochemical Codes Using Data from1-Day Contact of Water with Raw and Retorted Samples*

1. GEOCHEM

2. WATEQFC

* Average of duplicate analysis

because we included $HSiO_4^3$, SiO_4^4 , $CaH_3SiO_4^+$, $MgH_3SiO_4^+$, $Ca(H_3SiO_4)_2^0$, and $Mg(H_3SiO_4)_2^0$ species in the GEOCHEM database. The equilibrium constants for these species are from Essington and Spackman (in press).

The mineral reactions that control Ca and Mg activities in raw and retorted oil shale solid wastes are important. Such information may explain the alkalinity of oil shale waters. Major minerals identified by XRD analyses of raw and spent oil shale samples are listed in Table 4. These data suggest that processing oil shale at high temperature results in the decomposition of carbonate minerals (e.g., calcite and dolomite) and the production of oxides (e.g., periclase) and silicate minerals (e.g., akermanite and diopside). Similar results were reported by Park et al. (1979). Partial chemical analyses of waters that reacted with oil shale are listed in Table 5. These results show that processing oil shale at high temperature causes the pH of the water to increase from 8.05 to 12.34. Presumably, the processing of oil shale at

<u>Raw</u>	PPP3	PPP4	PPP6
Dolomite,	Dolomite,	Akermanite,	Akermanite,
CaMg(CO_) 3 2	CaMg(CO_)	Ca ₂ MgSi ₂ O ₇	Ca ₂ MgSi ₂ O ₇
Quartz,	Quartz,	Quartz,	Quartz,
sio ₂	sio ₂	sio	sio
Calcite,	Calcite,	Calcite,	Calcite,
CaCO 3	CaCO3	CaCO	CaCOz
Analcime,	Plagioclase,	Diopside,	Plagioclase,
NaAlSi20.H20	Na Ca Al Si O x (1-x) (2-x) (2+x) 8	CaMg(SiO ₃) ₂	Na Ca Al Si $(2+x)$ 8
Plagioclase,	Alkali-feldspar,	Alkali-feldspar,	Diopside,
Na Ca Al Si O X (2-x) 8	KALSI 0 3 B	KALSI 38	CaMg(SiO_)
K-feldspa r,	Illite,	Dolomite,	Alkali-feldspar,
KALSI 0 3 8	K-Al-Si-0 (OH) 4	CaMg(CO ₃)	KALSI 0
Siderite,	Siderite,	Plagioclase,	Periclase,
FeCO 3	FeCO3	Na Ca Al Si O x (1-x) (2-x) (2+x) 8	MgO
Pyrite,	Akermanite,	Periclase,	Anhydrite,
FeS ₂	Ca2 ^{MgSi20} 7	MgO	CaSO
			Dolomite,
			CaMg(CO ₃)
			Cristobalite,
			sio ₂

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Table 4. Major Minerals Identified in Raw and Retorted Oil Shale Solid Waste*

*Samples listed in order of decreasing abundance

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Samp1	e** pH	Ca	Mg	Na	К	CO 3	S0 4	C1	·····F	Мо
					<u>1</u> D	ay				
Raw	8.05 2.46	2.74	2.53	3.60	2.38	2.76	3.50	3.77	5.17	
PPP3	10.95	4.72	5.78	1.52	3.15	1.73	2.41	3.55	3.27	4.93
PPP6	11.94	2.18	4.95	1.50	2.26	1.77	2.06	2.25	4.07	4.56
					3 D	ays				
Raw	7.80 2.46	2.74	2.53	3.60	2.66	2.75	3.47	3.72	5.34	
PPP3	10.80	5.00	4.82	1.20	3.13	1.77	1.83	2.12	3.07	4.80
PPP6	11.60	2.29	BD***	1.56	2.17	2.31	1.87	2.22	4.07	4.51
					<u>7</u> D	ays				
Raw	8.20 2.57	2.67	2.47	3.52	2.62	2.40	3.70	3.70	5.20	
PPP3	10.60	3.72	5.08	0.89	3.09	1.89	1.77	1.89	2.88	4.75
PPP6	12.10	2.90	5.06	1.14	2.17	1.89	1.96	2.75	3.70	4.58
					14 D	ays				
Raw	8.24 2.40	2.65	3.42	3.60	2.56	2.30	3.95	3.67	5.25	
PPP3	10.40	4.74	5.38	1.18	3.05	1.98	1.77	3.01	2.74	4.75
PPP6	12.50	3.20	6.08	1.40	2.42	1.13	2.05	3.77	3.50	4.45

Table 5. Partial Chemical Analyses of Raw and Retorted Oil Shale Solid Waste Waters*

* Average of duplicate samples

** Except for pH, all units are -log mol/L

*** BD = Below detectable levels

high temperature causes production of oxide and silicate minerals. These minerals buffer the pH of oil shale solid waste above 11.00 (Garland et al. 1979; Kuo et al. 1979; Reddy and Lindsay 1986).

Ion activities computed by the GEOCHEM code are used to calculate ion activity products (IAPs) and are compared with equilibrium solubility products (Ksp) to evaluate minerals that control the solubility of Ca and Mg in PPP3 and PPP6 oil shale waters (Table 6). Processing oil shale at moderate temperatures to generate PPP3 did not produce many new mineral phases, except akermanite. Ion activity products of akermanite calculated for 1-, 7-, and 14-day reaction times show a high degree of undersaturation with respect to akermanite. This suggests that akermanite does not control the solubility of Ca and Mg in PPP3 shale waters. Processing oil shale at high temperatures to generate PPP6 shale produced several new mineral phases: akermanite, diopside, and periclase. Ion activity products of akermanite for PPP6 shale waters also suggest a high degree of undersaturation. However. with time, Ca^{2+} , Mg^{2+} , and $H_4SiO_4^0$ activities for PPP6 shale waters reached equilibrium with respect to diopside. This suggests that diopside controls the solubility of Ca and Mg in PPP6 shale waters. In addition, we observed that determination of alkalinity by acid titration in alkaline shale waters overestimates the carbonate and bicarbonate concentrations. This may be due to organic anions and anionic solution species of hydroxyl, boron, and silica. Therefore, we are developing a method to measure carbonate species accurately in alkaline oil shale waters.

for	
(IAP)	
Product	Shale
on Activity	n Spent Oil
K with Id	Reacted with
n of Equilibrium Solubility Product (e, Diopside, and Periclase in Waters
Comariso	Akermanit
Table 6.	

No.	Reaction		log K _{sp} *	10g ppp3	I AP** PPP6	
1.	Ca ₂ MgSi ₂ 0 ₇ + 6H ⁺ + H ₂ 0 ,	² 2Ca ²⁺ + Mg ²⁺ + 2H 4Si0 ⁰	46.10	35,02 36 85	44.26 12 71	A a
	(akermanite)		33.90	40.65	C .	c
2.	CaMg(SiO3)2 + 4H ⁺ + 2H ₂ O	‡ Ca ²⁺ + Mg ²⁺ + 2H 4SiOβ	21.60		23 . 58 22.43	A B
				21.40	U U)
e.	Mg0 + 2H ⁺	$\pm Mg^{2+} + H_20$	21.74		17.98	A a
	(periclase)			17.70	C1•/T	с
 *	aken from this study					

** Calculated from the ion activities computed by the GEOCHEM code;

A = 1 day; B = 7 days; C = 14 days.

Conclusions

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Our evaluation of GEOCHEM and WATEQFC geochemical models for their ability to predict water quality from an oil shale waste environment has produced the following:

- 1. Ion activities computed by GEOCHEM and WATEQFC show excellent agreement, with the exception of $H_4SiO_4^0$.
- 2. Critical evaluation of thermodynamic data for cations and anions that are important for oil shale solid wastes has been completed.
- X-ray diffraction analyses show that processing raw shale at high temperature produces silicate and oxide minerals (akermanite, diopside, and periclase).
- 4. Equilibrium solubility studies suggest that akermanite and periclase are too soluble to control the solubility of Ca and Mg. However, the solubility of Ca and Mg in oil shale solid waste waters may be controlled by diopside.

PART II

CRITICAL EVALUATION OF THE THERMODYNAMIC DATA FOR CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM AT 25°C, 0.1 MPa, AND ZERO IONIC STRENGTH

Introduction

The most important references to thermodynamic data on various elements include Garrels and Christ (1965), Wagman et al. (1968, 1982), Smith and Martell (1976), Parker et al. (1971), Stull and Prophet (1971), Naumov et al. (1971), and Karapet'yants and Karapet'yants (1970).

Typically, there are large differences among the free energy of formation (ΔG_f^o) values of these various compilers. Choosing the best value may be difficult, and an incorrect choice may introduce a significant error. In this report, we have attempted to review the available literature on thermodynamic, electrochemical, and solubility data of various compounds to obtain the most reliable values.

Selection Criteria

The free energy of formation (ΔG_f°) values that deviate widely from those in most other studies have been eliminated. In cases where the agreement of ΔG_f° values is poor, the original sources of the compilers were traced and compared with other available data to obtain the most reliable values. If solubility data were available, the ΔG_f° value for a species was calculated using selected ΔG_f° values of the products and reactants involved in the equilibrium expression.

Methods of Calculating Standard Free Energies of Formation $({}^{\Delta G}{}^{\circ}_{f})$

The standard free energies of formation of species (in solid phases, solution complexes, and ion pairs) compiled in this report were calculated from calorimetric, electrochemical, or solubility data. In cases where ΔG_{f}^{o} was derived from calorimetric data, the standard heat of reaction and entropy of reaction, ΔH_{r}^{o} and ΔS_{r}^{o} , were evaluated. The standard heat of formation (ΔH_{f}^{o}) and standard entropy (S^o) were calculated from equations:

$$\Delta H_{r}^{\circ} = \Sigma \Delta H_{f}^{\circ} \text{ (products)} - \Sigma \Delta H_{f}^{\circ} \text{ (reactants)}$$
(1)
$$\Delta S_{r}^{\circ} = \Sigma \Delta S^{\circ} \text{ (products)} - \Sigma \Delta S^{\circ} \text{ (reactants)}$$
(2)

The Gibbs free energy of reaction (ΔG_r^o) was calculated from the equations:

$$\Delta G_{r}^{\circ} = \Delta H_{r}^{\circ} - T\Delta S_{r}^{\circ}$$
(3)
$$\Delta G_{r}^{\circ} = \Sigma \Delta G_{f}^{\circ} \text{ (products)} - \Sigma \Delta G_{f}^{\circ} \text{ (reactants)}$$
(4)

where ΔG_{f}° is the standard free energy of formation at 298.15 K (25°C). If electrochemical data were available, ΔG_{r}° was calculated from the equation:

$$\Delta G_{r}^{\circ} = -nFE^{\circ}$$
(5)

where

n = Number of moles of electrons participating in the reaction F = Faraday constant (96.487 kJ volt⁻¹ or 23.061 kcal volt⁻¹) $E^{\circ} =$ Standard cell potential

When ΔG_{f}° values were available, ΔG_{r}° was calculated using equation 4. Once ΔG_{r}° was known, the equilibrium constant (K[°]) was calculated from the equation:

 $\Delta G_r^o = -RT \ln K^o$

(6)

where

K[°] = Activity equilibrium constant

R = Universal gas constant (0.00831 kJ/K mol or 0.001987 kcal/K mol)

T = Temperature in Kelvin

At standard conditions (298.15 K and 1 atm) equation 6 becomes

$$\log K^{\circ} = -\frac{\Delta G_{r}^{\circ}}{1.364} \quad (\Delta G_{f}^{\circ} \text{ in kcal/mole}), \text{ or }$$
(7)

$$\log K^{\circ} = - \frac{\Delta G_{r}^{\circ}}{5.708} \quad (\Delta G_{f}^{\circ} \text{ in } kJ/mole) \tag{8}$$

substituting equation 4 into equations 7 and 8 gives

$$\log K^{\circ} = -\frac{1}{1.364} \left[\Delta G_{f}^{\circ}(\text{products}) - \Sigma \Delta G_{f}^{\circ}(\text{reactants}) \right]$$
(9)

$$\log K^{\circ} = -\frac{1}{5.708} \left[\Sigma \Delta G_{f}^{\circ}(\text{products}) - \Sigma \Delta G_{f}^{\circ}(\text{reactants}) \right] \quad (10)$$

Discussion of Selected Values

The free energies of formation (ΔG_f°) for various anionic species (Sadiq and Lindsay 1979) are listed in Table 7. These data were used to calculate equilibrium constants.

Calcium

Selected ΔG_{f}° values for calcium species are summarized in Table 8. Equilibrium constants for reactions involving calcium are listed in Table 9.

Ca^{2+}

Recommended standard free energy of formation (ΔG_{f}°) values for the $Ca^{2^{+}}$ ion are summarized in Table 10. Wagman et al. (1982) reported a ΔG_{f}° value for $Ca^{2^{+}}$ from ΔH_{f}° and S[°] values. Naumov et al. (1971) listed a ΔG_{f}° value for $Ca^{2^{+}}$ from ΔH_{f}° for the following reaction:

$$Ca0(c) + 2H^{+} \leftrightarrow Ca^{2+} + H_{2}0$$

Sadiq and Lindsay (1979) reported a ΔG_{f}^{o} value for $Ca^{2^{+}}$ from pK = 5.19 for the following reaction:

$$Ca(OH)_2(c) \leftrightarrow Ca^{2+} + 2OH^{-}$$

They attributed their selection to Smith and Martell (1976) solubility data for $Ca(OH)_2(c)$. Furthermore, Sadiq and Lindsay discuss the uncertainties and errors involved in the electrochemical data on calcium. For this report, we used $\Delta G_f^o = -554.46$ kJ/mole (-132.52 kcal/mole) for Ca²⁺ after Sadiq and Lindsay (1979).

		ΔG	° f
No.	Species	kJ/mole	kcal/mole
1.	Br	-104.05	- 24 . 87
2.	CO ₂ (g)	-394.38	-94.26
3.	CO ₃ ²	-527.94	-126.18
4.	HCO ₃	-586.89	-140.27
5.	H ₂ CO ₃	-623.20	-148.95
6.	Cl	-131.25	-31.37
7.	С	0.00	0.00
8.	F	-284.22	-67.93
9.	н+	0.00	0.00
10.	ОН	-157.29	- 37.59
11.	H ₂ O	-2337.17	-56.69
12.	I	-51.80	-12.38
13.	NO	-37.74	-9.02
14.	NO ₃	-111.46	-26.64
15.	PO ₄	-1025.83	-245.18
16.	HPO ²	-1096.34	-262.03
17.	$H_2 PO_4$	-1137.42	-271.85
18.	H₃PO₄	-1149.68	- 274.78
19.	S0 ²	-744.54	-177.95
20.	SiO4	-1045.96	-249.99
21.	HSiO ₄	-1120.72	-267.86
22.	$H_2SiO_4^2$	-1177.00	-281.31
23.	H ₃ SiO ₄	-1252.77	-299.42
24.	H ₄ SiO ₄	-1308.17	-312.66

Table 7.	Free Energy of Formation (ΔG_f°) of Anionic Species
	Selected from Sadiq and Lindsay (1979) to Calculate
	Equilibrium Constants.

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Species $kJ/mole$ $kcal/mole$ ScI. Ca2+Solution Species1. Ca2+Solution Species2. CaHCO_3+1147.67274.303. CaCO_3+1147.67274.303. CaCO_3+1100.77263.094. CaSO_4+112.19313.625. CaCl+680.02162.536. CaCl_2+815.25194.857. CaNO_3+638.52152.618. Ca(NO_3)_2+774.40185.089. CaOH+179.18171.8910. Ca(OH)_2+869.06207.7111. CaHPO_4+699.88406.2813. CaPO_4+1617.16386.51II. Solid Species14. CaO (lime)603.29144.1915. Ca(OH)_2 (portlandite)897.50214.5016. CaSiO_3 (wollastonite)1549.71370.3917. CaSiO_3 (pseudowollastonite)1549.71370.3918. Ca_MgSi_2O_7 (akermanite)3681.08879.80		,o ′f	ΔG [°] f		
I. Solution Species1. Ca^{2^+} -554.46-132.522. $CaHCO_3^+$ -1147.67-274.303. $CaCO_3^0$ -1100.77-263.094. $CaSO_4^0$ -1312.19-313.625. $CaC1^+$ -680.02-162.536. $CaCl_2^0$ -815.25-194.857. $CaNO_3^+$ -638.52-152.618. $Ca(NO_3)^2$ -774.40-185.089. $CaOH^+$ -179.18-171.8910. $Ca(OH)_2^0$ -869.06-207.7111. $CaHPO_4^0$ -1666.40-398.2812. $CaH_2PO_4^+$ -1699.88-406.2813. $CaPO_4^-$ -1617.16-386.51II. Solid Species14. $CaO(1ime)$ -603.29-144.1915. $Ca(OH)_2$ (portlandite)-897.50-214.5016. $CaSiO_3$ (wollastonite)-1549.71-370.3917. $CaSiO_3$ (pseudowollastonite)-1544.27-369.0918. $Ca_2MgSi_2O_7$ (akermanite)-3681.08-879.80	Source	kcal/mole	kJ/mole	Species	
1. Ca^{2^+} -554.46 -132.52 2. CaHCO^+_3 -1147.67 -274.30 3. CaCO^0_3 -1100.77 -263.09 4. CaSO^0_4 -1312.19 -313.62 5. CaCl^+ -680.02 -162.53 6. CaCl^0_2 -815.25 -194.85 7. CaNO^+_3 -638.52 -152.61 8. $\operatorname{Ca}(\operatorname{NO}_3)^0_2$ -774.40 -185.08 9. CaOH^+ -179.18 -171.89 10. $\operatorname{Ca}(\operatorname{OH})^0_2$ -869.06 -207.71 11. CaHPO^4_4 -1699.88 -406.28 12. $\operatorname{CaH}_2\operatorname{PO}^+_4$ -1699.88 -406.28 13. CaPO^4 -1617.16 -386.51 <u>II. Solid Species</u> 14. $\operatorname{CaO}(\operatorname{lime})$ -603.29 -144.19 15. $\operatorname{Ca}(\operatorname{OH})_2$ (portlandite) -897.50 -214.50 16. CaSiO_3 (wollastonite) -1549.71 -370.39 17. CaSiO_3 (pseudowollastonite) -1544.27 -369.09 18. $\operatorname{Ca}_2\operatorname{MgSi}_2\operatorname{O}_7$ (akermanite) -3681.08 -879.80			tion Species	I. Solu	
2. $CaHCO_{3}^{+}$ -1147.67 -274.30 3. $CaCO_{3}^{+}$ -1100.77 -263.09 4. $CaSO_{4}^{0}$ -1312.19 -313.62 5. $CaC1^{+}$ -680.02 -162.53 6. $CaCl_{2}^{0}$ -815.25 -194.85 7. $CaNO_{3}^{+}$ -638.52 -152.61 8. $Ca(NO_{3})_{2}^{0}$ -774.40 -185.08 9. $CaOH^{+}$ -179.18 -171.89 10. $Ca(OH)_{2}^{0}$ -869.06 -207.71 11. $CaHPO_{4}^{0}$ -1666.40 -398.28 12. $CaH_{2}PO_{4}^{+}$ -1699.88 -406.28 13. $CaPO_{4}^{-}$ -1617.16 -386.51 <u>II. Solid Species</u> 14. CaO (lime) -603.29 -144.19 15. $Ca(OH)_{2}$ (portlandite) -897.50 -214.50 16. $CaSiO_{3}$ (wollastonite) -1549.71 -370.39 17. $CaSiO_{3}$ (pseudowollastonite) -1544.27 -369.09 18. $Ca_{2}MgSi_{2}O_{7}$ (akermanite) -3681.08 -879.80	A	-132.52	-554.46	Ca ²⁺	1.
3. $CaC0_{3}^{\circ}$ -1100.77 -263.09 4. $CaS0_{4}^{\circ}$ -1312.19 -313.62 5. $CaC1^{+}$ -680.02 -162.53 6. $CaC1_{2}^{\circ}$ -815.25 -194.85 7. $CaN0_{3}^{+}$ -638.52 -152.61 8. $Ca(NO_{3})_{2}^{\circ}$ -774.40 -185.08 9. $CaOH^{+}$ -179.18 -171.89 10. $Ca(OH)_{2}^{\circ}$ -869.06 -207.71 11. $CaHPO_{4}^{\circ}$ -1666.40 -398.28 12. $CaH_{2}PO_{4}^{+}$ -1699.88 -406.28 13. $CaPO_{4}^{-}$ -1617.16 -386.51 <u>II. Solid Species</u> 14. $CaO(1ime)$ -603.29 -144.19 15. $Ca(OH)_{2}$ (portlandite) -897.50 -214.50 16. $CaSiO_{3}$ (wollastonite) -1549.71 -370.39 17. $CaSiO_{3}$ (pseudowollastonite) -1544.27 -369.09 18. $Ca_{2}MgSi_{2}O_{7}$ (akermanite) -3681.08 -879.80	В	-274.30	-1147.67	CaHCO ⁺ ₃	2.
4. $CaSO_4^{\circ}$ -1312.19 -313.62 5. $CaCl^+$ -680.02 -162.53 6. $CaCl_2^{\circ}$ -815.25 -194.85 7. $CaNO_3^+$ -638.52 -152.61 8. $Ca(NO_3)_2^{\circ}$ -774.40 -185.08 9. $CaOH^+$ -179.18 -171.89 10. $Ca(OH)_2^{\circ}$ -869.06 -207.71 11. $CaHPO_4^{\circ}$ -1666.40 -398.28 12. $CaH_2PO_4^+$ -1699.88 -406.28 13. $CaPO_4^ -1617.16$ -386.51 II. Solid Species14. CaO (lime) -603.29 -144.19 15. $Ca(OH)_2$ (portlandite) -897.50 -214.50 16. $CaSiO_3$ (wollastonite) -1549.71 -370.39 17. $CaSiO_3$ (pseudowollastonite) -1544.27 -369.09 18. $Ca_2MgSi_2O_7$ (akermanite) -3681.08 -879.80	В	-263.09	-1100.77	CaCO ₃	3.
5. $CaC1^{+}$ 6. $CaC1_{2}^{0}$ 7. $CaN0_{3}^{+}$ 7. $CaN0_{3}^{+}$ 7. $CaN0_{3}^{+}$ 7. $CaN0_{3}^{+}$ 7. $CaN0_{3}^{+}$ 7. $CaN0_{3}^{+}$ 7. $CaN0_{3}^{+}$ 7. $Ca(N0_{3})_{2}^{0}$ 7. $CaOH^{+}$ 7. $CaOH^{+}$ 7. $CaOH^{+}$ 7. $CaOH^{+}$ 7. $CaHP0_{4}^{0}$ 7. $CaHP0_{4}^{-}$ 7. $CaHP0_{4}^{-}$ 7. $CaP0_{4}^{-}$ 7.	A	-313.62	-1312.19	CaSO ⁰	4.
6. $CaCl_{2}^{0}$ -815.25 -194.85 7. $CaNO_{3}^{+}$ -638.52 -152.61 8. $Ca(NO_{3})_{2}^{0}$ -774.40 -185.08 9. $CaOH^{+}$ -179.18 -171.89 10. $Ca(OH)_{2}^{0}$ -869.06 -207.71 11. $CaHPO_{4}^{0}$ -1666.40 -398.28 12. $CaH_{2}PO_{4}^{+}$ -1699.88 -406.28 13. $CaPO_{4}^{-}$ -1617.16 -386.51 <u>II. Solid Species</u> 14. CaO (lime) -603.29 -144.19 15. $Ca(OH)_{2}$ (portlandite) -897.50 -214.50 16. $CaSiO_{3}$ (wollastonite) -1549.71 -370.39 17. $CaSiO_{3}$ (pseudowollastonite) -1544.27 -369.09 18. $Ca_{2}MgSi_{2}O_{7}$ (akermanite) -3681.08 -879.80	А	-162.53	-680.02	CaCl ⁺	5.
7. $CaNO_3^+$ -638.52-152.618. $Ca(NO_3)_2^0$ -774.40-185.089. $CaOH^+$ -179.18-171.8910. $Ca(OH)_2^0$ -869.06-207.7111. $CaHPO_4^0$ -1666.40-398.2812. $CaH_2PO_4^+$ -1699.88-406.2813. $CaPO_4^-$ -1617.16-386.51II. Solid Species14. Ca0 (lime)-603.29-144.1915. $Ca(OH)_2$ (portlandite)-897.50-214.5016. CaSiO_3 (wollastonite)-1549.71-370.3917. CaSiO_3 (pseudowollastonite)-1544.27-369.0918. $Ca_2MgSi_2O_7$ (akermanite)-3681.08-879.80	С	-194.85	-815.25	CaCl ⁰	6.
8. $Ca(NO_3)_2^9$ -774.40 -185.08 9. $CaOH^+$ -179.18 -171.89 10. $Ca(OH)_2^9$ -869.06 -207.71 11. $CaHPO_4^9$ -1666.40 -398.28 12. $CaH_2PO_4^+$ -1699.88 -406.28 13. $CaPO_4^-$ -1617.16 -386.51 <u>II. Solid Species</u> 14. CaO (lime) -603.29 -144.19 15. $Ca(OH)_2$ (portlandite) -897.50 -214.50 16. $CaSiO_3$ (wollastonite) -1549.71 -370.39 17. $CaSiO_3$ (pseudowollastonite) -1544.27 -369.09 18. $Ca_2MgSi_2O_7$ (akermanite) -3681.08 -879.80 10. $CaM SiO_2$ (akermanite) -3651.08 -879.80	А	-152.61	-638.52	$CaNO_3^+$	7.
9. $CaOH^+$ 10. $Ca(OH)_2^0$ 10. $Ca(OH)_2^0$ 11. $CaHPO_4^0$ 12. $CaH_2PO_4^+$ 13. $CaPO_4^+$ 14. $CaO(1ime)$ 14. $CaO(1ime)$ 15. $Ca(OH)_2$ (portlandite) 16. $CaSiO_3$ (wollastonite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca(OH)_2$ (portlandite) 15. $CaSiO_3$ (wollastonite) 15. $CaSiO_3$ (pseudowollastonite) 15. $CaSiO_3$ (pseudowollastonite) 15. $Ca_2MgSi_2O_7$ (akermanite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca(OH)_2$ (pseudowollastonite) 15. $Ca_2MgSi_2O_7$ (akermanite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca_2MgSi_2O_7$ (akermanite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca(OH)_2$ (pseudowollastonite) 15. $Ca_2MgSi_2O_7$ (akermanite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca(OH)_2$ (pseudowollastonite) 15. $Ca_2MgSi_2O_7$ (akermanite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca(OH)_2$ (portlandite) 15. $Ca(OH)_2$ (pseudowollastonite) 15. $Ca(OH)_2$ (pseudowollastonit	С	-185.08	-774.40	$Ca(NO_3)_2^0$	8.
10. $Ca(OH)_{2}^{0}$ -869.06 -207.71 11. $CaHPO_{4}^{0}$ -1666.40 -398.28 12. $CaH_{2}PO_{4}^{+}$ -1699.88 -406.28 13. $CaPO_{4}^{-}$ -1617.16 -386.51 II. Solid Species14. Ca0 (lime) -603.29 -144.19 15. Ca(OH)_{2} (portlandite) -897.50 -214.50 16. CaSiO_{3} (wollastonite) -1549.71 -370.39 17. CaSiO_{3} (pseudowollastonite) -1544.27 -369.09 18. $Ca_{2}MgSi_{2}O_{7}$ (akermanite) -3681.08 -879.80 10. CaW Si20 (colspan="2"> -1144.19	D	-171.89	-179.18	CaOH ⁺	9.
11. $CaHPO_4^0$ -1666.40 -398.28 12. $CaH_2PO_4^+$ -1699.88 -406.28 13. $CaPO_4^ -1617.16$ -386.51 II. Solid Species14. Ca0 (lime) -603.29 -144.1915. $Ca(OH)_2$ (portlandite) -897.50 -214.50 16. $CaSiO_3$ (wollastonite) -1549.71 -370.39 17. $CaSiO_3$ (pseudowollastonite) -1544.27 -369.09 18. $Ca_2MgSi_2O_7$ (akermanite) -3681.08 -879.80	А	-207.71	-869.06	Ca(OH) ⁰ ₂	10.
12. $CaH_2PO_4^+$ -1699.88-406.2813. $CaPO_4^-$ -1617.16-386.51II. Solid Species14. Ca0 (lime)-603.2914. Ca0 (lime)-603.29-144.1915. Ca(OH)_2 (portlandite)-897.50-214.5016. CaSiO_3 (wollastonite)-1549.71-370.3917. CaSiO_3 (pseudowollastonite)-1544.27-369.0918. Ca_2MgSi_2O_7 (akermanite)-3681.08-879.8019. CaVA CiO-1144.19-3681.08-879.80	D	-398.28	-1666.40	CaHPO ⁰	11.
13. $CaPO_{4}^{-}$ -1617.16 -386.51 <u>II. Solid Species</u> 14. CaO (lime) -603.29 -144.19 15. Ca(OH) ₂ (portlandite) -897.50 -214.50 16. CaSiO ₃ (wollastonite) -1549.71 -370.39 17. CaSiO ₃ (pseudowollastonite) -1544.27 -369.09 18. Ca ₂ MgSi ₂ O ₇ (akermanite) -3681.08 -879.80 19. CaVA 210 (А	-406.28	-1699.88	CaH ₂ PO ⁺	12.
II. Solid Species14. Ca0 (lime) -603.29 -144.19 15. Ca(OH) ₂ (portlandite) -897.50 -214.50 16. CaSiO ₃ (wollastonite) -1549.71 -370.39 17. CaSiO ₃ (pseudowollastonite) -1544.27 -369.09 18. Ca ₂ MgSi ₂ O ₇ (akermanite) -3681.08 -879.80	. A	-386.51	-1617.16	CaPO ₄	13.
14. Ca0 (lime) -603.29 -144.19 15. Ca(OH) ₂ (portlandite) -897.50 -214.50 16. CaSiO ₃ (wollastonite) -1549.71 -370.39 17. CaSiO ₃ (pseudowollastonite) -1544.27 -369.09 18. Ca ₂ MgSi ₂ O ₇ (akermanite) -3681.08 -879.80			lid Species	<u>II. So</u>	
15. $Ca(OH)_2$ (portlandite)-897.50-214.5016. $CaSiO_3$ (wollastonite)-1549.71-370.3917. $CaSiO_3$ (pseudowollastonite)-1544.27-369.0918. $Ca_2MgSi_2O_7$ (akermanite)-3681.08-879.8010. $CaVA SiO_4$ (maximum bits)-214.50-369.09	С	-144.19	-603.29	CaO (lime)	14.
16. CaSi0 ₃ (wollastonite) -1549.71 -370.39 17. CaSi0 ₃ (pseudowollastonite) -1544.27 -369.09 18. Ca ₂ MgSi ₂ O ₇ (akermanite) -3681.08 -879.80 10. CaVA GiO -1140.00 -3145.42	С	-214.50	-897.50	Ca(OH) ₂ (portlandite)	15.
17. $CaSiO_3$ (pseudowollastonite)-1544.27-369.0918. $Ca_2MgSi_2O_7$ (akermanite)-3681.08-879.8010. $CaVASiO_7$ (akermanite)-3681.08-879.80	А	-370.39	-1549.71	CaSiO ₃ (wollastonite)	16.
18. $Ca_2MgSi_2O_7$ (akermanite) -3681.08 -879.80	А	-369.09	-1544.27	$CaSiO_3$ (pseudowollastonite)	17.
	E	-879.80	-3681.08	Ca ₂ MgSi ₂ 0 ₇ (akermanite)	18.
19. CamgS10 ₄ (monticellite) -2145.68 -512.83	E	-512.83	-2145.68	CaMgSiO4 (monticellite)	19.
20. Ca ₃ MgSi ₂ 0 ₆ (merwinite) -4339.56 -1037.18	E	-1037.18	-4339.56	Ca ₃ MgSi ₂ 0 ₆ (merwinite)	20.
21. Ca ₃ Si ₂ O ₇ (rankinite) -3761.30 -898.97	E	-898.97	-3761.30	Ca ₃ Si ₂ 0 ₇ (rankinite)	21.

Table 8.	Selected Standard Free Energies of Formation (ΔG_f°) of Ca
	Species at 25°C (298.15 K) and 1 atm (10^5 Pa)

			(ΔG_{f}^{o})	
Spec	ies	kJ/mole	kcal/mole	Source
		<u> </u>		
22.	β -Ca ₂ SiO ₄ (larnite)	-2190.99	-523.66	А
23.	γ -Ca ₂ SiO ₄ (calcium olivine)	-2201.28	-526.12	Α
24.	CaMg(SiO ₃) ₂ (diopside)	-3029.21	-724.00	E
25.	$CaSO_4$ (anhydrite)	-1324.15	-316.48	Α
26.	CaSO ₄ •2H ₂ O (gypsum)	-1799.83	-430.17	А
27.	CaCO ₃ •6H ₂ O (ikaite)	-25341.86	-607.52	А
28.	CaCO ₃ (aragonite)	-1129.93	-270.06	В
29.	CaCO ₃ (calcite)	-1130.80	-270.27	В
30.	$CaMg(CO_3)_2$ (dolomite)	-2168.36	-518.25	А
31.	$CaHPO_4$ (monetite)	-1690.17	-403.96	А
32.	CaHPO ₄ •2H ₂ 0 (brushite)	-2162.67	-516.89	Α
33.	$Ca(H_2PO_4)_2 \cdot H_20$ (c)	-3073.06	-734.48	А
34.	$\alpha Ca_3(PO_4)_2(c)$	-3860.58	-922.70	А
35.	β -Ca ₃ (PO ₄) ₂ (whitelockite)	-3880.12	-927.37	A
36.	$Ca_8H_2(PO_4)_6 \cdot 5H_2O$			
	(octacalcium phosphate)	-12311.92	-2942.62	А
37.	Ca ₁₀ (OH) ₂ (PO ₄) ₆ (hydroxyapatite)	-12678.60	-3030.26	A

Table 8.	Selected Standard Free Energies of Formation	(ΔG_{f}^{0}) of Ca
	Species at 25°C (298.15 K) and 1 atm (10^5 Pa)	, Continued

A = Sadiq and Lindsay (1979)

B = Plummer and Busenberg (1984)

C - CODATA (1987)

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D = Smith and Martell (1976)

E = Helgeson et al. (1978)

F = Wagman et al. (1982)

No.	Equilibrium Reaction	log K°
	I. Solid Species	
1.	$Ca0(c) + 2H^{+} \leftrightarrow Ca^{2^{+}} + H_{2}0$	33.00
2.	$Ca(OH)_{2}(c) + 2H^{+} \leftrightarrow Ca^{2^{+}} + 2H_{2}0$	23.02
3.	$CaSiO_3$ (wollastonite) + 2H ⁺ + H ₂ O + Ca ²⁺ + H ₄ SiO ₄ ⁰	13.27
4.	$CaSiO_3$ (pseudowollastonite) + $2H^+$ + $H_2O \leftrightarrow Ca^{2+}$ + $H_4SiO_4^0$	14.23
5.	$Ca_2MgSi_2O_7$ (akermanite) + $6H^+$ + H_2O \leftrightarrow	
	$2Ca^{2^{+}} + Mg^{2^{+}} + 2H_{4}Si0_{4}^{0}$	46.10
6.	$CaMgSiO_4$ (monticellite) + $4H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + H_4SiO_4^0$	30.32
7.	$Ca_{3}MgSi_{2}O_{6}$ (merwinite) + $4H^{+}$ + $2H_{2}O \Leftrightarrow$	
	$3Ca^{2+} + Mg^{2+} + 2H_4Si0_4^0$	-13.69
8.	Ca_3SiO_7 (rankinite) + $6H^+$ + $H_20 \Leftrightarrow 3Ca^{2+}$ + $2H_4SiO_4^0$	49.28
9.	β -Ca ₂ SiO ₄ (laramite) + 4H ⁺ \leftrightarrow 2Ca ²⁺ + H ₄ SiO ₄ ⁰	39.62
10.	γ -Ca ₂ SiO ₄ (calcium olivine) + 4H ⁺ \leftrightarrow 2Ca ²⁺ + H ₄ SiO ₄ ⁰	37.82
11.	$CaMg(SiO_3)_2$ (diopside) + $4H^+$ + $2H_2O$ ++	
	$Ca^{2^{+}} + Mg^{2^{+}} + 2H_4SiO_4^0$	21.60
12.	$CaSO_4(c) \Leftrightarrow Ca^{2^+} + SO_4^2^-$	-4.41
13.	$CaSO_4 \cdot 2H_2O$ (gypsum) + $Ca^{2^+} + SO_4^{2^-} + 2H_2O$	-4.64
14.	$CaCO_{3} \cdot 6H_{2}O$ (ikaite) $\Rightarrow Ca^{2^{+}} + CO_{3}^{2^{-}} + 6H_{2}O$	-6.24
15.	$CaCO_3$ (aragonite) \leftrightarrow Ca^{2^+} + $CO_3^{2^-}$	-8.33
16.	$CaCO_3$ (calcite) \Leftrightarrow Ca^{2^+} + $CO_3^{2^-}$	-8.48
17.	$CaMg(CO_3)_2$ (dolomite) \Leftrightarrow $Ca^{2^+} + Mg^{2^+} + CO_3^{2^-}$	-17.85
18.	$CaHPO_4$ (monetite) $\leftrightarrow Ca^{2^+} + HPO_4^{2^-}$	-6.90
19.	$CaHPO_4 \cdot 2H_2 0$ (brushite) $\leftrightarrow Ca^{2^+} + HPO_4^{2^-} + 2H_2 0$	-6.57
20.	$Ca(H_2(H_2PO_4)_2 \cdot H_2O(c) \leftrightarrow Ca^{2+} + 2H_2PO_4 + H_2O$	-1.14

Table 9. Equilibrium Constants for Reactions Involving Calcium at 25 $^{\circ}$ C (298.15 K) and 1 atm (10 5 Pa)

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No.	Equilibrium Reaction	log K°
01	$= (22) (22) + (22)^{2} + (22)^{3}$	- 25 50
21.	$\alpha - (a_3(FO_4)_2(C) \leftrightarrow 5Ca^2 + 2FO_4^2)$	-25.50
22.	β -Ca ₃ (PO ₄) ₂ (whitelockite) + 3Ca ²⁺ + 2PO ₄ ³⁻	-28.92
23.	$Ca_{8}H_{2}(PO_{4})_{6} \cdot 5H_{2}O$ (octacalcium phosphate) +	
	$8Ca^{2+} + 2H^{+} + 6PO_{4}^{3-} + 5H_{2}O$	-93.80
24.	$Ca_{10}(OH)_2(PO_4)_6$ (hydroxyapatite) $\leftrightarrow 10Ca^{2^+} + 6PO_4^{3^-} + 20H^-$	-116.40
	II. Solution Species	
95	$c_{2}^{2+} + u_{2}^{-} + c_{2}^{2} + c_{3}^{2}$	1 11

Table 9.	Equilibrium Constants for Reactions Involving Calcium
	at 25°C (298.15 K) and 1 atm (10 ⁵ Pa), Continued

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25.	$Ca^{2^{+}} + HCO_{3}^{-} \leftrightarrow CaHCO_{3}^{+}$	1.11
26.	$Ca^{2^+} + CO_3^{2^-} \leftrightarrow CaCO_3^{0}$	3.22
27.	$Ca^{2^+} + SO_4^{2^-} \leftrightarrow CaSO_4^{0}$	2.31
28.	$Ca^{2^+} + Cl^- \Leftrightarrow CaCl^+$	-1.00
29.	$Ca^{2^+} + 2C1^- \leftrightarrow CaC1^0_2$	-0.30
30.	$Ca^{2^{+}} + NO_{3}^{-} \leftrightarrow CaNO_{3}^{+}$	-4.80
31.	$Ca^{2^+} + 2NO_3^- \Leftrightarrow Ca(NO_3)_2^0$	-0.53
32.	$Ca^{2^+} + OH^- \Leftrightarrow CaOH^+$	1.30
33.	$Ca^{2^+} + 2OH^- \Leftrightarrow Ca(OH)^0_2$	0.00
34.	$Ca^{2^{+}} + HPO_{4}^{2^{-}} \leftrightarrow CaHPO_{4}^{0}$	2.74
35.	$Ca^{2^+} + H_2PO_4^- \leftrightarrow CaH_2PO_4^+$	1.40
36.	$Ca^{2^+} + PO_4^3 \Rightarrow CaPO_4^-$	6.46

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vestigator	kJ/mole	kcal/mole
Wagman et al. (1982) Naumov et al. (1971) Sadiq and Lindsay (1979)	- 553.58 - 552.70 - 554.46	-132.30 -132.10 -132.52

Table 10. Standard Free Energy of Formation of Ca^{2^+}

CaHC03+

Sadiq and Lindsay (1979) report $\Delta G_{f}^{\circ} = -1147.79$ kJ/mole (-274.44 kcal/mole) from pK = 1.13 for the following reaction:

$$CaHCO_3^+ \leftrightarrow Ca^{2+} + HCO_3^-$$

After Reardon et al. (1973), CODATA (1987) listed $\Delta G_{f}^{\circ} = -1145$ kJ/mole (-273.83 kcal/mole). Plummer and Busenberg (1982) reported log K = 1.11 for the following reaction:

 $Ca^{2^{+}} + HCO_{3}^{-} \leftrightarrow CaHCO_{3}^{+}$

These authors also made corrections for temperature, ionic strength, and solution complexes. Therefore, we selected log K of 1.11 for the above reaction after Plummer and Busenberg (1982) and calculated a ΔG_{f}^{o} value of -1147.67 kJ/mole (-274.30 kcal/mole) for CaHCO₃⁺.

$CaCO_3^0$

Naumov et al. (1971) reported $\Delta G_f^{\circ} = -1098.89$ kJ/mole (-262.64 kcal/mole) from pK = 3.20 for the reaction:

$$CaCO_3^0 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

after Garrels and Thompson (1962). CODATA (1987) listed $\Delta G_{f}^{\circ} = -1098.90$ kJ/mole (-262.64 kcal/mole). Sadiq and Lindsay (1979) adopted pK = 3.15 for the above reaction after Reardon and Langumuir (1974) and calculated $\hat{f}_{f}^{\circ} = -1100.40$ kJ/mole (-263.00 kcal/mole) for CaCO₃^o. Plummer and senberg (1982) reported log K = 3.22 for the reaction:

$$Ca^{2^+} + CO_3^2 \leftrightarrow CaCO_3^0$$

Because Plummer and Busenberg (1982) made reliable solubility measurements, we selected their log K value of 3.22 for the above reaction and calculated $\Delta G_{\rm f}^{\rm o} = -1100.77$ kJ/mole (-263.09 kcal/mole) for CaCO₃^o.

CaS0₄

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -1310.43$ kJ/mole (-313.20 kcal/mole) for the CaSO₄⁰ species from pK = 2.43 for the reaction:

$$CaSO_4^0 \leftrightarrow Ca^{2^+} + SO_4^2^-$$

Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -1298.10 \text{ kJ/mole}$ (-310.25 kcal/mole) for $CaSO_{4}^{\circ}$ from ΔH_{f}° and S° values. Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1312.19 \text{ kJ/mole}$ (-313.62 kcal/mole) from pK = 2.31 for the reaction after Ainsworth (1973). CODATA (1987) reported $\Delta G_{f}^{\circ} = -1311.35 \text{ kJ/mole}$ (-313.42 kcal/mole). Reported ΔG_{f}° values for $CaSO_{4}^{\circ}$ species are in good agreement. Therefore, we selected $\Delta G_{f}^{\circ} = -1312.19 \text{ kJ/mole}$ (-313.62 kcal/mole) for $CaSO_{4}^{\circ}$ after Sadiq and Lindsay (1979).

$CaC1^+$

Sadiq and Lindsay (1979) reported $\Delta G_f^{\circ} = -680.02$ kJ/mole (-162.53 kcal/mole) from pK = 1.0 listed by Harned and Owen (1958) for the reaction:

$$Ca^{2^+} + C1^- \leftrightarrow CaC1^+$$

No other information is available for this species. Therefore, we selected this ΔG_f^o value of -680.02 kJ/mole (-162.53 kcal/mole) for CaCl⁺.

CaCl⁰

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -816.96$ kJ/mole (-195.26 kcal/mole) for the CaCl₂^o species from Parker et al. (1971). CODATA (1987) reported $\Delta G_{f}^{\circ} = -815.25$ kJ/mole (-194.85 kcal/mole). No other information is available for this species. Therefore, we selected $\Delta G_{f}^{\circ} = -815.25$ kJ/mole (-194.85 kcal/mole) for CaCl₂^o after CODATA (1987).

$CaNO_3^+$

Sadiq and Lindsay (1979) listed $\Delta G_{f}^{\circ} = -638.52$ kJ/mole (-152.61 kcal/mole) for the CaNO₃⁺ species from Fedorov et al. (1974). No other information is available. Therefore, we selected $\Delta G_{f}^{\circ} = -638.52$ kJ/mole (-152.61 kcal/mole) after Sadiq and Lindsay (1979).

$Ca(NO_3)^0_2$

Sadiq and Lindsay (1979) listed $\Delta G_{f}^{\circ} = -751.69 \text{ kJ/mole}$ (-179.66 kcal/mole). CODATA (1987) reported a value of $\Delta G_{f}^{\circ} = -774.40 \text{ kJ/mole}$ (-185.08 kcal/mole) for the Ca(NO₃)⁰₂ species. No other information is available. Therefore, we selected $\Delta G_{f}^{\circ} = -774.40 \text{ kJ/mole}$ (-185.08 kcal/mole) for Ca(NO₃)⁹₂ after CODATA (1987).

CaOH⁺

Smith and Martell (1976) reported pK = 1.30 for the reaction:

 $CaOH^+ \leftrightarrow Ca^{2^+} + OH^-$

which gives $\Delta G_{f}^{\circ} = -719.18 \text{ kJ/mole} (-171.89 \text{ kcal/mole})$ for CaOH⁺ species. No other information is available. Therefore, we selected $\Delta G_{f}^{\circ} = -719.18 \text{ kJ/mole} (-171.89 \text{ kcal/mole})$ for CaOH⁺.

Ca(OH) 9

Sadiq and Lindsay (1979) reported that $\Delta G_f^{\circ} = -869.06$ kJ/mole 207.71 kcal/mole) from pK = 0.00 for the reaction:

No other information is available. Therefore, we selected $\Delta G_{f}^{\circ} = -869.06$ kJ/mole (-207.71 kcal/mole) after Sadiq and Lindsay (1979).

CaHP0⁰

Smith and Martell (1976) reported pK = 2.74 for the reaction:

$$CaHPO_4^0 \leftrightarrow Ca^{2^+} + HPO_4^{2^-}$$

Sadiq and Lindsay (1979) and calculated $\Delta G_{f}^{\circ} = -1666.40 \text{ kJ/mole} (-398.28 \text{ kcal/mole})$ for CaHPO₄^o form this reaction. We selected $\Delta G_{f}^{\circ} = -1666.40 \text{ kJ/mole}$ (-398.28 kcal/mole) after Smith and Martell (1974).

CaH,PO4

-

Sadiq and Lindsay (1979) listed $\Delta G_{f}^{\circ} = -1699.88$ kJ/mole (-406.28 kcal/mole) from pK = 1.41 from the reaction:

$$CaH_2PO_4^+ \leftrightarrow Ca^{2^+} + H_2PO_4^-$$

after Chughtai et al. (1968). No other information is available. Therefore, we selected $\Delta G_{f}^{\circ} = -1699.88 \text{ kJ/mole} (-406.28 \text{ kcal/mole})$ for $CaH_2PO_4^{+}$ after Sadiq and Lindsay (1979).

CaP0

Sadiq and Lindsay (1979) reported $\Delta G_f^{\circ} = -1617.16$ kJ/mole (-386.51 kcal/mole) from pK = 6.46 for the reaction:

$$CaPO_{4}^{-} \leftrightarrow Ca^{2}^{+} + PO_{4}^{3}^{-}$$

after Chughtai et al. (1968). No other information is available for this species. Therefore, we selected $\Delta G_{f}^{\circ} = -1617.16 \text{ kJ/mole}$ (-386.51 kcal/mole) for CaPO₄ after Sadiq and Lindsay (1979).

CaO (lime)

Wagman et al. (1982) reported $\Delta G_f^{\circ} = -604.03$ kJ/mole (-144.37 kcal/mole) for CaO(c) from ΔH_f° and S[°] values. Naumov et al. (1971)

listed $\Delta G_{f}^{\circ} = -603.92 \text{ kJ/mole} (-144.34 \text{ kcal/mole})$ for CaO(c) from ΔH_{f}° and S° values. Sadiq and Lindsay (1979) also reported $\Delta G_{f}^{\circ} = 603.58 \text{ kJ/mole}$ (-144.26 kcal/mole) from ΔH_{f}° and S° values. CODATA (1987) compared different CaO(c) ΔG_{f}° measurements and recommended $\Delta G_{f}^{\circ} = -603.29 \text{ kJ/mole}$ (-144.19 kcal/mole) for CaO(c). We selected $\Delta G_{f}^{\circ} = -603.29 \text{ kJ/mole}$ (-144.19 kcal/mole) for CaO(c) after CODATA (1987).

Ca(OH), (portlandite)

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -897.00 \text{ kJ/mole}$ (-214.39 kcal/mole) from ΔH_{f}° and S° values. Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -898.68 \text{ kJ/mole}$ (-214.79 kcal/mole). Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -898.49 \text{ kJ/mole}$ (-214.745 kcal/mole). 'CODATA (1987) recommended $\Delta G_{f}^{\circ} = -897.50 \text{ kJ/mole}$ (-214.50 kcal/mole) after examining the solubility and calorimetric data of Ca(OH)₂ (c). We selected the CODATA (1987) recommended ΔG_{f}° value for Ca(OH)₂(c).

CaSiO₃ (wollastonite)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = 1549.71$ kJ/mole (-370.39 kcal/mole). Helgeson et al. (1978) reported $\Delta G_{f}^{\circ} = -1545.73$ kJ/mole (-369.44 kcal/mole). Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -1549.66$ kJ/mole (-370.38 kcal/mole). Reported ΔG_{f}° values for wollastonite agree well. Therefore, we selected $\Delta G_{f}^{\circ} = -1549.71$ kJ/mole (-370.39 kcal/mole) for wollastonite after Sadiq and Lindsay (1979).

CaSi0₃ (pseudowollastonite)

Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -1544.70$ kJ/mole (-369.19 kcal/mole). Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1544.27$ kJ/mole (-369.09 kcal/mole). Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -1547.91$ kJ/mole (-369.96 kcal/mole). Reported ΔG_{f}° values for pseudowollastonite are in good agreement. Therefore, we selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

Ca₂MgSi₂O₇ (akermanite)

Helgeson et al. (1978) recommended $\Delta G_{f}^{o} = -3681.08$ kJ/mole (-879.80 kcal/mole) for akermanite from various solubility measurements. Wagman

et al. (1982) reported $\Delta G_{f}^{\circ} = -3679.84$ kJ/mole (-879.50 kcal/mole). Naumov et al. (1971) listed $\Delta G_{f}^{\circ} = -3679.84$ (-879.50 kcal/mole). Reported ΔG_{f}° values for akermanite are in general agreement. Therefore, we selected the ΔG_{f}° value recommended by Helgeson et al. (1978).

CaMgSiO₄ (monticellite)

Helgeson et al. (1978) reported $\Delta G_{f}^{\circ} = -2145.68$ kJ/mole (-512.83 kcal/mole) for monticellite. No other information is available for this compound. Therefore, we selected the ΔG_{f}° of Helgeson et al. (1978).

Ca₃MgSi₂O₆ (merwinite)

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Helgeson et al. (1978) reported $\Delta G_{f}^{\circ} = -4339.56$ kJ/mole (-1037.18 kcal/mole). Robie and Waldbaum (1968) reported a similar ΔG_{f}° value. Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -4340.23$ kJ/mole (-1037.34 kcal/mole). Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -4340.40$ kJ/mole (-1037.38 kcal/mole). Reported ΔG_{f}° values for merwinite are in general agreement. Therefore, we selected the ΔG_{f}° value recommended by Helgeson et al. (1978) for merwinite.

Ca₃Si₂O₇ (rankinite)

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -3761.30 \text{ kJ/mole}$ (-898.97 kcal/mole) from ΔH_{f}° and S[°] values. No other information is available for this compound. Therefore, we selected the one available ΔG_{f}° value for rankinite.

$\beta Ca_2 SiO_4$ (larnite)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -2190.99$ kJ/mole (-523.66 kcal/mole) from ΔH_{f}° and S[°] values. No other information is available for larnite. Therefore, we selected the Sadiq and Lindsay (1979) ΔG_{f}° value for larnite.

$\gamma Ca_2 SiO_4$ (calcium olivine)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -2201.28$ kJ/mole (-526.12 kcal/mole) from ΔH_{f}° and S[°] values. No other information is available

for calcium olivine. Therefore, we adopted the available ΔG_{f}° value for calcium olivine after Sadiq and Lindsay (1979).

CaMg(SiO₃), (diopside)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -3031.81 \text{ kJ/mole}$ (-724.62 kcal/mole) from ΔH_{f}° and S° values. Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -3032.02 \text{ kJ/mole}$ (-724.67 kcal/mole) from ΔH_{f}° and S° values. Robie and Waldbaum (1968) also reported similar ΔG_{f}° values for diopside. Helgeson et al. (1978) reported $\Delta G_{f}^{\circ} = -3029.21 \text{ kJ/mole}$ (-724.00 kcal/mole) from different solubility measurements and calorimetric data. Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -3032.00 \text{ kJ/mole}$ (-724.67 kcal/mole). There is good agreement among these reported ΔG_{f}° values for diopside. Therefore, we selected the ΔG_{f}° value for diopside of Helgeson et al. (1978).

CaSO₄ (anhydrite)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1324.15 \text{ kJ/mole} (-316.48 \text{ kcal/mole})$. Naumov et al. (1971) listed $\Delta G_{f}^{\circ} -1321.81 \text{ kJ/mole} (-315.92 \text{ kcal/mole})$. Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1321.79 \text{ kJ/mole}$ (-315.92 kcal/mole). Reported ΔG_{f}° values for anhydrite are in general agreement. Therefore, we selected the Sadiq and Lindsay (1979) ΔG_{f}° value for anhydrite.

$CaSO_4 \bullet 2H_2O$ (gypsum)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1799.83 \text{ kJ/mole} (-430.17 \text{ kcal/mole})$. Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1797.28 \text{ kJ/mole} (-429.56 \text{ kcal/mole})$. Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -1797.20 \text{ kJ/mole} (-429.54 \text{ kcal/mole})$. Reported ΔG_{f}° values for gypsum are in good agreement. We selected the Sadiq and Lindsay (1979) ΔG_{f}° value for gypsum.

$CaCO_3 \bullet H_2O$ (ikaite)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -2542.86$ kJ/mole (-607.52 kcal/mole). No other information is available for ikaite. Therefore, we selected the available ΔG_{f}° value for ikaite.

CaCO₃ (aragonite)

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1127.75$ kJ/mole (-269.54 kcal/mole). Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -1127.38$ kJ/mole (-269.45 kcal/mole). Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1129.14$ kJ/mole (-269.87 kcal/mole). Plummer and Busenberg (1982) made reliable solubility measurements of aragonite and reported pK = 8.33 for the reaction:

$$CaCO_3$$
 (aragonite) \leftrightarrow Ca^{2^+} + $CO_3^{2^-}$

These authors also made corrections for ionic strengths, temperature, and solution complexes. Therefore, we selected a pK of 8.33 for the above reaction after Plummer and Busenberg (1982) and calculated the ΔG_{f}° value for aragonite, using selected ΔG_{f}° values of $Ca^{2^{+}}$ and $CO_{3}^{2^{-}}$. The calculated ΔG_{f}° value for aragonite is -1129.93 kJ/mole (-270.06 kcal/mole).

CaCO₃ (calcite)

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1128.79$ kJ/mole (-269.79 kcal/mole) from ΔH_{f}° and S[°] values. Naumov et al. (1971) listed $\Delta G_{f}^{\circ} = -1128.34$ kJ/mole (-269.68 kcal/mole) from ΔH_{f}° and S[°] values. Several investigators examined the solubility of calcite and recommend the following pK values for the reaction CaCO₃ (calcite) $\neq Ca^{2^{+}} + CO_{3}^{2^{-}}$ listed in Table 11.

PR VELEOD IOL OBLOIDO DIODOIGUION	Table	11.	рΚ	Values	for	Calcite	Dissolution
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Investigator	рК
Smith and Martell (1976)	8.35
Sadiq and Lindsay (1979)	8.42
Plummer and Busenberg (1982)	8.48
CODATA (1987)	8.48

Plummer and Busenberg (1982) made reliable solubility measurements of calcite and made corrections for ionic strength, temperature, and solution complexes. Recently, CODATA (1987) compared solubility data

and calorimetric data of calcite and selected pK = 8.48 for the above reaction from Plummer and Busenberg (1982). Therefore, we selected pK =8.48 for the above reaction after Plummer and Busenberg (1982) and calculated the ΔG_{f}° value for calcite. The calculated ΔG_{f}° value for calcite is -1130.80 kJ/mole (-270.27 kcal/mole).

$CaMg(CO_3)_2$ (dolomite)

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -2163.40 \text{ kJ/mole}$ (-517.07 kcal/mole) from ΔH_{f}° and S° values. Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -2151.92 \text{ kJ/mole}$ (-514.32 kcal/mole) from ΔH_{f}° and S° values. Sadiq and Lindsay (1979) critically evaluated thermodynamic data of dolomite and reported $\Delta G_{f}^{\circ} = -2168.36 \text{ kJ/mole}$ (- 518.25 kcal/mole) for dolomite. We selected the Sadiq and Lindsay (1979) ΔG_{f}° value for dolomite.

CaHPO (monetite)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1690.17$ kJ/mole (-403.96 kcal/mole) from pK = 6.90 for the reaction:

$$CaHPO_4$$
 (monetite) $\leftrightarrow Ca^{2^+} + HPO_4^{2^-}$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1681.18 \text{ kJ/mole} (-401.82 \text{ kcal/mole})$ from ΔH_{f}° and S° values. Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -1680.00 \text{ kJ/mole}$ (-401.53 kcal/mole) from pK = 6.66 for the above reaction after Farr (1950). However, Sadiq and Lindsay (1979) reported that the Farr (1950) investigation had not included the CaHPO₄ species. Therefore, we selected the Sadiq and Lindsay (1979) ΔG_{f}° value for monetite.

$CaHPO_4 \cdot 2H_2O$ (brushite)

Naumov et al. (1971) reported $\Delta G_f^{\circ} = -2153.76$ kJ/mole (-514.76 kcal/mole) from pK = 6.57 for the reaction:

 $CaHPO_4 \cdot 2H_2O$ (brushite) $\leftrightarrow Ca^{2^+} + HPO_4^{2^-} + 2H_2O$

Sadiq and Lindsay (1979) adopted the above reaction and reported ΔG_{f}° - -2162.67 kJ/mole (-516.89 kcal/mole). Wagman et al. (1982) reported

 $\Delta G_{f}^{\circ} = -2154.58 \text{ kJ/mole} (-514.97 \text{ kcal/mole}) \text{ from } \Delta H_{f}^{\circ} \text{ and } \text{ S}^{\circ} \text{ values}.$ Because the Sadiq and Lindsay (1979) reported value is from solubility measurements, we adopted their ΔG_{f}° value for brushite.

$Ca(H_2PO_4)_2 \cdot H_2O(c)$

Naumov et al. (1971) reported $\Delta G_f^{\circ} = -3058.50$ kJ/mole (-731.00 kcal/mole) from $\Delta H_r^{\circ} = -160.20$ kJ/mole (-38.28 kcal/mole) for the reaction:

$$Ca(OH)_2(c) + 2H_3PO_4 \leftrightarrow Ca(H_2PO_4)_2 \cdot H_2O(c) + H_2O(c)$$

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{o} = -3073.06$ kJ/mole (-734.48 kcal/mole) from pK = 1.14 for the following reaction:

$$Ca(H_2PO)_2 \cdot H_20 \leftrightarrow Ca^{2^+} + 2H_2PO_4^- + H_2O$$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -3058.18 \text{ kJ/mole} (-730.92 \text{ kcal/mole})$ from ΔH_{f}° and S[°] values. Because Sadiq and Lindsay's (1979) ΔG_{f}° value is from solubility measurements, we selected it for $Ca(H_{2}PO_{4})_{2} \cdot H_{2}O$ (c).

$Ca_3(PO_4)_2(c)$

Naumov et al. (1971) reported $\Delta G_f^{\circ} = -3870.20$ kJ/mole (-925 kcal/mole) from ΔH_f° and S° values. Sadiq and Lindsay (1979) listed $\Delta G_f^{\circ} = -3860.58$ kJ/mole (-922.70 kcal/mole) and also recommended pK = 25.50 for the reaction:

$$Ca_{3}(PO_{4})_{2}(c) \leftrightarrow 3Ca^{2^{+}} + 2PO_{4}^{3^{-}}$$

No other information is available for this compound. Therefore, we adopted the ΔG_f^o value recommended by Sadiq and Lindsay (1979).

$\beta Ca_3(PO_4)_2$ (whitelockite)

Sadiq and Lindsay (1979) reported $\Delta G_f^{\circ} = -3880.12$ kJ/mole (-927.37 kcal/mole) from pK = 28.92 for the reaction:

$\beta Ca_3 (PO_4)_2 (whitlockite) \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$

No other information is available for this compound. Therefore, we selected the ΔG_f^o value recommended by Sadiq and Lindsay (1979).

$Ca_{8}H_{2}(PO_{4})_{6} \cdot 5H_{2}O$ (octacalcium phosphate)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -12311.92 \text{ kJ/mole} (-2942.62 \text{ kcal/mole})$ from solubility data. These authors also reported problems associated with calorimetric data of octacalcium phosphate. Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -12263.00 \text{ kJ/mole} (-2930.93 \text{ kcal/mole})$. We selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

Ca₁₀(OH)₂(PO₄)₆ (hydroxyapatite)

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -12684.21$ kJ/mole (-3031.60 kcal/mole) from ΔH_{f}° and S° values. Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -12678.60$ kJ/mole (-3030.26 kcal/mole) from pK = 116.40 for the reaction:

$$Ca_{10}(OH)_2(PO_4)_6$$
 (hydroxyapatite) + $10Ca^{2^+} + 6PO_4^{3^-} + 2OH^{-1}$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} - -12677.00$ kJ/mole (-3029.88 kcal/mole) from ΔH_{f}° and S[°] values. Because Sadiq and Lindsay (1979) reported their ΔG_{f}° value from solubility data, we selected it for hydroxyapatite.

Magnesium

Selected ΔG_{f}^{0} values for magnesium species are summarized in Table 12. Equilibrium constants for reactions involving magnesium are listed in Table 13.

Mg²+

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -454.80$ kJ/mole (-108.70 kcal/mole) from ΔH_{f}° and S° values. Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -455.26$ kJ/mole (-108.81 kcal/mole). Robie et al. (1978) listed $\Delta G_{f}^{\circ} = -454.80$ kJ/mole (-180.70 kcal/mole). Table 14 lists pK values for the reaction Mg(OH)₂(brucite) $\neq Mg^{2^{+}} + OH^{-}$. Sadiq and Lindsay (1979) used the pK reported by Hostetler (1963) and reported $\Delta G_{f}^{\circ} = -456.09$ kJ/mole (-109.01 kcal/mole). Further, these authors reported that Hostetler (1963) considered the MgOH⁺ complex in his solubility measurements. Therefore, we selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979) for Mg^{2⁺} species.

MgCO3

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -1002.47$ kJ/mole (-239.60 kcal/mole) from pK = 3.40 for the reaction:

 $MgCO_3^0 \rightarrow Mg^{2^+} + CO_3^{2^-}$

Sadiq and Lindsay (1979) reported $\Delta G_{\rm f}^{\circ} = -1002.53$ kJ/mole (-239.61 kJ/mole). No other information is available. Therefore, we selected the $\Delta G_{\rm f}^{\circ}$ value reported by Sadiq and Lindsay (1979).

		ΔG	ΔG [°] f		
No.	Species	kJ/mole	kcal/mole	Source	
	I. Solution	on Species			
1.	Mg2 ⁺	-456.09	-109 01	Α	
2.	MgCO ⁹	-1002 53	-239 61	Δ	
3.	MgHCO	-1049.10	-250 74	A	
4.	MgCl.	-718.44	-171.71	A	
5.	MgSO ²	-1213.36	-290.00	A	
6.	Mg (NO ₂)?	-678.94	-162.27	A	
7.	MgOH ² ^{+3²}	-627.93	-150.08	A	
8.	Mg(OH)	-770.73	-184.21	A	
9.	MgHPO 4	-1569.04	-375.01	A	
	<u>II. Soli</u>	d Species			
10.	MgO (periclase)	-569.20	-136.04	А	
11.	Mg(OH), (brucite)	-834.33	-199.41	A	
12.	MgSiO, (clinoenstatite)	-1461.93	-349.41	A	
13.	Mg_SiO_ (forsterite)	-2055.60	-491.30	A	
14.	Mg_Si_0_(OH) (chrysotile)	-4034.21	-964.20	Α	
15.	$Mg_3Si_0_1(OH)_2$ (talc)	-5525.22	-1320.56	Α	
16.	Mg ₂ ₈₂₅ Si ₂ O ₅ (OH) ₃ ₆₅ (antigorit	e) -3885.90	-928.75	В	
17.	Mg ₆ Si ₄ O ₁₀ (OH) ₈ (serpentine)	-8091.23	-1933.85	Α	
18.	Mg ₂ Si ₃ (OH) ₄ (sepiolite)	-4271.65	-1020.95	Α	
19.	MgSO ₄ (c)	-1153.95	-275.80	А	
20.	$MgSO_4 \cdot H_2O$ (c)	-1428.70	-341.46	Е	
21.	MgSO ₄ •H ₂ O (amorphous)	-1404.90	-335.78	Ē	
22.	$MgSO_4 \cdot 6H_2O(c)$	-2631.80	-629.01	Е	
23.	$MgSO_4 \cdot 7H_2O(c)$	-2871.50	-686.30	E	
24.	MgCO ₃ (magnesite)	-1026.62	-245.37	D	
25.	$MgCO_3 \cdot 3H_2O$ (nesquehonite)	-1726.61	-412.67	С	
26.	$MgCO_3 \cdot 5H_2O$ (lansfordite)	-2199.20	-525.62	Е	
27.	MgHPO ₄ •3H ₂ O (newberryite)	-2297.18	-549.04	А	
28.	$MgKPO_{4} \cdot 6H_{2}O$ (c)	-3248.08	-776.31	А	
29.	$MgNH_4PO_4 \cdot \tilde{6}H_2O$ (struvite)	-3059.50	-731.24	А	
30.	$Mg_3(PO_4)_2$ (c)	-3503.26	-837.30	А	
31.	$Mg_3(PO_4)_2 \cdot 8H_2O$ (boberrite)	-5460.08	-1304.99	A	
32.	$Mg_{3}(PO_{4})_{2} \cdot 22H_{2}O(c)$	-8769.70	-2096.01	A	
33.	$Mg_7Si_8O_{22}(OH)_2$ (anthophyllite)	-11364.58	-2716.20	С	

Table 12. Selected Standard Free Energies of Formation (ΔG_f°) of Mg Species at 25°C (298.15 K) and 1 atm (10⁵ Pa)

A = Sadiq and Lindsay (1979)

B = Hemley et al. (1977) C = Naumov et al. (1971)

D = Smith and Martell (1976)

E = Wagman et al. (1982)

No.	Equilibrium Reaction	log K°
	I. Solid Species	
1.	MgO (periclase) + $2H^{+} \rightarrow Mg^{2^{+}} + H_{2}O$	21.74
2.	$Mg(OH)_2$ (brucite) + $2H_2O \rightarrow Mg^{2+} + 2H_2O$	16.84
3.	$MgSiO_3$ (clinoenstatite) + $2H^+$ + $2H_2O \rightarrow Mg^{2+} + H_4SiO_4^0$	11.42
4.	Mg_2SiO_4 (forsterite) + $4H^+ \rightarrow 2Mg^{2+} + H_4SiO_4^0$	28.87
5.	$Mg_3Si_2O_5(OH)_4(chrysotite) + 6H^+ \rightarrow 3Mg^{2+} + 2H_4SiO_4^0 + H_2O$	32.87
6.	$Mg_3Si_4O_{10}(OH)_2(talc) + 4H_2O + 6H^{+} \stackrel{?}{\rightarrow} 3Mg^{2^+} + 4H_4SiO_4^0$	22.26
7.	$Mg_{2,825}Si_{2}O_{5}(OH)_{3,65}(antigorite) + 5.65H^{+} \stackrel{2}{\rightarrow}$	30.32
	$2.85 \text{Mg}^{2^+} + 4 \text{H}_4 \text{SiO}_4^0 + 0.65 \text{H}_2 \text{O}$	
8.	$Mg_6Si_4O_{10}(OH)_8$ (serpentine) + $12H^+ \stackrel{2}{\leftarrow} 6Mg^{2^+} + 4H_4SiO_4^0 + 2H_2O_4^0$	0 61.75
9.	$Mg_2Si_3O_6(OH)_4$ (sepiolite) + $2H_2O$ $4H^+ \div 2Mg^{2+} + 3H_4Si_4^0$	15.89
10.	$Mg_7Si_8O_{22}(OH)_2$ (anthophyllite) + 14H ⁺ + 8H ₂ O \neq	
	$7Mg^{2+} + 8H_4SiO_4^{\circ}$	69.78
11.	$MgSO_4$ (c) $\rightarrow Mg^{2^+} + SO_4^2$	8.18
12.	$MgSO_4 \cdot H_2O$ (c) $\stackrel{\rightarrow}{\leftarrow} Mg^{2^+} + SO_4^2 + H_2O$	1.60
13.	$MgSO_4 \cdot H_2O$ (amorphous) $\stackrel{2}{\leftarrow} Mg^{2^+} + SO_4^{2^-} + H_2O$	5.77
14.	$MgSO_4 \cdot 6H_2O$ (c) $\rightarrow Mg^{2^+} + SO_4^{2^-} + 6H_2O$	-1.40
15.	$MgSO_4 \cdot 7H_2O$ (c) $\rightarrow Mg^{2^+} + SO_4^{2^-} + 7H_2O$	-1.84
16.	$MgCO_3$ (magnesite) $\rightarrow Mg^{2^+} + CO_3^2$	-7.46
17.	$MgCO_3 \cdot 3H_2O$ (nesquehoite) $\stackrel{\rightarrow}{\leftarrow} Mg^{2^+} CO_3^2 + 3H_2O$	-5.43
18.	$MgCO_3 \cdot 5H_2O$ (lansfordite) $\stackrel{\rightarrow}{\leftarrow} Mg^{2^+} + CO_3^2^- + 5H_2O$	-5.12
19.	$MgHPO_4 \cdot 3H_2O$ (newberryite) + $H^+ \neq Mg^{2+} + H_2PO_4^- + 3H_2O$	1.38
20.	$MgKPO_{4} \cdot 6H_{2}O(c) + 2H^{+} \stackrel{\rightarrow}{\leftarrow} Mg^{2+} + K^{+} + H_{2}PO_{4}^{-} + 6H_{2}O$	8.93
21.	$MgNH_4PO_4 \cdot 6H_2O$ (struvite) + $2H^+ \rightarrow Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2^-$	0 6.40
22.	$Mg_3(PO_4)_2$ (c) + $4H^+ \div 3Mg^{2+} + 2H_2PO_4^-$	24.51
23.	$Mg_3(PO_4)_2 \cdot 8H_2O$ (boberrite) + $4H^+ \stackrel{\rightarrow}{\leftarrow} 3Mg^{2^+} + 2H_2PO_4^- + 8H_2O$	14.10
24	M_{σ} (PO) .22H O (c) + $4H^{+} \rightarrow 3M_{\sigma}2^{+} + 2H PO^{-} + 22H O$	16 01

Table 13. Equilibrium Constants for Reactions Involving Magnesium at 25 $^{\circ}$ C (298.15 K) and 1 atm (10 5 Pa)

No.	Equilibrium Reaction	log K [°]
	II. Solution Species	
25.	$Mg^{2^+} + CO_3^2 MgCO_3^0$	3.23
26.	$Mg^{2^+} + CO_3^2 \xrightarrow{\rightarrow} MgHCO_3^+$	1.06
27.	$Mg^{2^+} + 2Cl^- \downarrow MgCl_2^{0}$	-0.03
28.	$Mg^{2^+} + SO_4^{2^-} \stackrel{2}{\rightarrow} MgSO_4^0$	2.23
29.	$Mg^{2^+} + 2NO_3^- \stackrel{\rightarrow}{\leftarrow} Mg(NO_3)_2^0$	-0.01
30.	$Mg^{2^+} + H_2 O \stackrel{\rightarrow}{\rightarrow} MgOH^+ + H^+$	-11.45
31.	$Mg^{2^+} + 2H_2O \stackrel{\rightarrow}{\rightarrow} Mg(OH)^{0}_2 + 2H^+$	-27.99
32.	$Mg^{2^+} + H_2PO_4^- \xrightarrow{\rightarrow} MgHPO_4^0 + H^+$	-4.29

Table 13. Equilibrium Constants for Reactions Involving Magnesium at 25° C (298.15 K) and 1 atm (10^5 Pa), Continued

Table 14. pK Values for Brucite Dissolution

Investigator	рК
Robie et al. (1978) Hostetler (1963) Smith and Martell (1976)	11.06 11.15 11.15
Smith and Martell (1976)	11.15

MgHC0⁺

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{o} = -1049.10$ kJ/mole (-250.74 kcal/mole) from pK 1.07 for the reaction:

$$MgHCO_3^+ \rightarrow Mg^{2^+} + HCO_3^-$$

Smith and Martell (1976) reported pK = 0.95 for the above reaction. No other information is available for this species. Therefore, we selected the ΔG_{f}^{o} value reported by Sadiq and Lindsay (1979).

MgC19

Sadiq and Lindsay (1979) reported $\Delta G_f^{\circ} = -718.44$ kJ/mole (-171.71 kcal/mole) from the reaction:

 $Mg^{2^+} + 2C1^- \neq MgC1_2^0$

No other information is available. Therefore, we selected ΔG_f° value reported by Sadiq and Lindsay (1979).

MgSO4

i te

Naumov et al. (1971) listed $\Delta G_f^{\circ} = -1211.82$ kJ/mole (-289.63 kcal/mole) from ΔH_f° and pK = 2.23 for the reaction:

$$MgSO_4^0 \xrightarrow{} Mg^{2^+} + SO_4^2^-$$

Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -1212.21$ kJ/mole (-289.72 kcal/mole) from ΔH_{f}° and S[°] values. Smith and Martell (1976) reported a similar pK

value for the above reaction. Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1213.36 \text{ kJ/mole}$ (-290.00 kcal/mole) from pK = 2.23 for the above reaction. Reported ΔG_{f}° as well as pK values are very consistent. We selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

$Mg(NO_3)_2^0$

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -678.94$ kJ/mole (-162.27 kcal/mole). No other information was available. We adopted the only available ΔG_{f}° value for Mg(NO₃)⁰₂.

MgOH⁺

Naumov et al. (1971) reported $\Delta G_f^{\circ} = -627.60$ kJ/mole (-150.00 kcal/mole). Smith and Martell (1976) reported pK = 2.58 for the reaction:

$$MgOH^{+} \neq Mg^{2} + OH^{-}$$

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -627.93$ kJ/mole (-150.08 kcal/mole) from the above pK value. We selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

Mg(OH) 9

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -770.73$ kJ/mole (-184.21 kcal/mole). Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -769.40$ kJ/mole (-183.90 kcal/mole). No other information is available. Therefore, we selected Sadiq and Lindsay's (1979) reported ΔG_{f}° value.

MgHPO₄

Smith and Martell (1976) reported pK = 2.91 for the reaction:

 $MgHPO_4^0 \rightarrow Mg^{2^+} + HPO_4^{2^-}$

Sadiq and Lindsay adopted a similar pK value and reported $\Delta G_{f}^{\circ} = -1569.04$ kJ/mole (-375.01 kcal/mol). We adopted the ΔG_{f}° value of Sadiq and Lindsay (1979).

MgO (periclase)

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -569.44$ kJ/mole (-136.10 kcal/mole). Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -569.20$ kJ/mole (-136.04 kcal/mole). Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -569.43$ kJ/mole (-136.10 kcal/mole). Reported ΔG_{f}° values are in general agreement. We selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

Mg(OH)₂ (brucite)

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -833.58$ kJ/mole (-199.23 kcal/mole). Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -834.33$ kJ/mole (-199.41 kcal/mole). Reported ΔG_{f}° values are in good agreement. We selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

MgSiO₃ (clinoenstatite)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1461.93 \text{ kJ/mole} (-349.41 \text{ kcal/mole})$. Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1462.09 \text{ kJ/mole}$ (-349.45 kcal/mole). No other information was available. Therefore, we selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

Mg₂SiO₄ (forsterite)

Naumov et al. (1971) listed $\Delta G_{f}^{\circ} = -2053.34$ kJ/mole (-490.76 kcal/mole) from ΔH_{f}° and S[°] values. Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -2055.60$ kJ/mole (-491.30 kcal/mole). Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -2055.10$ kJ/mole (-491.18 kcal/mole). We used the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

$Mg_3Si_2O_5(OH)_4$ (chrysotile)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -4034.21 \text{ kJ/mole} (-964.20 \text{ kcal/mole})$. Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -4037.80 \text{ kJ/mole}$ (-965.06 kcal/mole). No other information is available. Therefore, we selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

$Mg_3Si_4O_{10}(OH)_2$ (talc)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -5525.22 \text{ kJ/mole} (-1320.56 \text{ kcal/mole}) \text{ from } \Delta H_{f}^{\circ}$ and S° values. Wagman et al. (1982) reported ΔG_{f}° = -5542.70 kJ/mole (-1324.74 kcal/mole). Sadiq and Lindsay (1979) critically evaluated the calorimetric data for talc. We selected their recommended ΔG_{f}° value for talc.

$Mg_{2.825}Si_{2}O_{5}(OH)_{3.65}$ (antigorite)

Hemley et al. (1977) reported $\Delta G_{f}^{\circ} = -3885.90$ kJ/mole (-928.75 kcal/mole) from the solubility and calorimetric data. No other information was available. Therefore, we selected the only available ΔG_{f}° value for antigorite.

Mg₆Si₄O₁₀(OH)₈ (serpentine)

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -8076.04 \text{ kJ/mole} (-1930.22 \text{ kcal/mole}) \text{ from } \Delta H_{f}^{\circ}$ and S° values. Sadiq and Lindsay (1979) listed $\Delta G_{f}^{\circ} = -8091.23 \text{ kJ/mole} (-1933.85 \text{ kcal/mole})$. No other information was available. Therefore, we selected the Sadiq and Lindsay (1979) ΔG_{f}° value.

$Mg_2Si_3O_6(OH)_4$ (sepiolite)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{o} = -4271.65$ kJ/mole (-1020.95 kcal/mole) from pK = 40.1 for the reaction:

$$Mg_2Si_3O_6(OH)_4(c) + 6H_2O \rightarrow 2Mg^{2^+} + 3H_4SiO_4^0 + 4OH^-$$

No other information was available. Therefore, we selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

MgSO₄ (c)

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -1165.79 \text{ kJ/mole} (-278.63 \text{ kcal/mole}) from <math>\Delta H_{f}^{\circ}$ and S[°] values. Sadiq and Lindsay (1979) listed $\Delta G_{f}^{\circ} = -1153.95 \text{ kJ/mole} (-275.80 \text{ kcal/mole}) from <math>\Delta H_{f}^{\circ}$ and S[°] values. Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1170.60 \text{ kJ/mole} (-279.78 \text{ kcal/mole}).$

Sadiq and Lindsay (1979) compared ΔH_{f}° and S° values reported by different investigators for $MgSO_{4}$ (c). These authors also discussed problems associated with calorimetric data. We selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

$MgSO_4 \cdot H_2O(c)$

Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -1428.70$ kJ/mole (-341.46 kcal/mole) from ΔH_{f}° and S[°] values. No other information was available. Therefore, we selected the only available value for MgSO₄·H₂O (c).

$MgSO_4 \cdot H_2O$ (amorphous)

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1404.90$ kJ/mole (-335.78 kcal/mole). No other information was available. We selected the only available ΔG_{f}° value.

$MgSO_4 \cdot 6H_2O$ (c)

Naumov et al. (1971) reported $\Delta G_f^{\circ} = -2631.31$ kJ/mole (-628.90 kcal/mole) from pK = 1.58 for the reaction:

$$MgSO_4 \cdot 6H_2O$$
 (c) $\rightarrow Mg^{2^+} + SO_4^{2^-} + 6H_2O$

Wagman et al. (1982) reported that $\Delta G_{f}^{\circ} = -2631.80 \text{ kJ/mole}$ (-629.01 kcal/mole) from ΔH_{f}° and S[°] values. Reported ΔG_{f}° values agree very well. We selected the Wagman et al. (1982) ΔG_{f}° value.

$MgSO_4 \cdot 7H_2O$ (c)

Naumov et al. (1971) reported $\Delta G_{f}^{o} = -2870.22$ kJ/mole (-686.00 kcal/mole) from pK = 1.92 for the reaction:

$$MgSO_4 \cdot 7H_2O$$
 (c) $\rightarrow Mg^{2^+} + SO_4^{2^-} + 7H_2O$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -2871.50 \text{ kJ/mole}$ (-686.30 kcal/mole) from ΔH_{f}° and S[°] values. Reported ΔG_{f}° values are in good agreement. We selected the ΔG_{f}° value reported by Wagman et al. (1982).

MgCO₃ (magnesite)

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -1012.27$ kJ/mole (-241.94 kcal/mole) from $\Delta G_{f}^{\circ} = 2.76$ kJ/mole (-0.66 kcal/mole) for the reaction:

$$MgCO_3 \cdot 3H_2O$$
 (c) $\rightarrow MgCO_3$ (c) $+ 3H_2O$

Sadiq and Lindsay (1979) reported ΔG_{f}^{o} = -1026.62 kJ/mole (-245.37 kcal/mole) from pK = 7.46 for the reaction:

$$MgCO_3$$
 (c) $\rightarrow Mg^{2^+} + CO_3^{2^-}$

after Smith and Martell (1976). Wagman et al. (1982) reported ΔG_{f}° = -1012.10 kJ/mole (-241.90 kcal/mole) from ΔH_{f}° and S° values. We selected pK = 7.46 for the above reaction after Smith and Martell (1976) and calculated ΔG_{f}° = -1026.62 kJ/mole (-245.37 kcal/mole) for magnesite.

 $MgCO_3 \cdot 3H_2O$ (nesquehonite)

Naumov et al. (1971) reported $\Delta G_{f}^{o} = -1726.61$ kJ/mole (-412.67 kcal/mole) from pK = 5.59 for the reaction:

$$MgCO_3 \cdot 3H_2O \rightarrow Mg^{2^+} + CO_3^2 + 3H_2O$$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1726.10$ kJ/mole (-412.55 kcal/mole) from ΔH_{f}° and S[°] values. We selected the ΔG_{f}° value reported by Naumov et al. (1971).

$MgCO_3 \cdot 5H_2O$ (lansfordite)

Naumov et al. (1971) reported $\Delta G_{f}^{\circ} = -2200.24$ kJ/mole (-525.87 kcal/mole) from $\Delta G_{f}^{\circ} = -0.71$ kJ/mole (-0.171 kcal/mole) for the reaction:

$$MgCO_3 \cdot 5H_2O$$
 (c) $\rightarrow MgCO_3 \cdot 3H_2O$ (c) $+ 2H_2O$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -2199.20$ kJ/mole (-525.62 kcal/ mole) from ΔH_{f}° and S[°] values. Reported ΔG_{f}° values agree with each other well. No other information was available. We selected the ΔG_{f}° value reported by Wagman et al. (1982).

$MgHPO_4 \cdot 3H_2O$ (newberryite)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{o} = -2297.18$ kJ/mole (-549.04 kcal/mole) from pK = 5.82 for the reaction:

$$MgHPO_4 \cdot 3H_2O \rightarrow Mg^{2+} + HPO_4^2 + 3H_2O$$

No other information was available. We selected the only available ΔG_{f}° value after Sadiq and Lindsay (1979).

$MgKPO_4 \cdot 6H_2O$ (c)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -3248.08$ kJ/mole (-776.31 kcal/mole) from pK = 10.62 for the reaction:

$$MgKPO_{4} \cdot 6H_{2}O (c) \stackrel{\rightarrow}{\leftarrow} Mg^{2^{+}} + K^{+} + PO_{4}^{3^{-}} + 6H_{2}O$$

No other information was available. We selected the only available ΔG_{f}^{o} value after Sadiq and Lindsay (1979).

MgNH₄PO₄•6H₂O (struvite)

Sadiq and Lindsay (1979) reported $\Delta G_f^o = -3059.50$ kJ/mole (-731.24 kcal/mole) from pK = 13.15 for the reaction:

$$MgNH_4PO_4 \cdot 6H_2O$$
 (c) $\rightarrow Mg^{2^+} + NH_4^+ + PO_4^{3^-} + 6H_2O$

No other information was available. We selected the ΔG_f° value reported by Sadiq and Lindsay (1979) for struvite.

$Mg_3(PO_4)_2$ (c)

Naumov et al. (1971) reported $\Delta G_f^{\circ} = -3548.45$ kJ/mole (-848.10 kcal/mole) from $\Delta H_f^{\circ} = -464.34$ kJ/mole (-110.98 kcal/mole) for the reaction:

$3MgO(c) + P_2O_5$ (orthorhombic) $\rightarrow Mg_3(PO_4)_2$ (c)

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -3503.26$ kJ/mole (-837.30 kcal/mole) from ΔH_{f}° and S° values. Furthermore, these authors also compared ΔH_{f}° and S° values for this reaction reported by different investigators. Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -3538.70$ kJ/mole (-845.77 kcal/mole). We adopted the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

$Mg_3(PO_4)_2 \cdot 8H_2O$ (boberrite)

Smith and Martell (1976) reported pK = 25.00 for the reaction:

$$Mg_3(PO_4)_2 \cdot 8H_2O$$
 (c) $\rightarrow 3Mg^2 + 2PO_4^3 + 8H_2O$

Sadiq and Lindsay (1979) adopted above pK value and reported ΔG_{f}° = -5460.08 kJ/mole (-1304.99 kcal/mole). No other information was available. We selected the only available ΔG_{f}° value.

 $Mg_{3}(PO_{4})_{2} \cdot 22H_{2}O$ (c)

Sadiq and Lindsay (1979) used pK = 23.10 for the reaction:

$$Mg_{3}(PO_{4})_{2} \cdot 22H_{2}O$$
 (c) $\rightarrow 3Mg^{2^{+}} + 2PO_{4}^{3^{-}} + 22H_{2}O$

and reported $\Delta G_{f}^{\circ} = -8769.70$ kJ/mole (-2096.01 kcal/mole). No other information was available. We adopted the only available ΔG_{f}° value.

Mg₇Si₈O₂₂(OH)₂ (anthophyllite)

Naumov et al. (1971) reported $\Delta G_f^{\circ} = -11364.58$ kJ/mole (-2716.20 kcal/mole) from $\Delta H_r^{\circ} = -304.93$ kJ/mole (-72.88 kcal/mole) for the reaction:

7MgO (c) + 8SiO₂(
$$\alpha$$
quartz) + H₂O \rightarrow Mg₇(Si₄O₁₁)(OH)₂ (c)

No other information was available. We selected the only available ΔG_{f}° value for anthophyllite.

Sodium

Selected ΔG_{f}^{0} values for sodium species are summarized in Table 15. Equilibrium constants for reactions involving sodium are listed in Table 16.

Na^+

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -261.88$ kJ/mole (-62.59 kcal/ mole) for Na⁺ from ΔH_{f}° and S[°] values. Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -261.90$ kJ/mole (-62.59 kcal/mole) for Na⁺. No other information is available for this species. Therefore, we selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979).

NaC1°

Sadiq and Lindsay (1979) reported $\Delta G_f^{\circ} = -393.13 \text{ kJ/mole} (-93.96 \text{ kcal/ mole})$ from Garrels and Christ (1965). Wagman et al. (1982) reported $\Delta G_f^{\circ} = -393.13 \text{ kJ/mole} (-93.96 \text{ kcal/mole})$ from ΔH_f° and S° values. We selected the ΔG_f° value suggested by Sadiq and Lindsay (1979) for NaCl°.

NaHCO₃

Sadiq and Lindsay (1979) reported ΔG_f^o = -850.18 kJ/mole (-203.20 kcal/ mole) from pK = 0.25 for the reaction:

 $NaHCO_3^0 \rightarrow Na^+ + HCO_3^-$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -849.70 \text{ kJ/mole} (-203.10 \text{ kcal/mole})$ from ΔH_{f}° and S[°] values. Reported ΔG_{f}° values for NaHCO₃[°] agree very well. Therefore, we selected the ΔG_{f}° value recommended by Sadiq and Lindsay (1979) for NaHCO₃[°].

$Na_2CO_3^0$

Sadiq and Lindsay (1979) reported $\Delta G_f^{\circ} = -1051.77$ kJ/mole (-251.38 kcal/ mole) from Garrels and Christ (1965) and Karapet'yants and

	••••••	ΔG [°] f		
No.	Species	kJ/mole	kcal/mole	Source
1.	Na ⁺	-261.88	-62.59	А
2.	NaCl ⁰	-393.13	-93.96	А
3.	NaHCO ⁰	-850.18	-203.20	А
4.	$Na_2CO_3^0$	-1051.77	-251.38	А
5.	NaOH ⁰	-418.02	-99.91	А
6.	$NaSO_{4}$	-1010.39	-241.49	А
7.	$Na_2SO_4^0$	-1268.36	-303.14	В
8.	$NaNO_{3}^{0}$	-373.15	-89.18	В
9.	NaH ₂ PO ⁰	-1392.17	-332.73	В
10.	к+	-282.46	-67.51	А
11.	KC1º	-409.74	-97.93	А
12.	KHCO3	-870.04	-207.94	В
13.	K ₂ CO ₃	-1092.78	-261.18	А
14.	KOH 0	-436.90	-104.42	А
15.	KH ₂ PO ⁰	-1421.10	-339.65	А
16.	KS04	-1031.85	-246.62	А

Table 15. Selected Standard Free Energies of Formation (ΔG_f^o) of Sodium and Potassium Solution Species at 25°C (298.15 K) and 1 atm (10⁵ Pa).

A = Sadiq and Lindsay (1979) B = Wagman et al. (1982)

No.	Equilibrium Reaction	log K
1.	$Na^+ + C1^- \leftrightarrow NaC1^0$	0.00
2.	$Na^{+} + CO_2(g) + H_2O \leftrightarrow NaHCO_3^{\circ} + H^{+}$	-7.58
3.	$Na^{+} + CO_2(g) + H_2O \leftrightarrow NaCO_3 + 2H^{+}$	-16.89
4.	$Na^{+} + H_2 O \leftrightarrow NaOH^{0} + H^{+}$	-14.20
5.	$Na^{+} + SO_{4}^{2^{-}} \leftrightarrow NaSO_{4}^{-}$	0.70
6.	$2Na^+ + SO_4^2 \leftrightarrow Na_2SO_4^0$	0.00
7.	$2Na^{+} + CO_2(g) + H_2O \leftrightarrow Na_2CO_3^{\circ} + 2H^{+}$	-18.14
8.	$Na^+ + NO_3^- \Leftrightarrow NaNO_3^0$	-0.03
9.	$Na^{+} + H_2PO_4^{-} \leftrightarrow NaH_2PO_4^{0}$	-1.25
10.	K ⁺ + C1 ⁻ ↔ KC1°	-0.70
11.	$K^{+} + CO_2(g) + H_2O \leftrightarrow KHCO_3^{\circ} + H^{+}$	-7.71
12.	$2K^{+} + CO_2(g) + H_2O \Leftrightarrow K_2CO_3^0 + 2H^{+}$	-18.17
13.	$K^+ + H_2 O \Leftrightarrow KOH^0 + H^+$	-14.50
14.	$K^+ + H_2 PO_4^2 + KH_2 PO_4^-$	0.21
15.	K^+ $SO_4^2^- \leftrightarrow KSO_4^-$	-0.85

Table 16. Equilibrium Constants for Reactions Involving Sodium and Potassium Species at 25°C (298.15 K) and 1 atm (10⁵ Pa)

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Karapet'yants (1970). Wagman et al. (1982) listed $\Delta G_{f}^{\circ} = -1051.64$ kJ/mole (-251.35 kcal/ mole) from ΔH_{f}° and S[°] values. We selected the value recommended by Sadiq and Lindsay (1979).

NaOH⁰

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{o} = -418.02$ kJ/mole (-99.91 kcal/mole) from pK = 0.20 for the reaction:

$$Na^+ + OH^- \rightarrow NaOH^0$$

after Smith and Martell (1976). Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -419.15 \text{ kJ/mole}$ (-100.18 kcal/mole) from ΔG_{f}° values. Therefore, we selected ΔG_{f}° value suggested by Sadiq and Lindsay (1979) for NaOH^o.

NaSO_

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1010.39$ kJ/mole (-241.49 kcal/mole) from pK = 0.70 for the reaction:

$$NaSO_{4}^{-} \rightarrow Na^{+} SO_{4}^{2^{-}}$$

after Smith and Martell (1976). Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1010.61 \text{ kJ/mole}$ (-241.54 kcal/mole) from ΔH_{f}° and S° values. No other information is available. We selected the value reported by Sadiq and Lindsay (1979).

Na₂SO₄

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1268.36$ kJ/mole (-303.14 kcal/mole) for Na₂SO₄^o. No other information is available. We selected the available ΔG_{f}° value for Na₂SO₄^o.

NaNO₃

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = 373.15 \text{ kJ/mole}$ (-89.18 kcal/mole) for NaNO₃^o from ΔH_{f}° values and S^o values. No other information is available. We selected the ΔG_{f}° value recommended by Wagman et al. (1982) for NaNO₃^o.

NaH, PO4

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1392.17$ kJ/mole (-332.73 kcal/mole) from ΔH_{f}° and S[°] values. No other information is available for this species. We selected the available ΔG_{f}° value for NaH₂PO₄[°].

Potassium

Selected ΔG_{f}^{0} values for potassium species are summarized in Table 15. Equilibrium constants for reactions involving potassium are listed in Table 16.

<u>K</u>+

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -282.46 \text{ kJ/mole} (-67.51 \text{ kcal/mole}) \text{ from } \Delta H_{f}^{\circ}$ and S[°] values. Wagman et al. (1982) reported ΔG_{f}° = -282.27 kJ/mole (-67.70 kcal/mole) from ΔH_{f}° and S[°] values. We selected the ΔG_{f}° value recommended by Sadiq and Lindsay (1979).

KC1º

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -409.74$ kJ/mole (-97.93 kcal/mole) from pK = 0.70 for the reaction:

 $K^+ + C1^- \rightarrow KC1^\circ$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -414.49 \text{ kJ/mole} (-99.06 \text{ kcal/ mole})$ from ΔH_{f}° and S° values. We selected the ΔG_{f}° value reported by Sadiq and Lindsay (1979) for KCl°.

KHCO₃

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -870.04$ kJ/mole (-207.94 kcal/mole) from ΔH_{f}° and S[°] values. No other information is available. We selected the available ΔG_{f}° value for KHCO₃[°].

$K_2CO_3^0$

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1092.78$ kJ/mole (-261.18 kcal/mole). Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -1094.36$ kJ/mole

(-261.55 kcal/mole) from ΔH_{f}° and S[°] values. Therefore, we selected the ΔG_{f}° value recommended by Sadiq and Lindsay (1979) for $K_{2}CO_{3}^{\circ}$.

KOH 0

Sadiq and Lindsay (1979) reported ΔG_{f}° = -436.90 kJ/mole (-104.42 kcal/mole) from pK = 0.50 for the reaction:

$$K^+ + OH^- \rightarrow KOH^0$$

Wagman et al. (1982) reported $\Delta G_{f}^{\circ} = -440.50 \text{ kJ/mole} (-105.28 \text{ kcal/mole})$ from ΔH_{f}° and S° values. Because Sadiq and Lindsay (1979) reported their ΔG_{f}° value from solubility measurements, we selected their value for KOH°.

KH2PO4

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1421.10 \text{ kJ/mole} (-339.65 \text{ kcal/mole})$ from ΔH_{f}° and S° values. Wagman et al. (1982) reported ΔG_{f}° = -1413.55 kJ/mole (-337.84 kcal/mole) from ΔH_{f}° and S° values. Sadiq and Lindsay (1979) critically evaluated the ΔG_{f}° values for $K_{2}H_{2}PO_{4}^{\circ}$.

KS0₄

Sadiq and Lindsay (1979) reported $\Delta G_{f}^{\circ} = -1031.85$ kJ/mole (-246.62 kcal/mole) from pK = 0.85 for the reaction:

$$KSO_4^- \stackrel{2}{\rightarrow} K^+ + SO_4^2^-$$

No other information is available. We selected the available ΔG_f° value for KSO_4° .

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