

CONTRIBUTIONS TO THE SOLUTION OF THE

PROBLEM OF DOLOMITE GENESIS

By

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A Thesis submitted to the Faculty and the Board of Trustees
of the Colorado School of Mines in partial fulfillment of the
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ABSTRACT

The basic contribution of thermodynamics to the solution of the problem of dolomite genesis at earth surface conditions is considered by this author to be the determination of the CaO-MgO-CO₂-H₂O system at 25°C, P_{total} = 1 atm, and P_{CO₂} = 10⁻³ atm. In this study the ternaries, i.e., the three-component systems, of the above four-component system were determined by reference to literature data, by experimentally obtaining the free energy of formation of huntite, and by deducing the stable states within the compositional regions CaO-MgO-CO₂, CaO-MgO-Ca(OH)₂-Mg(OH)₂, and MgO-MgCO₃-MgCO₃·3H₂O-Mg(OH)₂ by means of a calculation scheme introduced in this report.

The composition of the stable solution phases in the ternaries were either deduced from solubility data in the literature or determined from calculations involving successive approximations of the appropriate complex equilibria problems.

The free energy of formation of huntite, $\Delta G_{f, 25^\circ\text{C}, \text{CaMg}_3(\text{CO}_3)_4}^\circ = -915 \pm 3$ kcal/mole, was determined from emf measurements of the following galvanic cells at 25°C.

| | | | | |
|-----------------------------|---|--------------|-------------------------------------|----|
| Ca-amalgam(a ₁) | CaCO ₃ (c) | (satd.soln), | Ag ₂ CO ₃ (s) | Ag |
| Mg-amalgam(a ₂) | MgCO ₃ · 3H ₂ O(s) | (satd.soln), | Ag ₂ CO ₃ (s) | Ag |
| Ca-amalgam(a ₁) | CaMg ₃ (CO ₃) ₄ (s) | (satd.soln), | Ag ₂ CO ₃ (s) | Ag |
| Mg-amalgam(a ₂) | CaMg ₃ (CO ₃) ₄ (s) | (satd.soln), | Ag ₂ CO ₃ (s) | Ag |

Applicability of the above procedure was first verified by determining the free energy of formation of dolomite, $\Delta G_{f,25^{\circ}\text{C},\text{CaMg}(\text{CO}_3)_2}^{\circ} = -519 \pm 1$ kcal/mole, which agreed, within the experimental precision, with values found in the literature.

The calculation scheme introduced in this study is a technique for the determination of the stable phases and the calculation of their respective amounts for any specified bulk composition in multicomponent systems. The required experimental information is a list of the potentially stable phases and their free energies of formation at the temperature and pressure of interest. All combinations of potentially stable phases are initially considered as being possible stable states, but some of these possibilities are rejected by considering the list of potentially stable compounds. Others are eliminated on the basis of the specified bulk composition and the stoichiometry of the reactions producing each assemblage of phases. Finally that combination which results from those reactions producing the greatest overall decrease in the free energy of the system is selected as the stable state.

Using the free energy of formation of huntite determined in this study, it was ascertained that the compound is not potentially stable at 25°C and $P_{\text{total}} = 1$ atm. Therefore, this compound can not represent any portion of

a stable state in the CaO-MgO-CO_2 system at 25°C , $P_{\text{total}} = 1 \text{ atm}$ and $P_{\text{CO}_2} = 10^{-3} \text{ atm}$. The stable states for the compositional region CaO-MgO-CO_2 were deduced, by application of the calculation scheme, to exist between $\text{CO}_2\text{-CaMg(CO}_3)_2$, $\text{CaCO}_3\text{-CaMg(CO}_3)_2\text{-MgCO}_3$, $\text{CaCO}_3\text{-MgO}$, and $\text{CaMg(CO}_3)_2\text{-MgO}$. Also, the alkemade lines for the compositional regions $\text{CaO-MgO-Mg(OH)}_2\text{-Ca(OH)}_2\text{-Ca(OH)}_2$ and $\text{MgO-MgCO}_3\text{-MgCO}_3\cdot 3\text{H}_2\text{O-Mg(OH)}_2$ were deduced to exist between $\text{Ca(OH)}_2\text{-MgO}$ and $\text{MgCO}_3\cdot 3\text{H}_2\text{O-MgO}$ respectively.

It is suggested that further experimental data for the quaternary system $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ be determined prior to considering complex systems which might be more directly applicable to the genesis of specific dolomite deposits.

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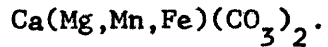
INTRODUCTIONIdentification of DolomiteDescription

The mineral dolomite is characterized by a definite internal structure and a range of chemical and physical properties. A description of the latter can be found in any standard mineralogy text such as Hurlbut (1955). Goldsmith and Graf (1958) reported that dolomite is a compound of calcium and magnesium carbonate with the mole ratio of calcium to magnesium equal to one, and is also, a solid solution of calcium, magnesium, manganese, and iron carbonate. The internal structure is represented by the space group $R\bar{3}(C_3^2i)$ (Graf and Lamar, 1955).

Geologic Occurrence

According to data collected by Goldsmith and Graf (1958) and to data reviewed by Dunbar and Rodgers (1958), very few natural carbonates can be represented as $CaMg(CO_3)_2$, i.e., as a double cation carbonate in which the Ca/Mg ratio is one. Isomorphous double cation carbonates have been identified in nature which range from $CaMg(CO_3)_2$ to $CaMn(CO_3)_2$ and $CaFe(CO_3)_2$. Thus the composition of the natural double cation carbonates of the dolomite

structure can best be represented by the compositional formula



Pettijohn (1957) points out that dolomite is usually associated with such minerals as calcite, aragonite, magnesite, anhydrite, and gypsum and more rarely with huntite, halite, and various ore minerals such as cerussite and smithsonite.

There appear to be four main types of dolomite deposits. The first type can be characterized as widespread deposits of dolomite extending over large distances and showing such stratigraphic relations as unconformity, vertical alternation, and facies change with other non-dolomitic rocks. Such deposits are exemplified by the Manitou dolomite of early Ordovician age in the Sawatch Range of Colorado. This deposit was described by Johnson (1944) as widespread siliceous dolomites and dolomitic limestones exhibiting an unconformable relationship with underlying Cambrian quartzite and overlying Ordovician and Devonian formations. Also, an example of this type deposit is the cyclic repetition of limestone and dolomite rocks observed near Chareton, Maryland, (Sarin, 1962). A second type is characterized by masses of dolomite which have irregular shapes and which appear to be related to the structural control of fracture systems. Krutsky (1959) described a deposit of limestone which contains irregular masses of dolomitic limestone definitely related to the fracture system. Hewett (1931) described dolomite in the Goodsprings district, Nevada which resulted from dolomilization of limestones along faults and fractures. A third type is depicted by Landes (1946) who described Devonian and Ordovician deposits of porous dolomitic limestone that are clearly related to buried erosional

surfaces. The fourth type of dolomite deposit is that which occurs in recent sediments. Alderman and Skinner (1957) described dolomite - calcite sediments which are presently being formed in a number of saline lakes in the South East province of South Australia. Taft (1961) described crystal - line authigenic dolomite in recent shallow-water marine sediments along the southern coast of Florida. Wells (1962) described recent dolomite associated with gypsum in sediment on a tidal flat in the Persian Gulf.

Origin of Dolomite

There appear to be as many different proposals for the origin of dolomite as there are descriptions of dolomite deposits in the literature. These varied proposals, however, can be grouped into the following three categories: dissolution of solid phases, "wet" secondary origin, and "wet" primary origin. The following discussion of laboratory and field evidence will serve to exemplify these three categories and to illustrate the reasonableness of such a categorization.

The first category, dissolution of solid phases, is exsolution, or unmixing, of metastable magnesium-rich calcites to yield dolomite as one of the products. Graf and Goldsmith (1955) and Harker and Tuttle (1955b) experimentally determined that magnesium-rich calcites are metastable phases at $T < 600^{\circ}\text{C}$ and $P >$ decomposition pressure for the carbonates. This means that at these conditions the following reaction is spontaneous to the right.



Since magnesium-rich calcites are known to exist in nature, (Goldsmith,

Graf, and Joensuu, 1955), it appears plausible that dissolution of magnesium-rich calcites could produce natural dolomite. Further justification for this genesis comes from Goldsmith (1957) and Baron and Favre (1958), who experimentally obtained dolomite from exsolution of magnesium-rich calcites at temperatures and pressures expected within the earth's crust. Field evidence for such a genesis would be observation of crystals of calcite and dolomite exhibiting an intimate association similar to the perthitic intergrowths of the feldspar minerals.

The second category, "wet" secondary origin, is usually meant to involve the reaction of aqueous Mg^{+2} with solid calcium carbonate to produce dolomite. But one can also include in this category the reaction of two or more solid phases to yield dolomite, because most authors would include an "intermediary" aqueous solution for the purpose of increasing the rate of reaction.

Berg and Borisova (1961) unsuccessfully attempted to crystallize dolomite from aqueous solutions within the $Na^{+1}, Mg^{+2}, Ca^{+2} \mid CO_3^{-2}, SO_4^{-2} - H_2O$ system at $25^\circ C$ and $P_{CO_2} = 1 \text{ atm}$. Thus, the authors concluded that some naturally occurring dolomite must have been formed by means of a "secondary" mechanism. Faust and Callaghan (1948) deduced that the reaction $2CaCO_3(s) + Mg_{aq.a_1}^{+2} \longrightarrow CaMg(CO_3)_2(d) + Ca_{aq.a_2}^{+2}$ is spontaneous to the right at the conditions of temperature, partial pressure of CO_2 , and concentrations of Mg^{+2} and Ca^{+2} found in sea water.

Garrels, Thompson, and Siever (1960), on the basis of solubility studies, concluded that the stable solid Ca and/or Mg carbonate in presence of sea water is dolomite and that the oceans are supersaturated with respect

to this phase. Thus, according to these authors, calcite and aragonite on the sea floor should react with the Mg^{+2} in sea water to form dolomite. By saturating aqueous solutions of various initial concentrations of Ca^{+2} and Mg^{+2} with calcite and dolomite, Kramer (1958) determined that at the temperature and pressure of normal sea water dolomite formation requires a Ca^{+2} "deficient" sea water. The above author notes that, due to such processes as precipitation of $CaCO_3$ which decreases the Ca^{+2} concentration of sea water, dolomite formation by reaction of Mg^{+2} with solid $CaCO_3$ is certainly possible. Rosenberg and Holland (1964) introduced solid calcite, solid magnesite, and solid dolomite into aqueous solutions containing various initial concentrations of Ca^{+2} and Mg^{+2} within the temperature range of 275° to $420^\circ C$ and at P_{CO_2} large enough to prevent formation of $Mg(OH)_2$. The solutions which yielded dolomite are those with a high Ca^{+2}/Mg^{+2} ratio. Thus, these authors conclude that the process of dolomitization of calcite above $275^\circ C$ must involve solutions in which the concentration of Ca^{+2} predominates over that of Mg^{+2} . Yanateva (1950, 1954) performed solubility studies of dolomite, calcite, and magnesite at $T = 0^\circ, 25^\circ, 55^\circ,$ and $70^\circ C$ and $P_{CO_2} = 1.2 \times 10^{-3}$ atm and also at 1 atm in the systems $CaCO_3 - MgCO_3 - H_2O$ and $Ca(HCO_3)_2 - Mg(HCO_3)_2 - CaSO_4 - MgSO_4$. From these experiments the above author concluded that the formation of dolomite could be represented by a reaction such as $2CaCO_{3(s)} + MgSO_{4(s)} \xrightarrow{H_2O} CaMg(CO_3)_2(d) + CaSO_{4(s)}$ at some stage in the metamorphosis of brines.

Even though the conditions for dolomite stability have not yet been clearly delineated, it is apparent from the above studies that some natural dolomite could have been formed at the temperatures and pressures on or

within the earth's crust by means of processes classified within the "wet" secondary category. Further justification for such a general process comes from Graf and Goldsmith (1956) who actually produced dolomite in the laboratory at $200^{\circ}\text{C} < T < 300^{\circ}\text{C}$ by reacting magnesium calcites and mixtures of aragonite and calcite with aqueous Mg^{+2} .

In the field, if one observes a deposit of dolomite with such characteristics as primary structures transected by dolomite rhombs, shadowy patterns of original clastic, bioclastic, or oolitic texture, structural control of dolomite distribution, calcite-dolomite boundaries that transgress bedding planes, and dolomitic fossils, then one can propose with some degree of confidence that the processes by which dolomite formed can be classified within the category of "wet" secondary origin. On the basis of such field evidence Faust and Callaghan (1948) proposed such an origin for dolomite in tuff beds of the Currant Creek magnesite deposits in Nevada. Krutsky (1959) described irregular layers of dolomite that followed the fracture system in limestone and proposed that Mg^{+2} in hot ascending aqueous solutions reacted with the calcite to produce dolomite. Curtis, Evans, Kinsman, and Shearman (1963) described recent sediments of the Persian Gulf in which calcite graded into dolomite within the first 15 cm of depth. These authors postulated an early diagenic replacement of calcite to yield dolomite.

The third category, "wet" primary origin, involves the direct precipitation of dolomite from an aqueous solution. Solubility studies of calcite, magnesite, and dolomite have been performed in order to ascertain the compositions of solutions from which dolomite should precipitate. Garrels,

Thompson, and Siever (1960) measured the pH of solutions saturated with respect to calcite, dolomite, huntite, magnesite, and hydromagnesite at 25°C. From these data these authors calculated the $\frac{A_{Ca}^{+2}}{A_{Mg}^{+2}}$ ratio in solutions saturated with respect to dolomite at various P_{CO_2} . Rosenberg and Holland (1964) determined the concentrations of solutions that were saturated with respect to dolomite by dissolving dolomite in solutions containing relatively large initial concentrations of Ca^{+2} and Mg^{+2} at 275°C to 420°C. Yanateva (1949) determined the concentrations of those solutions saturated with respect to dolomite by performing solubility experiments in the system $Ca^{+2}, Mg^{+2} \mid CO_3^{-2}, SO_4^{-2} - H_2O$ at 25°C and $P_{CO_2} = 1$ atm. Yanateva (1956), from solubility experiments of calcite, magnesite, and dolomite at $T = 0^\circ, 25^\circ, 55^\circ, \text{ and } 70^\circ C$ and $P_{CO_2} = 1$ atm and also 1.2×10^{-3} atm, concluded that the congruent or incongruent solubility of dolomite was a function of P_{CO_2} .

Numerous attempts to precipitate dolomite from such aqueous solutions as those described above have met with success only at $T \geq 150^\circ C$ and $P_{CO_2} > 1$ atm. Medlin (1959) precipitated dolomite from solutions of $MgCl_2$, $CaCl_2$, and urea at elevated P_{CO_2} and $150^\circ C \leq T < 250^\circ C$.

If one observes in the field that dolomite is associated with evaporites, that dolomite occurs as unfossiliferous thin laminations interbedded with thin laminations of calcite, then it would seem reasonable to suspect a "wet" primary origin for that dolomite. Sarin (1962) observed a cyclic repetition of limestone and dolomite lenses which were a few centimeters thick and postulated that the dolomite precipitated from an aqueous solution of high salinity. Graf, Eardley, and Shimp (1959) described thin

laminations of nearly pure and fossil-free unconsolidated dolomite located one foot below the surface of the Great Salt Lake Desert. They proposed that the dolomite precipitated from shallow evaporating waters isolated from the Great Salt Lake.

Major contributions for the justification of a "wet" primary origin for natural dolomite are the observations of Alderman (1958), Alderman and Skinner (1957), and Skinner, Skinner, and Rubin (1963). These authors reported that dolomite is presently being precipitated in shallow water lagoons of above normal salinity in South East Australia. Taft (1961) proposed a "wet" primary origin for euhedral dolomite crystals occurring in carbonate sediments now accumulating in shallow sea water along the southern coast of Florida.

Problem of Dolomite Genesis

Any conclusion regarding the origin of a natural deposit of dolomite should obviously be based on all available geologic evidence, i.e., field and laboratory data. As noted above, one can usually reach a conclusion on the basis of field data as to which one of the three general categories the origin of a specific deposit of dolomite belongs. If either the "wet" primary or secondary origin is selected, then there still remains a large, if not infinite, number of specific processes possible within either of the two general categories. A number of investigators have attempted to be more specific in their choice of a process by citing field evidence such as other minerals associated in time and place with dolomite. For example Strakhov (1958) postulated the precipitation of dolomite during the salinification of lake or lagoon waters with high CO₂ content. The resulting formation is

a distinctly bedded dolomite of normal composition exhibiting no or little calcite, traces of lamellar crystals of gypsum, and rare or absent organic remains. Curtis, Evans, Kinsman, and Shearman (1963) described a deposit of dolomite associated with aragonite, calcite, and anhydrite in recent sediments of the Persian Gulf. Due to the vertical distribution and mutual relationships of such minerals they proposed an early diagenetic replacement of calcite by the magnesium-rich pore liquids to produce dolomite.

The contributions which laboratory experiments can make to the solution of the problem of mineral genesis are (1) to limit the number of possible processes, (2) to verify as plausible a specific process chosen on the basis of field data, and (3) to point out additional field data which should be observed in order to substantiate the choice of a specific process. An example of the last is laboratory evidence which shows that intergrowths of calcite and dolomite in the field would substantiate exsolution of metastable magnesium-rich calcites to produce natural dolomite. An example of the second contribution is a report of Faust and Callaghan (1948), who hypothesized on the bases of field data specific process for origin of the dolomite associated with the Currant Creek magnesite deposits of Nevada. They state that ascending hydrothermal solutions obtained magnesium and bicarbonate ions in their passage through preexisting dolomitic rocks. Upon reaching porous calcitic tuff beds, $\text{CO}_2(\text{g})$ was evolved from solution and the aqueous Mg^{+2} replaced the Ca^{+2} in the calcite to produce dolomite. The above authors cited laboratory data in the literature delineating the $\text{Ca}^{+2}/\text{Mg}^{+2}$ ratio for which the reaction $2\text{CaCO}_3(\text{c}) + \text{Mg}^{+2} \rightarrow \text{CaMg}(\text{CO}_3)_2(\text{d}) + \text{Ca}^{+2}_{(\text{aq.})}$ is spontaneous to the right at $P = 1 \text{ atm}$ and $T = 25^\circ$ and 38.8°C .

Faust and Callaghan concluded that the above reaction will proceed spontaneously to the right with the $\text{Ca}^{+2}/\text{Mg}^{+2}$ ratio and pressure and temperature conditions which they proposed for the ascending solutions. Faust (1949) states that laboratory data in the literature support the thesis that dolomite exhibits both congruent and incongruent solubility, depending on the variables T , P_{CO_2} , and concentration of other ions in solution. Thus, the above authors concluded that there are two possible mechanisms for origin of the magnesium-rich hydrothermal solutions, which they postulated as being essential for the origin of the dolomite associated with the Currant Creek magnesite deposits. First, dolomite could dissolve congruently and calcite could precipitate later as the temperature was decreased to yield a magnesium-rich solution. Second, dolomite could dissolve incongruently to yield a magnesium-rich solution.

As noted above, laboratory data can also contribute to the solution of mineral genesis problems by limiting the number of possible processes. The following laboratory studies are examples of this contribution. Yanateva (1950) published results of carbonate mineral solubility studies in the systems $\text{CaCO}_3 - \text{MgCO}_3 - \text{H}_2\text{O}$ and $\text{Ca}^{+2}, \text{Mg}^{+2} \mid \text{CO}_3^{-2}, \text{SO}_4^{-2} - \text{H}_2\text{O}$. As previously noted, Garrels, Thompson, and Siever (1960) calculated the $A_{\text{Ca}^{+2}} / A_{\text{Mg}^{+2}}$ ratio of solutions saturated with respect to dolomite on the basis of equilibrium pH measurements. From such studies limits may be placed on the possible processes proposed for the origin of natural dolomite.

As stated and exemplified above, the investigator should rely on both field and laboratory evidence as a basis for proposing a plausible processes for the origin of a dolomite deposit. It is this author's opinion that such

laboratory data of paramount importance are (1) thermodynamic data and (2) kinetic data. The thermodynamic data are used to delineate the range of conditions for mineral stability, i.e., temperature, pressure, and bulk composition. Kinetic data lead to the determination of possible mechanisms for mineral genesis.

Discussion of Thesis Problem

An Approach to the Problem of Dolomite Genesis

The purpose of this thesis is twofold.

- 1) To report an experimental free energy of formation of huntite, which will add to the list of known thermodynamic data. and
- 2) To contribute to the understanding of the applicability of such thermodynamic data to complex chemical systems.

These two contributions should aid in the selection of plausible mechanisms for dolomite genesis.

As previously stated, there appears to be ample field evidence supporting each of the three general categories, namely, dissolution of solid phases, "wet" secondary origin, and "wet" primary origin. But there are insufficient laboratory data substantiating the above three categories, especially at low temperatures and pressures. For example, field data support the hypothesis that some dolomite has been formed at low temperatures and pressures, but no investigator has been able to produce dolomite in the laboratory at earth surface conditions of temperature and pressure. Also, there are contradictory statements in the literature concerning the solubility of dolomite at low

temperatures and pressures. Yanateva (1954) concluded that the type of solubility of dolomite, i.e., whether congruent or incongruent, is a function of P_{CO_2} . On the other hand Garrels, Thompson, and Siever (1960) contend their data indicate that the type of dolomite solubility is not a function of P_{CO_2} . For reasons such as these, this thesis will be restricted to determination of thermodynamic data at 25°C and $P_{\text{CO}_2} = 10^{-3}$ atm, which closely approximate that of earth surface conditions. This does not mean that the supporting laboratory data, thermodynamic or kinetic, are complete at the higher temperatures and pressures corresponding to hydrothermal conditions.

The problem of the thermodynamic stability of dolomite at earth surface conditions involves the following two questions.

- (1) Is dolomite a potentially stable phase at 25°C $P_{\text{CO}_2} = 10^{-3}$ atm, and $P_{\text{total}} = 1$ atm?
- (2) If so, for what bulk compositions is dolomite a stable phase?

The question of potential stability can be answered by referring either to the one-component system $\text{CaMg}(\text{CO}_3)_2$ or to thermodynamic data.

The question concerning bulk composition should be considered as follows. For any system, no matter how complex to contain bulk compositions for which dolomite is a stable phase, Ca, Mg, C, and O_2 must be present either as components or as constituents of components. If the "wet" primary or secondary origin is considered, then H_2 must also be present. The Ca-Mg oxides, hydroxides, and carbonates of interest in this study can be represented by bulk compositions within the $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ system, which is a subsystem of the relatively more complex five component system $\text{Ca-Mg-C-O}_2\text{-H}_2$. In this writer's opinion it is imperative that we first understand the $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ system,

before considering the stability of dolomite in the relatively more complex systems found in lakes, lagoons, sea-water, or hydrothermal solutions.

Potential Stability of Dolomite

The phase diagram for the one component system $\text{CaMg}(\text{CO}_3)_2$ has not been previously determined at 25°C and 1 atm total pressure. Therefore, it was necessary to refer to published thermodynamic data in order to ascertain whether or not dolomite is potentially stable at these conditions. The logic is as follows. If the reaction $\text{CaCO}_3(\text{c}) + \text{MgCO}_3(\text{m}) \xrightarrow[1 \text{ atm}]{25^\circ\text{C}} \text{CaMg}(\text{CO}_3)_2(\text{d})$ is spontaneous to the right and if the reactants are potentially stable at these conditions, then dolomite is a potentially stable phase at 25°C and 1 atm.

$$\begin{aligned} & \text{CaCO}_3(\text{c}) + \text{MgCO}_3(\text{m}) \xrightarrow[1 \text{ atm}]{25^\circ\text{C}} \text{CaMg}(\text{CO}_3)_2(\text{d}) \\ \Delta G_R &= \Delta G_{f,\text{Dolomite}}^\circ - \Delta G_{f,\text{Calcite}}^\circ - \Delta G_{f,\text{Magnesite}}^\circ \\ &= (-516600 \pm 500) - (-269908 \pm 300) - (-241920 \pm 550) \\ &= -4772 \pm 1400 \text{ cal.} \end{aligned}$$

$\text{CaCO}_3(\text{c})$ is a potentially stable phase at these conditions since it is the stable state for the one component system CaCO_3 (Figure 1). The potential stability of $\text{MgCO}_3(\text{m})$ must be determined from thermodynamic data. Since the reaction $\text{MgO}(\text{s})(1 \text{ atm}) + \text{CO}_2(\text{g})(10^{-3} \text{ atm}) \xrightarrow{25^\circ\text{C}} \text{MgCO}_3(\text{s})(1 \text{ atm})$ is spontaneous to the right and since the reactants are potentially stable at these conditions, $\text{MgCO}_3(\text{s})$ is potentially stable. (Table 1)

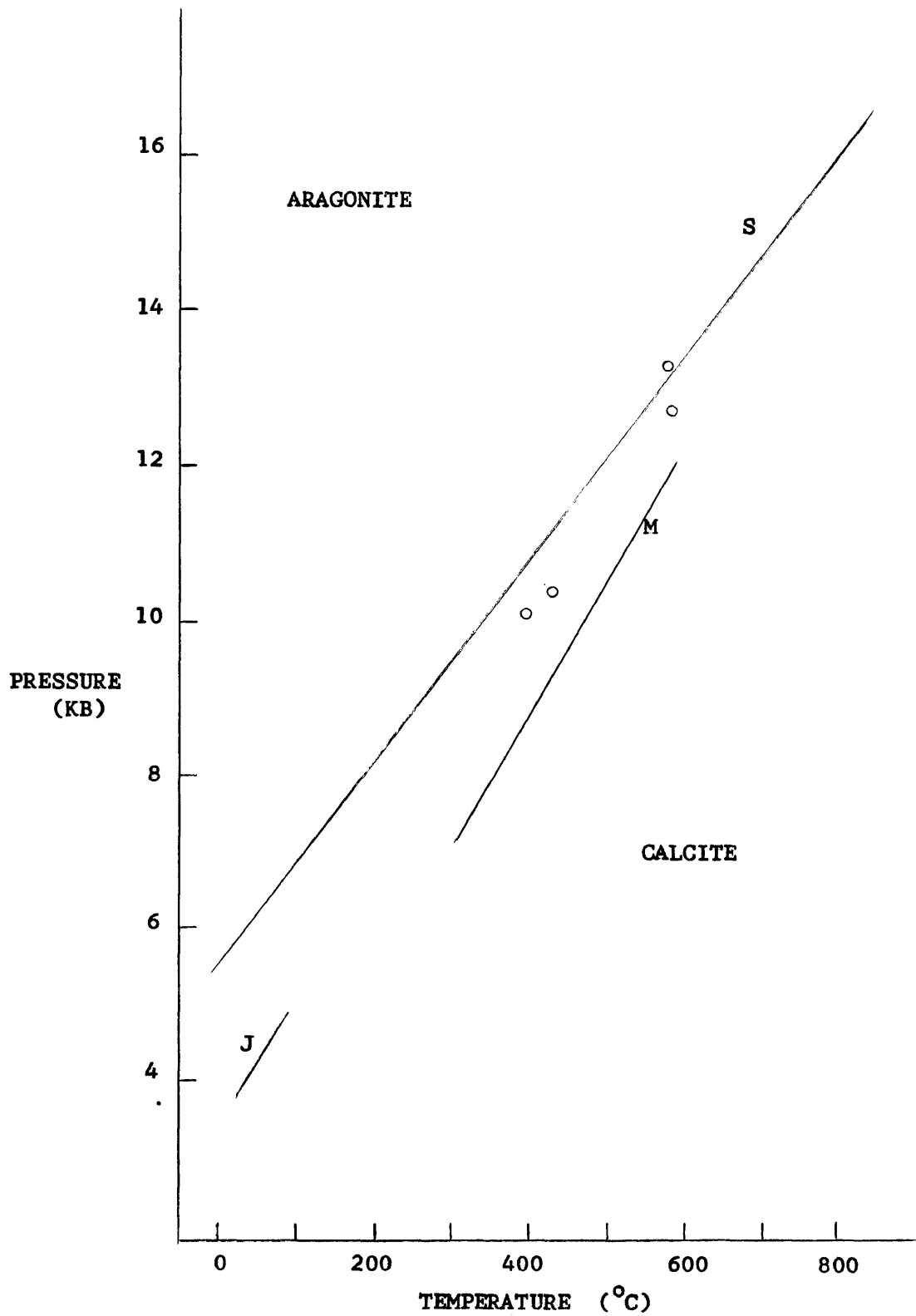
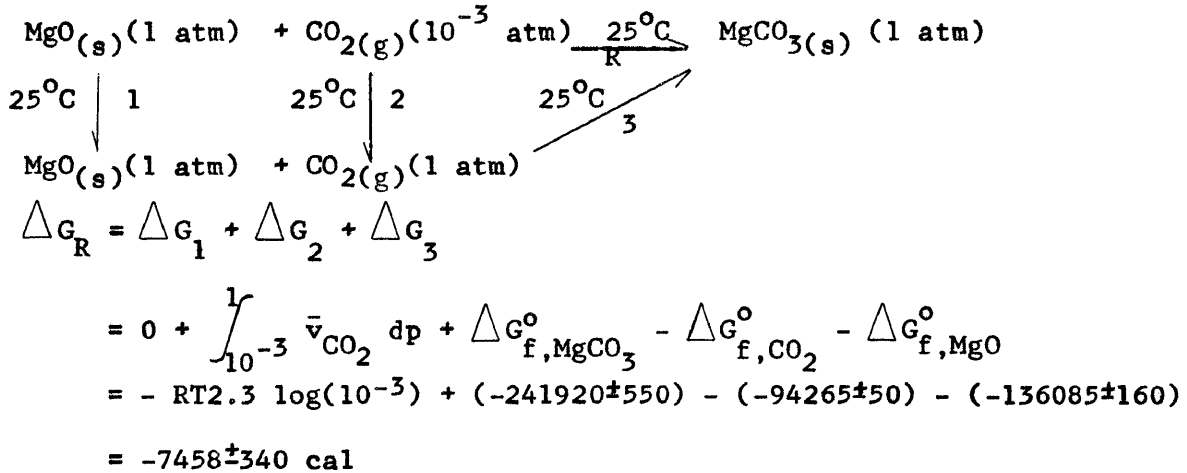


Figure 1. - CaCO₃ System: o - Clark (1957); J - Jamieson (1953);
M - MacDonald (1956); S - Simmons and Bell (1963).

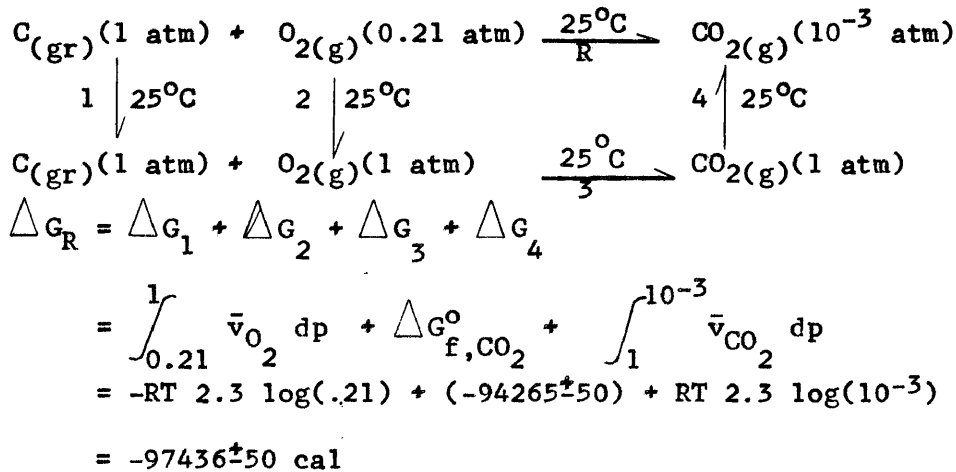
TABLE 1

Free Energy of Formation Data

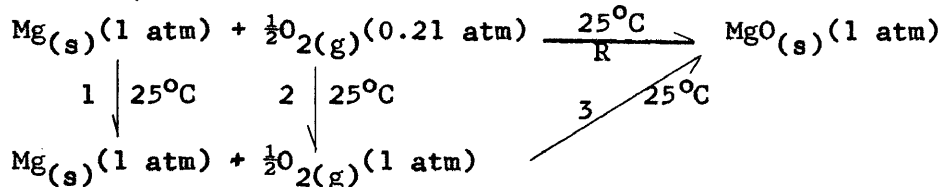
| <u>FORMULA</u> | $\Delta G_{f,25}^{\circ}$ (cal/mole) | <u>REFERENCE</u> |
|---|--------------------------------------|--------------------------------------|
| H ₂ O(l) | -56691 ± 15 | Langmuir (1964, 1965) |
| OH ⁻ (aq) | -37595 | Rossini (1952) |
| CO ₂ (g) | -94265 ± 50 | Langmuir (1964, 1965) |
| H ₂ CO ₃ (aq) | -148596 ± 55 | Harned and Davis (1943) |
| HCO ₃ ⁻ (aq) | -140290 ± 60 | Harned and Bonner (1945) |
| CO ₃ ⁻² (aq) | -126200 ± 70 | Harned and Scholes (1941) |
| Ca ⁺² (aq) | -132250 ± 350 | Langmuir (1964, 1965) |
| Mg ⁺² (aq) | -108760 ± 300 | Stephenson (1946) |
| CaO(s) | -144351 ± 350 | Langmuir (1965) |
| MgO(s) | -136085 ± 160 | Langmuir (1964, 1965) |
| Ca(OH) ₂ (s) | -214670 ± 500 | Langmuir (1965) |
| Mg(OH) ₂ (s) | -200021 ± 550 | Langmuir (1964, 1965) |
| CaCO ₃ (c) | -269908 ± 300 | Langmuir (1964) |
| MgCO ₃ (s) | -241920 ± 550 | Langmuir (1964, 1965) |
| MgCO ₃ ·3H ₂ O(s) | -412658 ± 500 | Langmuir (1964, 1965) |
| MgCO ₃ ·5H ₂ O(s) | -525851 ± 600 | Langmuir (1964, 1965) |
| 3MgCO ₃ ·Mg(OH) ₂ ·3H ₂ O(s) | -1100118 ± 2100 | Langmuir (1964, 1965) |
| MgCO ₃ ·Mg(OH) ₂ ·3H ₂ O(s) | -612483 ± 1100 | Langmuir (1964, 1965) |
| CaMg(CO ₃) ₂ (s) | -516600 ± 500 | Langmuir (1964) |
| CaMg ₃ (CO ₃) ₄ (s) | -1007000 | Garrels, Thompson, and Siever (1960) |



$\text{CO}_{2(g)}$ is potentially stable at 25°C and P_{O_2} equal to that in the atmosphere, (0.21 atm), since the ΔG of the following reaction is less than zero. (Table 1)



$\text{MgO}_{(s)}$ is potentially stable at 25°C and $P_{\text{O}_2} = 0.21 \text{ atm}$ since the ΔG of the following reaction is less than zero. (Table 1)

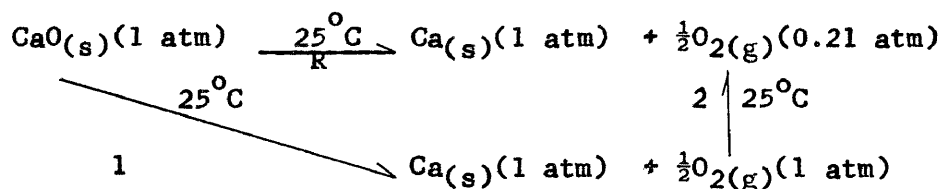


$$\begin{aligned}
 \Delta G_R &= \Delta G_1 + \Delta G_2 + \Delta G_3 \\
 &= \int_{0.21}^1 \frac{1}{2} \bar{v}_{O_2} dp + \Delta G_{f, MgO}^{\circ} \\
 &= \frac{1}{2} RT 2.3 \log(0.21) + (-136058 \pm 160) \\
 &= -135856 \pm 160 \text{ cal}
 \end{aligned}$$

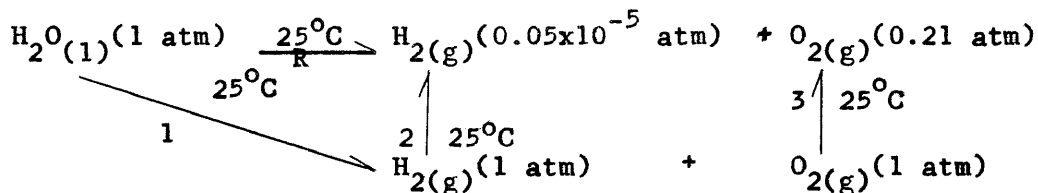
Therefore, since $\text{CaCO}_3(\text{c})$ and $\text{MgCO}_3(\text{m})$ are potentially stable phases at 25°C , $P_{\text{CO}_2} = 10^{-3}$ atm, and $P_{\text{total}} = 1$ atm, and since $\Delta G > 0$ for the reaction $\text{CaCO}_3(\text{c}) + \text{MgCO}_3(\text{m}) \xrightarrow[1 \text{ atm}]{25^\circ\text{C}} \text{CaMg}(\text{CO}_3)_2(\text{d})$, dolomite is a potentially stable phase at these conditions. Thus the first question concerning the thermodynamic stability of dolomite at earth surface conditions has been answered.

Potential Stability of Components

It was previously stated that the four-component system $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$, (not the relatively more complex five-component system $\text{Ca-Mg-C-O}_2\text{-H}_2$), was the fundamental system to consider for the purpose of this study. But this statement was made assuming that the chosen components are all potentially stable at earth surface conditions. In order to verify this, one can perform calculations similar to those used for ascertaining the potential stability of dolomite. As noted above, MgO and CO_2 were determined to be potentially stable at these conditions of temperature and pressure.



$$\begin{aligned}
 \Delta G_R &= \Delta G_1 + \Delta G_2 \\
 &= -\Delta G_{f, \text{CaO}}^\circ + \int_1^{0.21} \frac{1}{2} \bar{v}_{\text{O}_2} dp \\
 &= -(-144351 \pm 350) + \frac{1}{2} RT 2.3 \log (.21) \\
 &= +144149 \pm 350 \text{ cal}
 \end{aligned}$$



$$\begin{aligned}
 \Delta G_R &= \Delta G_1 + \Delta G_2 + \Delta G_3 \\
 &= -\Delta G_{f, \text{H}_2\text{O}}^\circ + \int_1^{.05 \times 10^{-5}} \bar{v}_{\text{H}_2} dp + \int_1^{0.21} \bar{v}_{\text{O}_2} dp \\
 &= -(-56691) + RT 2.3 \log (.05 \times 10^{-5}) + RT 2.3 \log (.21) \\
 &= +47647 \text{ cal}
 \end{aligned}$$

Even though $\text{H}_2\text{O}(1)$ does not spontaneously decompose into the elements, it is not necessarily a potentially stable phase. If the $P_{\text{H}_2\text{O}}$ in the atmosphere $< P_{\text{H}_2\text{O}}(\text{eq.})$ at 25°C , the system can further lower its free energy by the process $\text{H}_2\text{O}(1) \xrightarrow{25^\circ\text{C}} \text{H}_2\text{O}(\text{g})$. But since "wet" origins of dolomite are to be considered, it will be assumed that $P_{\text{H}_2\text{O}} \geq P_{\text{H}_2\text{O}}(\text{eq.})$ at 25°C . Since $\text{CaO}(\text{s})$, $\text{MgO}(\text{s})$, $\text{H}_2\text{O}(1)$ and $\text{CO}_2(\text{g})$ do not spontaneously decompose into the elements, and since $\text{H}_2\text{O}(1)$ does not undergo a phase change, then each is potentially stable at 25°C , $P_{\text{total}} = 1 \text{ atm}$, $P_{\text{CO}_2} = 10^{-3} \text{ atm}$, $P_{\text{H}_2} = 0.05 \times 10^{-5} \text{ atm}$, and $P_{\text{O}_2} = 0.21 \text{ atm}$.

Evaluation of Literature Data for CaO-MgO-CO₂-H₂O System

The above serves to illustrate that $\text{CaMg}(\text{CO}_3)_2(\text{d})$, $\text{CaO}(\text{s})$, $\text{CO}_2(\text{g})$, and

H_2O (l) are potentially stable phases at 25°C , $P_{\text{CO}_2} = 10^{-3}$ atm, $P_{\text{H}_2} = .05 \times 10^{-5}$, $P_{\text{O}_2} = 0.21$ atm, and $P_{\text{total}} = 1$ atm. The question remaining unanswered concerns the stability of dolomite, i.e., what are the bulk compositions in the $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ system for which dolomite is a stable phase at the above conditions? The approach taken in this study will be to determine the stable states for the four three-component systems involved.

Various investigators have attempted to determine the potential stability of compounds in the above ternary systems from crystallization and solubility experiments. As it is possible that due to the rate of reaction a metastable phase could be obtained, the results of such experiments must be checked whenever possible by reference to appropriate one-component systems or by recourse to thermodynamic data. If a compound is experimentally obtained at a specific temperature and pressure and if it is the only solid phase within the system, its potential stability need not be checked by thermodynamic data. Thus, the potential stability needs to be verified only for those compounds which are in systems containing more than one solid phase.

CaO-CO₂-H₂O System. Baron and Favre (1958) studied the $\text{CaO-CO}_2\text{-H}_2\text{O}$ system and reported $\text{CaCO}_3(\text{c})$ and $\text{Ca(OH)}_2(\text{s})$ as the only compounds obtained by crystallization experiments at $P_{\text{CO}_2} = 10^{-3}$ atm and 25°C . Kindyakov, Khodhlova, and Lapchinskaya (1958) studied the $\text{CaCO}_3\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system at 25°C and reported no solid solutions or binary salts. Yanateva and Rossonskaya (1961) and Miller (1952) determined the composition of the aqueous solution saturated with respect to $\text{CaCO}_3(\text{c})$ at 25°C and $P_{\text{CO}_2} = 10^{-3}$ atm. This

indicates that calcite might be a potentially stable phase in the CaO-CO₂-H₂O system at these conditions. Hume (1925) reported the existence of CaCO₃·6H₂O and CaCO₃·5H₂O in aqueous solutions of 20% sucrose at temperatures less than 10.4°C and greater than 17.0°C, respectively. Mackenzie (1923) reported the dehydration of CaCO₃·6H₂O at 5°C and above. Tschirivinsky (1907) reported the existence of CaCO₃·3H₂O and CaCO₃·5H₂O in nature and CaCO₃·6H₂O in the laboratory. Baron and Favre (1958) proposed a phase diagram for CaCO₃-H₂O in which the stable carbonate at 25°C and P_{CO₂} = 10⁻³ atm is anhydrous CaCO_{3(c)}. Based on the above it is assumed in this study that the possible potentially stable solid phases are CaCO_{3(c)} and Ca(OH)_{2(s)}.

Since Ca(OH)_{2(s)} is the only compound reported for the CaO-H₂O binary, its potential stability is verified without recourse to thermodynamic data. CaCO_{3(c)}, as noted above, is the stable state for the one component system CaCO₃ at 25°C, P_{CO₂} = 10⁻³ atm, and P_{total} = 1 atm.

Since CaCO_{3(c)} and Ca(OH)₂ are potentially stable phases, one must now consider the solutions saturated with respect to these compounds.

Garrels (1960) calculated the concentration of the solution saturated with respect to CaCO_{3(c)} and reported that the calculated values showed "excellent agreement" with the experimental values. The bulk composition of this solution saturated with respect to CaCO_{3(c)} at P_{CO₂} = 10⁻³ atm is 2.24x10⁻³ weight percent CaO and 4.4x10⁻³ weight percent CO₂.

Haslam, Calengaret, and Taylor (1924) determined the solubility of Ca(OH)₂ in H₂O_(l) to be 0.173 weight percent and 0.134 weight percent at 10°C and 42°C, respectively, from which the value of 0.156 weight percent at 25°C is interpolated.

This author can find no reference in the literature concerning the solubility of $\text{CO}_2(\text{g})$ in $\text{H}_2\text{O}(\text{l})$ at 25°C and $P_{\text{CO}_2} = 10^{-3}$ atm. But, if it is initially assumed that the activity coefficients of the dissolved constituents are one, the solubility of $\text{CO}_2(\text{g})$ in $\text{H}_2\text{O}(\text{l})$ can be calculated on the basis of the reported equilibrium constants for the appropriate equilibria.

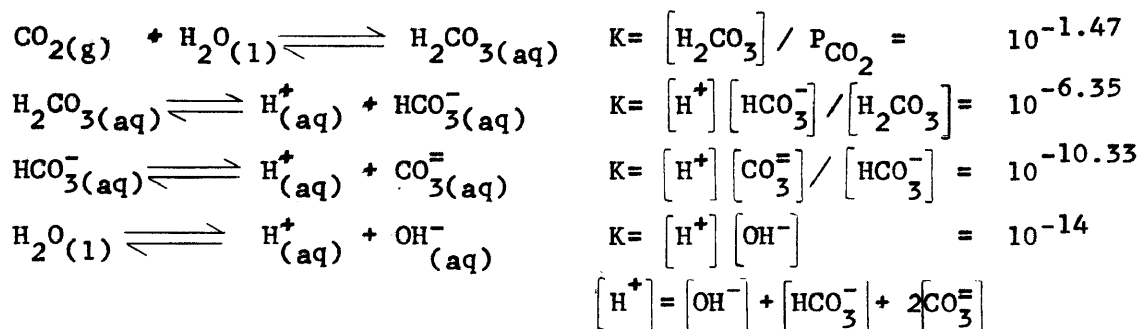
(Table 2)

TABLE 2

Equilibrium Constants Calculated from Free Energy Data

| EQUILIBRIA | K |
|--|---------------|
| $\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{+2}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})}$ | $10^{-11.5}$ |
| $\text{Ca}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Ca}^{+2}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})}$ | $10^{-5.33}$ |
| $\text{CaCO}_3(\text{c}) \rightleftharpoons \text{Ca}^{+2}_{(\text{aq})} + \text{CO}_3^{-2}_{(\text{aq})}$ | $10^{-8.43}$ |
| $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{Mg}^{+2}_{(\text{aq})} + \text{CO}_3^{-2}_{(\text{aq})} + 3\text{H}_2\text{O}(\text{l})$ | $10^{-5.62}$ |
| $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$ | $10^{-1.47}$ |
| $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^{+}_{(\text{aq})} + \text{HCO}_3^{-}_{(\text{aq})}$ | $10^{-6.37}$ |
| $\text{HCO}_3^{-}_{(\text{aq})} \rightleftharpoons \text{H}^{+}_{(\text{aq})} + \text{CO}_3^{-2}_{(\text{aq})}$ | $10^{-10.38}$ |

The calculations are as follows.



If the above equations are solved simultaneously, then

$[H^+] = 10^{-5.41}$ M, $[H_2CO_3] = 10^{-4.47}$ M, $[HCO_3^-] = 10^{-4.81}$ M, $[CO_3^{2-}] = 10^{-9.75}$ M, and $[OH^-] = 10^{-8.59}$ M. The ionic strength of this solution can now be determined.

$$\mu = \frac{1}{2} [H^+] (1)^2 + \frac{1}{2} [OH^-] (1)^2 + \frac{1}{2} [HCO_3^-] (1)^2 + \frac{1}{2} [CO_3^{2-}] (2)^2 = 21.2 \times 10^{-6}$$

At this ionic strength the activity coefficients of the dissolved constituents can be calculated using the Debye-Huckel equation.

$$\log \gamma_i = \frac{-A (Z_i)^2 (\mu)^{\frac{1}{2}}}{1 + (a^{\circ}) (B) (\mu)^{\frac{1}{2}}}$$

The value of A and B in aqueous solutions at 25°C are reported by Manov, Bates, Hamer and Acree (1943) as 0.5085 and 0.3281×10^8 respectively. As noted by Klotz (1950) the values of a° for H^+ , CO_3^{2-} , HCO_3^- , and OH^- are 9×10^{-8} , 4.5×10^{-8} , 4×10^{-8} , and 3.5×10^{-8} , respectively. The values of the activity coefficients as determined by the above method are as follow. $\gamma_H = 0.999$, $\gamma_{HCO_3^-} = 0.999$, $\gamma_{CO_3^{2-}} = 0.984$, $\gamma_{OH^-} = 0.984$. It is evident that the error in assuming activity coefficients equal to one is negligible.

The solubility of $CO_2(g)$ in $H_2O(l)$ can now be determined on the basis of the concentrations calculated above.

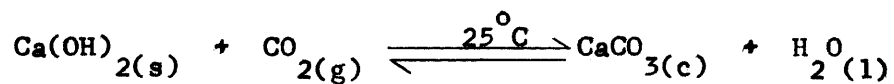
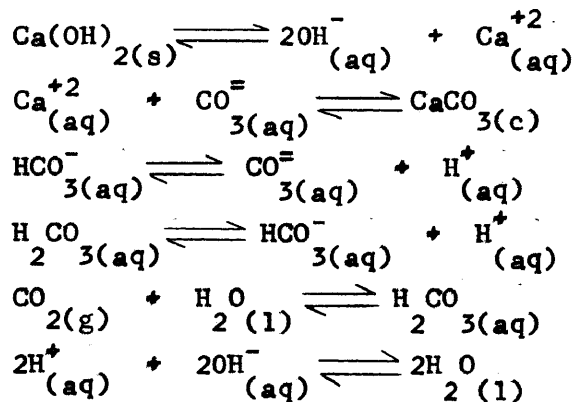
$$[CO_2]_{(aq) \text{ total}} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = 4.95 \times 10^{-5} \text{ M}$$

This concentration of CO_2 can be expressed as 2.18×10^{-4} weight percent CO_2 .

Ellis (1959) reported the equilibrium constant for the process

$CO_{2(aq)} \rightleftharpoons CO_{2(g)}$ as a function of temperature, e.g., $K = P_{CO_2} / X_{CO_2}$ 1.7×10^3 at 25°C. At $P_{CO_2} = 10^{-3}$ atm the approximate weight percent of $CO_{2(aq)}$ is calculated to be 1.44×10^{-4} , which agrees with that calculated above.

Before determining the composition of the solution saturated with respect to $\text{CaCO}_3(\text{c})$ and Ca(OH)_2 , it will be necessary to determine whether or not $\text{CO}_2(\text{g})$ at $P_{\text{CO}_2} = 10^{-3}$ atm will exist in equilibrium with the solution saturated simultaneously with respect to $\text{CaCO}_3(\text{c})$ and $\text{Ca(OH)}_2(\text{s})$ at 25°C . (Table 1)



$$\Delta G_R^{\circ} = -RT \ln(1/P_{CO_2})$$

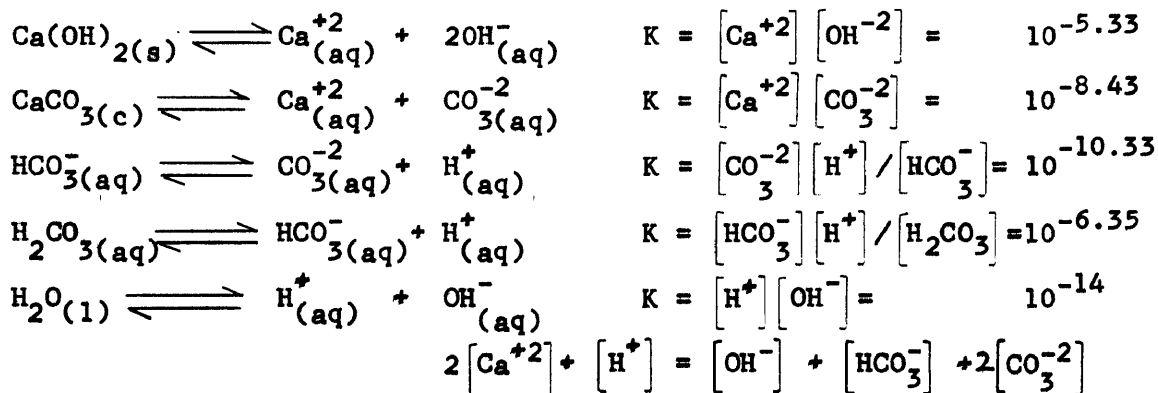
$$\begin{aligned} \Delta G_R^{\circ} &= \Delta G_f^{\circ}, H_2O + \Delta G_f^{\circ}, CaCO_3 - \Delta G_f^{\circ}, CO_2 - \Delta G_f^{\circ}, Ca(OH)_2 \\ &= (-56691 \pm 15) + (-269908 \pm 300) - (-94265 \pm 10) - (-214670 \pm 500) \end{aligned}$$

$$\log P_{CO_2} = (-17664 \pm 825) / RT \cdot 2.3$$

$$P_{CO_2} = 10^{-12.94 \pm .6}$$

If there is any CO_2 in the gas phase within the $CaO-H_2O-CO_2$ system, the $P_{CO_2} = 10^{-3}$ atm. Thus, since 10^{-3} atm $>$ $P_{(eq.)CO_2} = 10^{-12.9}$ atm, there will be no $CO_2(g)$ above the solution saturated with respect to $CaCO_3(c)$ and $Ca(OH)_2(s)$. This situation may be realized as a liquid solution with a piston, which is impervious to CO_2 and equivalent to 10^{-3} atm, sitting on the liquid surface.

No data in the literature could be found pertaining to the composition of the aqueous solution saturated simultaneously with respect to $Ca(OH)_2$ and $CaCO_3(c)$, but the composition of this solution can be calculated if it is initially assumed that the activity coefficients of the ions in solution are unity.



If the above equations are solved simultaneously, one sees that

$$\begin{aligned} [Ca^{+2}] &= 10^{-1.98} \text{ M}, [CO_3^{-2}] = 10^{-6.45} \text{ M}, [OH^{-}] = 10^{-1.68} \text{ M}, \\ [HCO_3^{-}] &= 10^{-8.43} \text{ M}, [H_2CO_3] = 10^{-18.76} \text{ M}, \text{ and } [H^{+}] = 10^{-12.32} \text{ M}, \end{aligned}$$

The ionic strength of this solution can now be determined.

$$\mu = \frac{1}{2}[\text{Ca}^{+2}](2)^2 + \frac{1}{2}[\text{H}^+] + \frac{1}{2}[\text{OH}^-] + \frac{1}{2}[\text{CO}_3^{-2}](2)^2 + \frac{1}{2}[\text{HCO}_3^-] = 3.39 \times 10^{-2}$$

Using this value for the ionic strength and σ_a for Ca^{+2} equal to 6×10^{-8}

(Klotz, 1950), the Debye-Huckel equation results in the following activity coefficients: $\gamma_{\text{Ca}^{+2}} = 0.532$, $\gamma_{\text{H}^+} = 0.874$, $\gamma_{\text{OH}^-} = 0.840$, $\gamma_{\text{CO}_3^{-2}} = 0.508$, and $\gamma_{\text{HCO}_3^-} = 0.844$.

Since the activity coefficients for Ca^{+2} and CO_3^{-2} are significantly different from the assumed value of one, a series of successive approximations are made. If it is initially assumed that $\gamma_{\text{Ca}^{+2}} = \gamma_{\text{CO}_3^{-2}} = 0.5$ and $\gamma_{\text{OH}^-} = \gamma_{\text{H}^+} = \gamma_{\text{HCO}_3^-} = 0.9$, the following concentrations are calculated. $[\text{Ca}^{+2}] = 10^{-2.09}$ M, $[\text{CO}_3^{-2}] = 10^{-6.75}$ M, $[\text{OH}^-] = 10^{-1.80}$ M, $[\text{HCO}_3^-] = 10^{-7.51}$ M, $[\text{H}_2\text{CO}_3] = 10^{-17.25}$ M, and $[\text{H}^+] = 10^{-12.29}$ M. The ionic strength of this solution is 2.43×10^{-2} . Based on this ionic strength, the following activity coefficients are calculated by the Debye-Huckel equation.

$\gamma_{\text{Ca}^{+2}} = 0.572$, $\gamma_{\text{H}^+} = 0.885$, $\gamma_{\text{OH}^-} = 0.859$, $\gamma_{\text{CO}_3^{-2}} = 0.553$, and $\gamma_{\text{HCO}_3^-} = 0.854$. Since these values do not differ significantly from those assumed, the error in the calculated concentrations is negligible. Thus the calculations determining the composition of the solution which is saturated simultaneously with respect to $\text{Ca}(\text{OH})_2$ and $\text{CaCO}_3(\text{c})$ will be based on the concentrations determined from the assumption that $\gamma_{\text{Ca}^{+2}} = \gamma_{\text{CO}_3^{-2}} = 0.5$ and $\gamma_{\text{H}^+} = \gamma_{\text{OH}^-} = \gamma_{\text{HCO}_3^-} = 0.9$. The result of such a calculation gives a weight percent CaO of 0.0456 and a weight percent CO_2 of 8.34×10^{-7} .

From the above information the phase diagram for the $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ system at these conditions can be constructed (Figure 2).

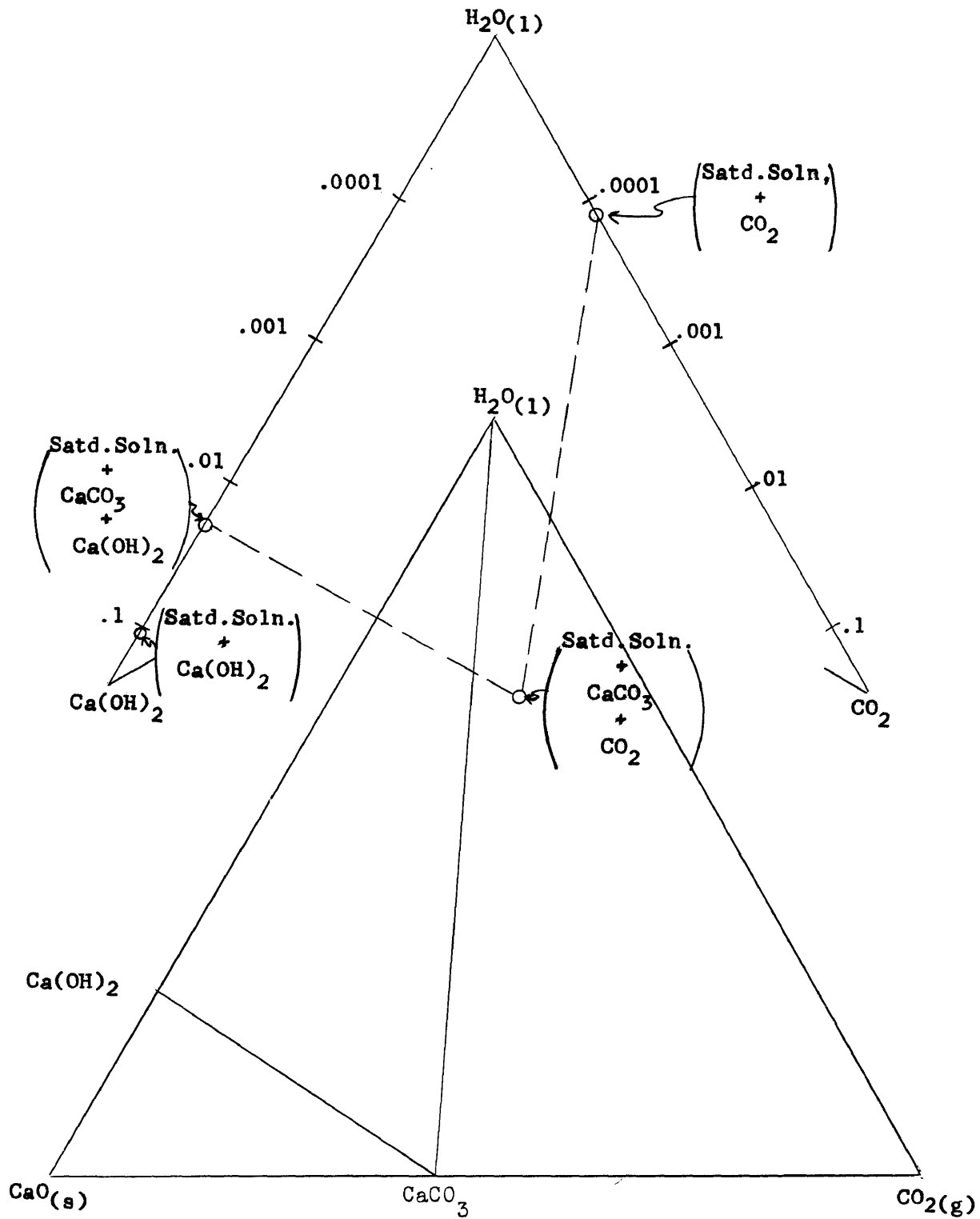


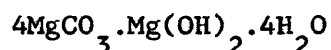
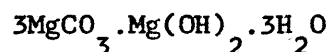
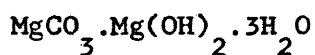
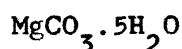
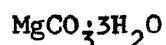
Figure 2. - $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ System (25°C , $P_{\text{total}} = 1 \text{ atm}$, $P_{\text{CO}_2} = 10^{-3} \text{ atm}$)

MgO-CO₂-H₂O System. Leitner (1910) reported the existence of the following six hydrates of magnesium carbonate: MgCO₃.3H₂O, MgCO₃.4H₂O, MgCO₃.5H₂O, MgCO₃.Mg(OH)₂.3H₂O, 3MgCO₃.Mg(OH)₂.3H₂O, and 3MgCO₃.Mg(OH)₂.21H₂O. The existence of all but two of these compounds, MgCO₃.4H₂O and 3MgCO₃.Mg(OH)₂.21H₂O, has been verified by other authors. Levi (1925) identified 3MgCO₃.Mg(OH)₂.3H₂O as a product that formed on the walls of tanks containing boiling aqueous solutions of magnesium carbonate. Halla (1962) reported the solubility product constants for MgCO₃.5H₂O and MgCO₃.3H₂O. Yanateva, Rapport, Rossonskaya, and Ustinova (1961) reported that within the CaCO₃-MgCO₃-H₂O system the coexistent solid phases at 14^o C, 14-55^o C, and above 55^o C are MgCO₃.5H₂O and CaCO_{3(c)}, MgCO₃.3H₂O and CaCO_{3(c)}, and 4MgCO₃.Mg(OH)₂.4H₂O and CaCO_{3(c)}, respectively. Pashak (1960) obtained a patent for the use of MgCO₃.Mg(OH)₂.3H₂O as a source of Mg for production of light metals. Nishimura (1928) reported the reaction of MgCO₃.3H₂O and Mg(OH)₂ with H₂O_(l) to yield 4MgCO₃.Mg(OH)₂.4H₂O and 3MgCO₃.Mg(OH)₂.3H₂O, respectively. Terada (1928) investigated the solubility of magnesium carbonate in aqueous solutions saturated with respect to CO_{2(g)}. The above author's solubility data indicate a transition between MgCO₃.5H₂O and MgCO₃.3H₂O at 13.5^o C. Baron and Favre (1958) investigated the MgO-CO₂-H₂O system and reported MgCO₃ and MgCO₃.3H₂O as the compounds obtained by crystallization experiments at 25^o C and P_{CO₂} = 10⁻³ atm. These authors also reported the presence of 4MgCO₃.Mg(OH)₂.4H₂O at T > 70^o C. Faust (1949) determined the concentration of the solution saturated with respect to MgCO₃.3H₂O at 25^o C and P_{CO₂} = 10⁻³ atm, which indicates the potential stability of the tri-hydrate. Garrels, Thompson, and Siever (1960) determined the solubility product of 3MgCO₃.Mg(OH)₂.3H₂O and calculated the

$a_{Ca} + 2/a_{Mg} + 2$ ratio of solutions saturated with respect to this compound at various $P_{CO_2} \leq 10^{-8}$ atm.

Therefore, the existence of five of the seven ternary compounds reported for the $MgO-CO_2-H_2O$ system have been verified by more than one investigator. For the purpose of this study, these five compounds, listed below, will be considered as possible potential stable phases at $25^\circ C$,

$P_{total} = 1$ atm, $P_{H_2O} > P_{H_2O}(eq)$ and $P_{CO_2} = 10^{-3}$ atm.



Since $Mg(OH)_2$ and $MgCO_{3(s)}$ are the only compounds reported for their respective binaries, the potential stability of these compounds is verified without recourse to thermodynamic data.

As seen above, the experimental evidence indicates that $MgCO_3 \cdot 3H_2O$, not $MgCO_3 \cdot 5H_2O$, is the potentially stable hydrate at $25^\circ C$, $P_{total} = 1$ atm, and $P_{CO_2} = 10^{-3}$ atm. If this is the case, then $MgCO_3 \cdot 3H_2O$ can not decompose into the potentially stable phases $MgCO_3$ and $H_2O(1)$. (Table 1)

$$MgCO_3 \cdot 3H_2O(s) \xrightarrow[1 \text{ atm}]{25^\circ C} MgCO_3(s) + 3H_2O(1)$$

$$\Delta G_R^0 = 3 \Delta G_{f, MgCO_3}^0 - \Delta G_{f, MgCO_3 \cdot 3H_2O}^0$$

$$= 3(56691 \pm 15) + (-241920 \pm 550) - (-412658 \pm 500) = +665 \pm 1095 \text{ cal.}$$

If $MgCO_3 \cdot 5H_2O$ is not a potentially stable phase at these conditions, then $MgCO_3 \cdot 5H_2O$ will decompose into the potentially stable phases $MgCO_3$ and $H_2O(1)$.

$$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}(\text{s}) \xrightarrow[1 \text{ atm}]{25^\circ\text{C}} \text{MgCO}_3(\text{s}) + 5\text{H}_2\text{O}(\text{l})$$

$$\Delta G_R^\circ = \Delta G_{f, \text{MgCO}_3}^\circ + 5 \Delta G_{f, \text{H}_2\text{O}}^\circ - \Delta G_{f, \text{MgCO}_3 \cdot 5\text{H}_2\text{O}}^\circ$$

$$= (-241920 \pm 550) + 5(-56691 \pm 15) - (-525851 \pm 600) = -9524 \pm 1225 \text{ cal}$$

It is apparent from the above calculations that $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ is not potentially stable at these conditions and that the available free energy data are not of sufficient precision to come to a conclusion concerning the potential stability of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. But, based on the experimental data noted above of Terada (1928), Baron and Favre (1958), Faust (1949), and Yanateva, Rapoport, Rossonskaya and Ustinova (1961), it will be assumed in this study that $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is potentially stable at 25°C , $P_{\text{total}} = 1 \text{ atm}$, and $P_{\text{H}_2\text{O}} > P_{\text{H}_2\text{O}(\text{eq.})}$.

If $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ is not potentially stable at 25°C and $P_{\text{total}} = 1 \text{ atm}$, then it will decompose into the potentially stable phases $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$.

$$\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O} \xrightarrow[1 \text{ atm}]{25^\circ\text{C}} \text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s}) + \text{Mg}(\text{OH})_2(\text{s})$$

$$\Delta G_R^\circ = \Delta G_{f, \text{MgCO}_3 \cdot 3\text{H}_2\text{O}}^\circ + \Delta G_{f, \text{Mg}(\text{OH})_2}^\circ - \Delta G_{f, \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}}^\circ$$

$$= (-412658 \pm 500) + (-200021 \pm 550) - (-612483 \pm 1100) = -196 \pm 2150 \text{ cal}$$

Since it is not possible to make a decision on the basis of the above calculations, it will be assumed that the results of the solubility and crystallization experiments are valid, i.e., $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}(\text{s})$ is not potentially stable at 25°C and $P_{\text{total}} = 1 \text{ atm}$.

The results of the experiments reviewed above are contradictory as to whether or not $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}(\text{s})$ is potentially stable at these conditions. Since free energy data are available, it may be possible to determine

if the compound will spontaneously decompose at these conditions.

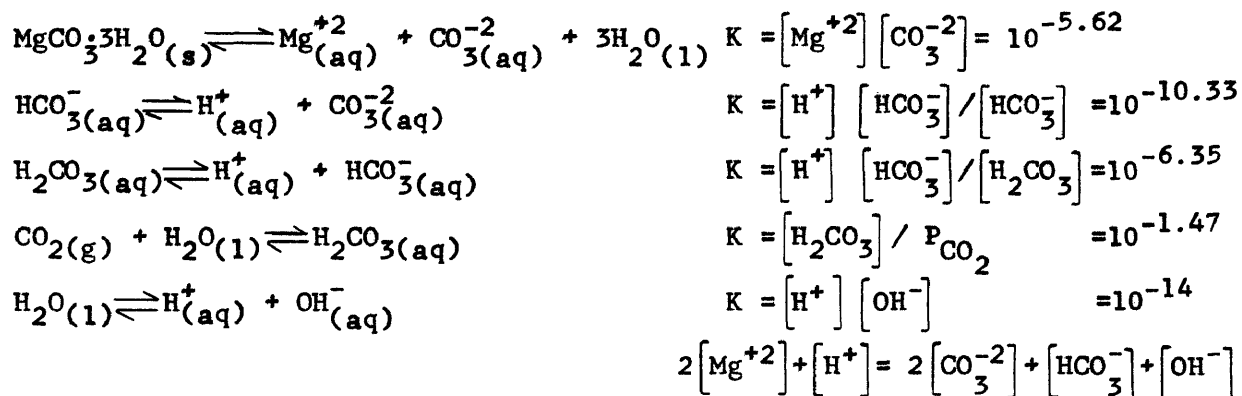
$$\begin{aligned}
 & 3\text{MgCO}_3 \cdot \text{Mg}(\text{OH}) \cdot 3\text{H}_2\text{O}(\text{s}) \xrightarrow[1 \text{ atm}]{25^\circ\text{C}} \text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s}) + \text{Mg}(\text{OH})_2(\text{s}) + 2\text{MgCO}_3(\text{s}) \\
 \Delta G_R^\circ &= \Delta G_f^\circ, \text{MgCO}_3 \cdot 3\text{H}_2\text{O} + \Delta G_f^\circ, \text{Mg}(\text{OH})_2 + 2 \Delta G_f^\circ, 3\text{MgCO}_3 \cdot \text{Mg}(\text{OH}) \cdot 3\text{H}_2\text{O} \\
 &= (-412658 \pm 500) + (-200021 \pm 550) + 2(-241920 \pm 550) - (-1100118 \pm 2100) \\
 &= + 3599 \pm 4250 \text{ cal.}
 \end{aligned}$$

Since the free energy data are not sufficiently precise to come to a conclusion and with no clear indication from other experiments, it will be assumed in this study that the compound is not potentially stable at 25°C and $P_{\text{total}} = 1 \text{ atm}$.

Since there are no free energy data available in the literature for $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, the experimental results of Baron and Favre (1958) will be assumed valid, i.e., this compound is not potentially stable at $T < 70^\circ\text{C}$ and $P_{\text{total}} = 1 \text{ atm}$.

Therefore, only three of the nine compounds that have been reported for the $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$ system will be considered in this study as potentially stable phases at 25°C , $P_{\text{total}} = 1 \text{ atm}$, $P_{\text{H}_2\text{O}} > P_{\text{H}_2\text{O}}(\text{eq.})$, and $P_{\text{CO}_2} = 10^{-3} \text{ atm}$. These compounds are $\text{Mg}(\text{OH})_2(\text{s})$, $\text{MgCO}_3(\text{s})$, and $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s})$.

The bulk composition of the solution saturated with respect to $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ can be determined by the following calculation. If it is initially assumed that the activity coefficients of the ions in solution are one, then the following expressions for the equilibrium constants are valid.



If the above equations are solved simultaneously, then

$[\text{Mg}^{+2}] = 10^{-2.24}$ M, $[\text{H}^{+}] = 10^{-8.89}$ M, $[\text{CO}_3^{-2}] = 10^{-3.38}$ M, $[\text{HCO}_3^{-}] = 10^{-1.94}$ M, $[\text{OH}^{-}] = 10^{-5.11}$ M, and $[\text{H}_2\text{CO}_3] = 10^{-4.47}$ M. The ionic strength of this solution can now be calculated.

$$I = \frac{1}{2} [\text{Mg}^{+2}] (2)^2 + \frac{1}{2} [\text{H}^{+}] + \frac{1}{2} [\text{CO}_3^{-2}] (2)^2 + \frac{1}{2} [\text{HCO}_3^{-}] + \frac{1}{2} [\text{OH}^{-}] = 1.8 \times 10^{-2}.$$

The activity coefficients of the ions can be calculated by Debye Huckel equation using this value for the ionic strength and a° for Mg^{+2} equal to 8×10^{-8} as reported by Klotz (1950) $\gamma_{\text{Mg}^{+2}} = 0.630$, $\gamma_{\text{H}^{+}} = 0.897$, $\gamma_{\text{CO}_3^{-2}} = 0.593$, $\gamma_{\text{HCO}_3^{-}} = 0.876$, and $\gamma_{\text{OH}^{-}} = 0.876$.

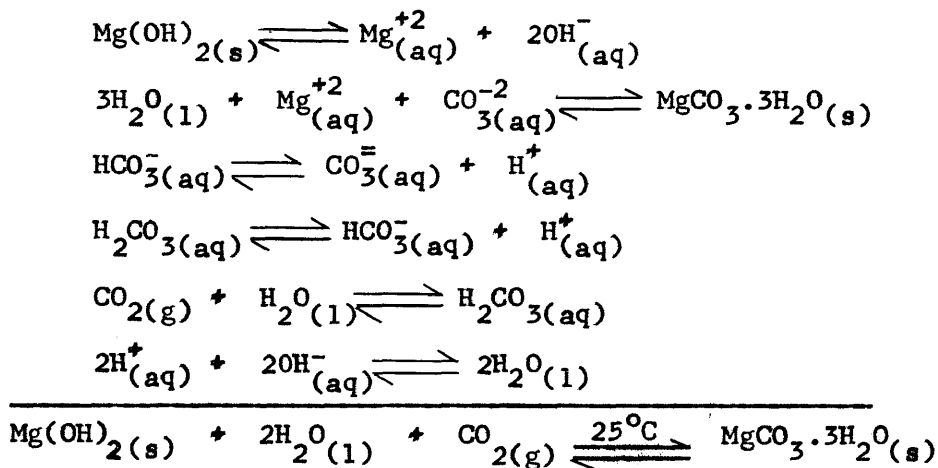
Since these activity coefficients differ significantly from one, a series of successive approximations is employed in order to determine activity coefficients that do not differ significantly from those assumed. Such approximations, similar to those used to calculate the concentration of the solution saturated with respect to $\text{Ca}(\text{OH})_2(\text{s})$ and $\text{CaCO}_3(\text{c})$, yield the following result. The bulk composition of the solution which is saturated with respect to $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is 0.0293 weight percent MgO and 0.0678 weight percent CO_2 .

It should be noted that the calculated $[\text{Mg}^{+2}]$ does differ significantly from the solubility of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ as reported by Kline (1929), i.e., $.07 \times 10^{-3}$

weight percent MgO at 25°C and $P_{\text{CO}_2} = 10^{-3}$ atm, but agrees with that reported in the Handbook of Chemistry and Physics (1965), i.e., .0377 weight percent CaO at 25°C.

The bulk composition of the solution saturated with respect to $\text{Mg}(\text{OH})_2(\text{s})$ at 25°C and $P_{\text{total}} = 1$ atm is 7×10^{-4} weight percent MgO. This value is calculated from the solubility value of 0.0099 g $\text{Mg}(\text{OH})_2$ per liter of solution as reported by Travers (1929).

Before the composition of the solution saturated simultaneously with respect to $\text{Mg}(\text{OH})_2$ and $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is determined, the following will be considered. The question as to whether or not $\text{CO}_2(\text{g})$ at 10^{-3} atm will exist in equilibrium with the solution saturated with respect to $\text{Mg}(\text{OH})_2(\text{s})$ and $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ can be answered on the basis of the following calculation.



$$\Delta G_R^\circ = -RT \ln 1/P_{\text{CO}_2}$$

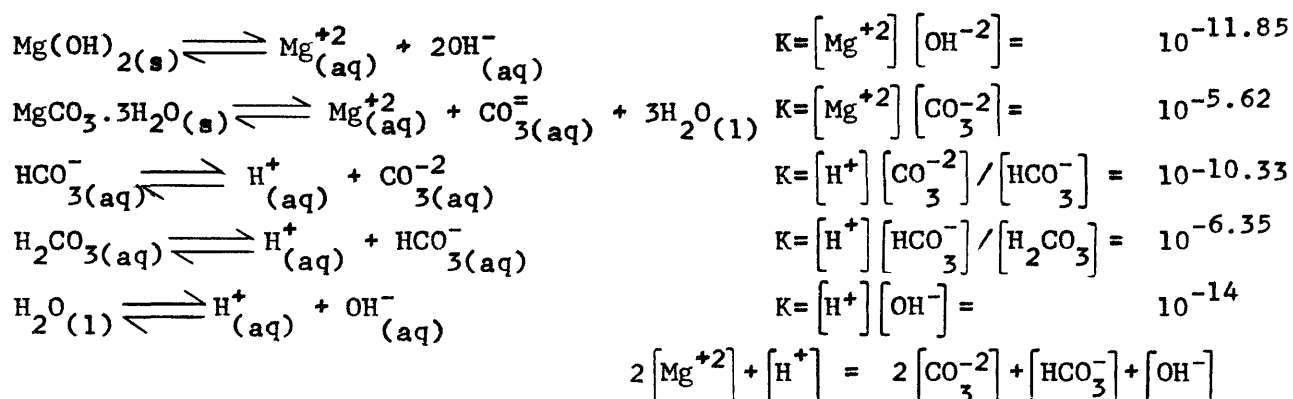
$$\begin{aligned}
 \Delta G_R^\circ &= \Delta G_{\text{f}, \text{MgCO}_3 \cdot 3\text{H}_2\text{O}}^\circ - \Delta G_{\text{f}, \text{Mg}(\text{OH})_2}^\circ - 2 \Delta G_{\text{f}, \text{H}_2\text{O}}^\circ - \Delta G_{\text{f}, \text{CO}_2}^\circ \\
 &= (-412658 \pm 500) - (-200021 \pm 550) - 2(-56691 \pm 15) - (-94265 \pm 50)
 \end{aligned}$$

$$RT \ 2.3 \log P_{\text{CO}_2} = -184990$$

$$P_{\text{CO}_2} = 10^{-134}$$

If there is any CO_2 in the gas phase within the $\text{MgO-CO}_2\text{-H}_2\text{O}$ system, the $P_{\text{CO}_2} = 10^{-3}$ atm. Thus, since 10^{-3} atm $>$ $P_{(\text{eq.})\text{CO}_2} = 10^{-134}$ atm, there will be no $\text{CO}_2(\text{g})$ above the solution saturated with respect to $\text{CaCO}_3(\text{c})$ and $\text{Ca}(\text{OH})_2(\text{s})$. This situation may be realized as a liquid solution with a piston, which is impervious to $\text{CO}_2(\text{g})$ and is equivalent to 10^{-3} atm, sitting on the liquid surface.

If it is assumed that the activity coefficients of the ions in solution are one, then one can calculate the composition of the above solution.



If the above equations are solved simultaneously, then

$$\begin{aligned} [\text{Mg}^{+2}] &= 10^{-2.24} \text{ M}, \quad [\text{OH}^{-}] = 10^{-4.74} \text{ M}, \quad [\text{H}^{+}] = 10^{-9.25} \text{ M}, \quad [\text{CO}_3^{-2}] = 10^{-4.42} \text{ M}, \\ [\text{HCO}_3^{-}] &= 10^{-2.06} \text{ M}, \quad \text{and} \quad [\text{H}_2\text{CO}_3] = 10^{-5.09} \text{ M}. \end{aligned}$$

The ionic strength of this solution can now be determined.

$$\mu = \frac{1}{2} [\text{Mg}^{+2}] (2)^2 + \frac{1}{2} [\text{OH}^{-}] + \frac{1}{2} [\text{H}^{+}] + \frac{1}{2} [\text{CO}_3^{-2}] (2)^2 + \frac{1}{2} [\text{HCO}_3^{-}] = 12.29 \times 10^{-3}.$$

At this value of ionic strength the activity coefficients of the ions can be calculated by the Debye Huckel equation. The activity coefficients are as follows. $\gamma_{\text{Mg}^{+2}} = 0.670$, $\gamma_{\text{OH}^{-}} = 0.894$, $\gamma_{\text{H}^{+}} = 0.901$, $\gamma_{\text{CO}_3^{-2}} = 0.641$, and $\gamma_{\text{HCO}_3^{-}} = 0.895$.

Since the computed activity coefficients of Mg^{+2} and CO_3^{-2} are significantly different from one, a series of successive approximations are used.

Such approximations, similar to those previously used to calculate the concentration of the solution saturated with respect to $\text{Ca(OH)}_2(\text{s})$ and $\text{CaCO}_3(\text{c})$, yield the following result.

The bulk composition of the solution which is saturated simultaneously with respect to Mg(OH)_2 and $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is 0.0202 weight percent MgO and 0.0310 weight percent CO_2 .

The above information concerning the potentially stable phases in the $\text{MgO-CO}_2\text{-H}_2\text{O}$ system is plotted in Figure 3 and the stable states graphically illustrated for all bulk compositions except those occurring within the compositional region $\text{MgO-MgCO}_3\text{-MgCO}_3 \cdot 3\text{H}_2\text{O-Mg(OH)}_2$.

CaO-MgO-H₂O System. No data could be found in the literature for the $\text{CaO-MgO-H}_2\text{O}$ system at 25°C , $P_{\text{total}} = 1 \text{ atm}$, and $P_{\text{H}_2\text{O}} \cong P_{\text{H}_2\text{O}(\text{eq})}$. However, tentative conclusions can be drawn from experiments at other temperatures and pressures. Doman, Barr, McNally, and Alper (1963) and Rankin and Merwin (1916) reported limited solubility in the CaO-MgO binary at 1600° and 1400°C , respectively. Osborn and Muan (1960) reported only limited solubility of approximately 1% MgO in CaO at 1000°C . Baron and Favre (1958) reported no compounds in the $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ system at 25°C which would indicate any potentially stable compounds other than Ca(OH)_2 and Mg(OH)_2 in the $\text{CaO-MgO-H}_2\text{O}$ subsystem. Harker and Tuttle (1955a,b) investigated the $\text{CaO-MgO-H}_2\text{O}$ system and reported no compounds or solid solutions in the CaO-MgO binary at $T \geq 600^\circ\text{C}$. Weir (1955) presented a "proposed" phase diagram for the $\text{Ca(OH)}_2\text{-H}_2\text{O}$ system at 21°C and $0 \leq P \leq 10^4 \text{ atm}$. At 21°C and $P_{\text{total}} = 1 \text{ atm}$ the potentially stable phases are $\text{Ca(OH)}_2(\text{s})$, aqueous solution saturated

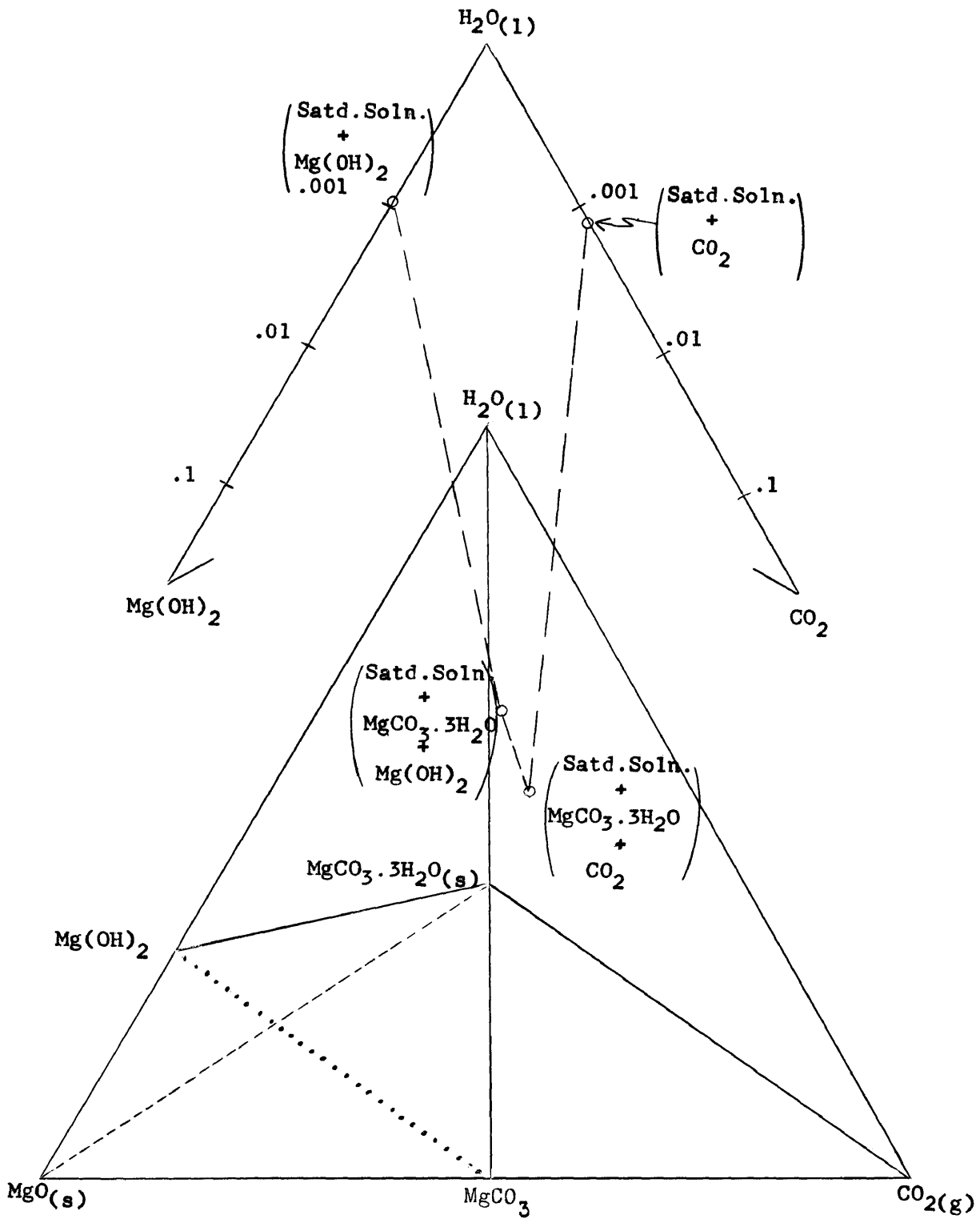
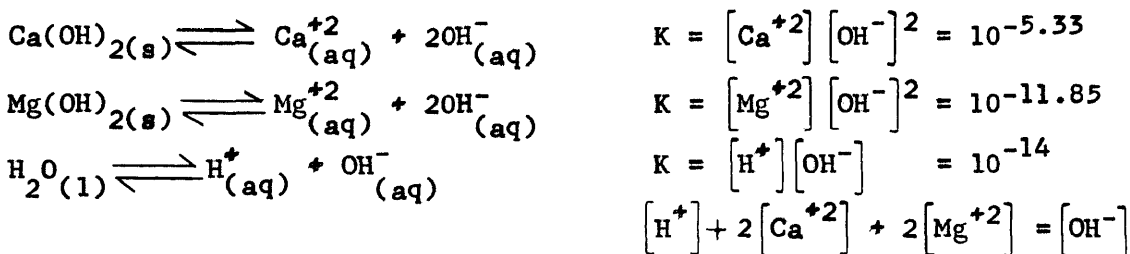


Figure 3. - MgO-CO₂-H₂O System (25°C, P_{total} = 1 atm, P_{CO₂} = 10⁻³ atm)

with respect to Ca(OH)_2 , and $\text{H}_2\text{O}(1)$.

On the basis of the above it will be assumed that the only compounds in the $\text{CaO-MgO-H}_2\text{O}$ system at 25°C , $P_{\text{total}} = 1 \text{ atm}$, and $P_{\text{H}_2\text{O}} \geq P_{\text{H}_2\text{O}(\text{eq})}$ are Mg(OH)_2 and Ca(OH)_2 , the potential stabilities of which have been previously verified.

The solubilities of $\text{Ca(OH)}_{2(s)}$ and $\text{Mg(OH)}_{2(s)}$ in $\text{H}_2\text{O}(1)$ at 25°C have been noted above. The composition of the solution saturated simultaneously with respect to Ca(OH)_2 and Mg(OH)_2 can be calculated if one initially assumes that the activity coefficients of the dissolved constituents are one. (Table 2)



If these equations are solved simultaneously, then

$$[\text{Ca}^{+2}] = 10^{-1.98} \text{ M}, [\text{Mg}^{+2}] = 10^{-8.30} \text{ M}, [\text{H}^{+}] = 10^{-12.32} \text{ M}, \text{ and } [\text{OH}^{-}] = 10^{-1.68} \text{ M}.$$

The ionic strength of this solution can now be calculated.

$$\mu = \frac{1}{2} [\text{Ca}^{+2}] (2)^2 + \frac{1}{2} [\text{Mg}^{+2}] (2)^2 + \frac{1}{2} [\text{OH}^{-}] + \frac{1}{2} [\text{H}^{+}] = 1.26 \times 10^{-2}.$$

At this value of the ionic strength the activity coefficients of the ions in solution can be calculated by the Debye Huckel equation. The values are as follows. $\gamma_{\text{Ca}^{+2}} = 0.644$, $\gamma_{\text{Mg}^{+2}} = 0.662$, $\gamma_{\text{H}^{+}} = 0.908$, and $\gamma_{\text{OH}^{-}} = 0.893$.

Since $\gamma_{\text{Ca}^{+2}}$ and $\gamma_{\text{Mg}^{+2}}$ are significantly less than one, a series of successive approximations are employed in order to determine activity coefficients that agree with that assumed. Such approximations, similar to those

previously used to calculate the concentrations of the solution saturated with respect to $\text{Ca(OH)}_2(\text{s})$ and $\text{CaCO}_3(\text{c})$, yield the following result. The composition of this solution is 0.83 weight percent CaO and 0.281×10^{-7} weight percent MgO.

The above information concerning the potentially stable phases in the CaO-MgO-H₂O system is plotted in Figure 4 and the stable states graphically illustrated for all bulk compositions except those occurring within the compositional region CaO-MgO-Mg(OH)₂-Ca(OH)₂.

CaO-MgO-CO₂ System. Harker and Tuttle (1955a) deduced the stable states for the CaO-MgO-CO₂ system at $T \geq 600^\circ\text{C}$ from decomposition pressure data, the compounds being $\text{CaCO}_3(\text{c})$, MgCO_3 , and $\text{CaMg}(\text{CO}_3)_2(\text{d})$. The potential stability of these phases at 25°C , $P_{\text{total}} = 1 \text{ atm}$, and $P_{\text{CO}_2} = 10^{-3} \text{ atm}$ has been discussed above. Faust (1953) described a new compound, huntite, as $\text{CaMg}_3(\text{CO}_3)_4$ and as a "chalky white probable metastable phase deposited by cool ground waters in cavities in rocks composed of magnesite and dolomite." Skinner (1958) described a field occurrence of this compound as having been precipitated from descending surface waters in a dolomite deposit. Danilova (1959) described huntite occurring in fissures along a contact between dolomitized limestone and quartz mica shales and hypothesized that the huntite was formed by interaction of low-temperature hydrothermal solutions and carbonate wall-rocks. Pobeguín (1960) described huntite associated with magnesite, aragonite, dolomite, and illite in the coatings of concretions and suggests an origin at ambient temperature and atmosphere pressure. Vitaliano and Beck (1963) report a field occurrence of huntite in veinlets

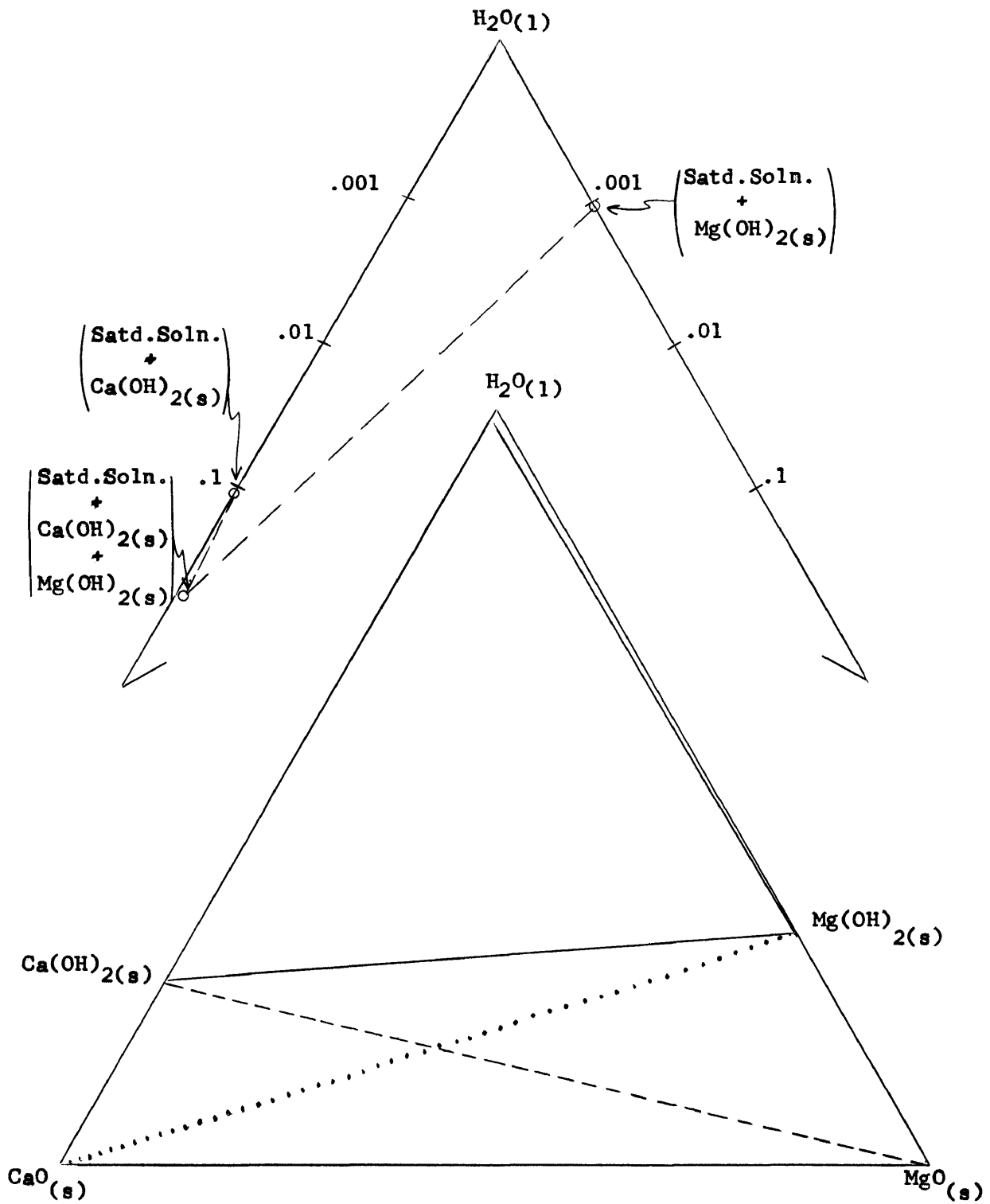


Figure 4. - CaO-MgO-H₂O System (25°C, P_{total} = 1 atm)

in a dolomite formation and hypothesized that it precipitated from solutions percolating downward from the surface. On the basis of such field observations, it seems plausible that huntite is a potentially stable phase at earth surface conditions of temperature and pressure.

As previously noted, Garrels, Thompson, and Siever (1960) determined the solubility products of various carbonates including huntite. Due to the suspected presence of calcite these authors expressed doubt in the accuracy of the solubility product of huntite and thus, in the calculated free energy of formation of huntite. Because of this uncertainty in the accuracy of the free energy data and because the only other information is geologic supposition, it is not possible to come to a conclusion regarding the potential stability of huntite.

From the above information it is not possible to deduce the stable states for the CaO-MgO-CO_2 system at 25°C , $P_{\text{total}} = 1 \text{ atm}$, and $P_{\text{CO}_2} = 10^{-3} \text{ atm}$.

Summary

As previously stated, it is the writer's opinion that it is imperative to understand the $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ system before attempting to understand relatively more complex systems, such as lakes, lagoons, sea water, or hydrothermal solutions.

From the above evaluation of the literature data it is evident that more information is required before the stable states can be determined for the ternary systems, CaO-MgO-CO_2 , $\text{CaO-CO}_2\text{-H}_2\text{O}$, $\text{MgO-CO}_2\text{-H}_2\text{O}$, and $\text{CaO-MgO-H}_2\text{O}$, at temperatures and pressures simulating earth surface conditions. For example, the potential stability of a number of compounds has been assumed on the

basis of sketchy experimental evidence. Also, no experiments have been performed, the results of which would indicate the stable states for the compositional regions $\text{MgO-MgCO}_3\text{-MgCO}_3\cdot 3\text{H}_2\text{O-Mg(OH)}_2$, $\text{CaO-MgO-Mg(OH)}_2\text{-Ca(OH)}_2$, and CaO-MgO-CO_2 . Also, as noted in the previous discussion, there are no reliable laboratory data indicating whether or not huntite is a potentially stable phase at temperatures and pressures simulating earth surface conditions.

Thus, as previously noted, the objective of this thesis is two-fold.

- 1) To report the experimentally determined free energy of formation of huntite which adds to the list of known thermodynamic data,
- 2) To contribute to the understanding of the applicability of such thermodynamic data to complex systems. This was accomplished by application of a calculation scheme, which was developed in this study, to the problem of determining the stable states for the above compositional regions.

CALCULATION SCHEME

If a combination of phases is to represent the stable state for a bulk composition, then no reactions can occur between these phases which would lower the free energy of the system at that temperature and pressure. Therefore, it follows that one should be able to determine the stable state for a system from thermodynamic data. A calculation scheme has been developed for just such a purpose, i.e., for the prediction of the stable state from free energy data.

DescriptionIdentification of the Calculation Scheme

This technique consists of the application of three rules for the determination of the stable phases and the calculation of their respective amounts for any specified bulk composition in a multicomponent system. The required experimental data are a list of the potentially stable phases in the system at the temperature and pressure of interest and a list of their respective free energies of formation as functions of temperature, pressure,

and composition. From these data, that assemblage of phases can be determined which will represent the stable state for any specified bulk composition at any temperature and pressure.

Outline of Calculation Scheme

The question to be answered is "What is the stable state for a given bulk composition in a system at a given temperature and pressure?" Each phase that has been shown to exist at the temperature and pressure of interest is only potentially stable. This is because the criteria for chemical stability are not only temperature and pressure, but also bulk composition. The bulk composition of the system must be specified in order to determine the stability of any one of these potentially stable phases. Therefore, first one must consider each one of the phases in the system at the temperature and pressure of interest as possibly being one of the stable phases for any bulk composition. This means that initially all combinations of potentially stable phases are considered as possible stable states. The maximum number of phases in any combination is determined by the phase rule. From this list of possible stable states one can select the stable state for a particular bulk composition by sequentially applying the three rules described below.

The first rule can be stated as follows. "Any combination of potentially stable phases which includes phases that will react spontaneously to produce any of the potentially stable phases as the only product, thereby lowering the free energy of the system, can not be a possible stable state". Thus the first rule is used to reject some combinations which

can not be possible stable states for any bulk composition. These combinations which will be rejected are identified by considering the list of potentially stable phases in the system. For example, A and B can not represent any portion of a stable state if there exists a potentially stable phase which is composed of just A and B in any ratio.

The second rule which is used to eliminate other combinations as possible stable states, can be stated as follows. "All phases in any particular combination must be produced from the specified bulk composition and the limiting reactants are those components which do not appear as such in that combination."

Thus, by considering the stoichiometry of the reactions producing the potentially stable phases from the components, one can derive a series of simple equations which are used to test whether or not the bulk composition can produce that particular assemblage of phases.

The following will serve to exemplify this second rule. The bulk composition is T_A , T_B , and T_C , where T_i is equal to the total number of moles of component i . The test equations for the combination B, AC, ABC_2 are derived as follows. Since C and A do not appear as such in the combination, then

$$T_C = (AC) + 2(ABC_2)$$

and

$$T_A = (AC) + (ABC_2),$$

where (AC) and (ABC_2) represent the number of moles of AC and ABC_2 in the combination. Solving these two equations for the two unknowns (AC) and (ABC_2) one obtains

$$(ABC_2) = T_C - T_A$$

$$(AC) = 2T_A - T_C.$$

Also, since B appears in the combination, then

$$(B) = T_B - (ABC_2) = T_B - T_C + T_A,$$

where (B) is the number of moles of B in the combination. Since $(ABC_2) >$

0, $(AC) > 0$, and $(B) > 0$, the test equations are

$$T_C - T_A > 0,$$

$$2T_A - T_C > 0, \text{ and}$$

$$T_B - T_C + T_A > 0.$$

In order for the bulk composition, T_A, T_B , and T_C , to have produced this combination, all three test equations must be satisfied.

Finally the third rule is used to select that assemblage of phases which is the stable state. This rule is based on the concept that the system at constant temperature and pressure always seeks a minimum in free energy. Therefore, "The stable state is that combination which has resulted from those reactions producing the greatest decrease in the free energy of the system."

It should be noted at this point that the first rule is not necessary for determining the stable state for any bulk composition. The principle upon which the first and third rules are based is that the system at constant temperature and pressure always seeks a minimum in free energy. Therefore, those combinations which are ruled out as possible stable states by the first rule would also be eliminated by the third rule. This can be exemplified by considering the absolute free energy scale of a system noted in Figure 5. The combination A,B,CD would be ruled out as a

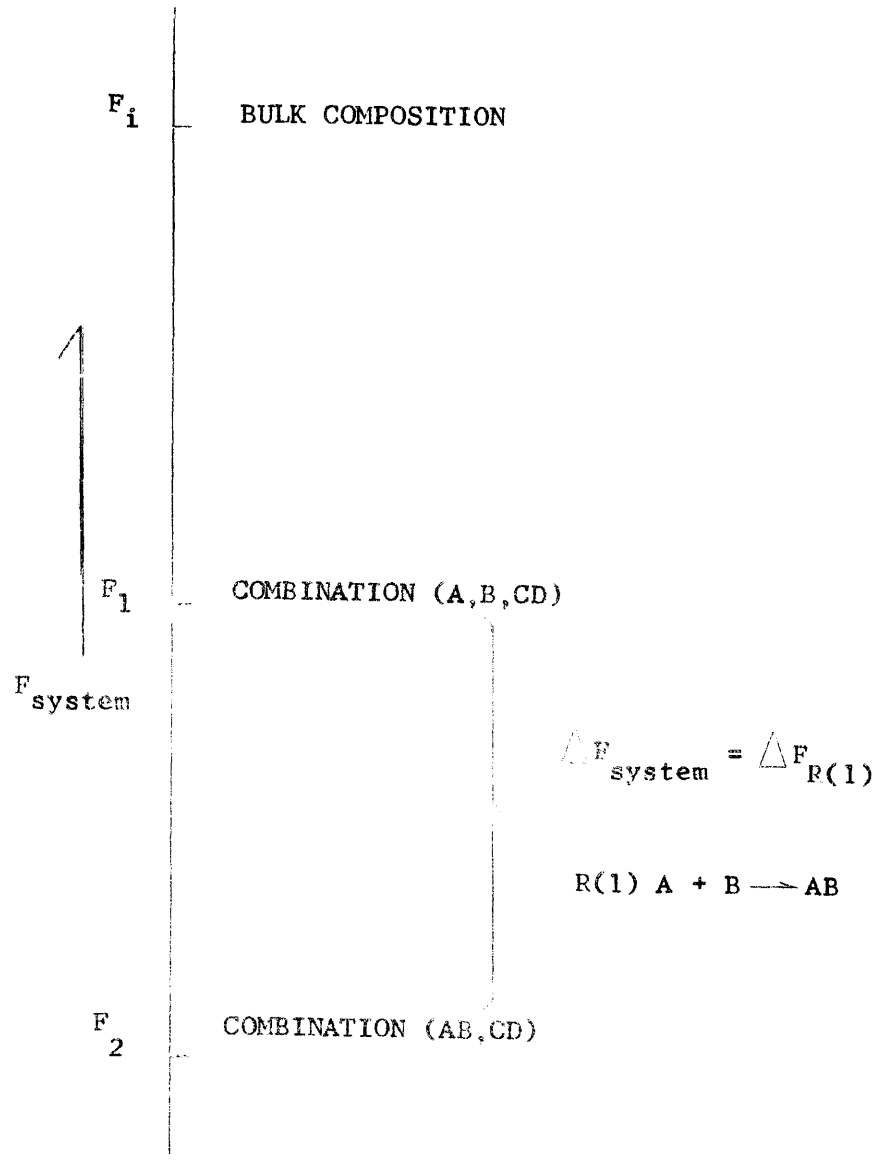


Figure 5. - Absolute Free Energy Scale

possible stable state since the potentially stable phase AB exists. But if the first rule had not been applied, the third rule would have chosen the combination AB,CD instead of A,B,CD because the former combination resulted from those reactions producing the greater decrease in the free energy of the system.

The reason for applying the first rule is that it only has to be used once for any given system and this eliminates many combinations that never have to be tested by the second or third rules. Thus, if the first rule is applied, much time and effort are saved by reducing the number of necessary calculations for determining the stable state for any specified bulk composition.

Summary

As outlined above, if experimental information is available from which the potential stability of the reported phases and their free energies of formation at the temperature and pressure of interest can be deduced, then one can easily calculate the stable assemblage of phases for any specified bulk composition.

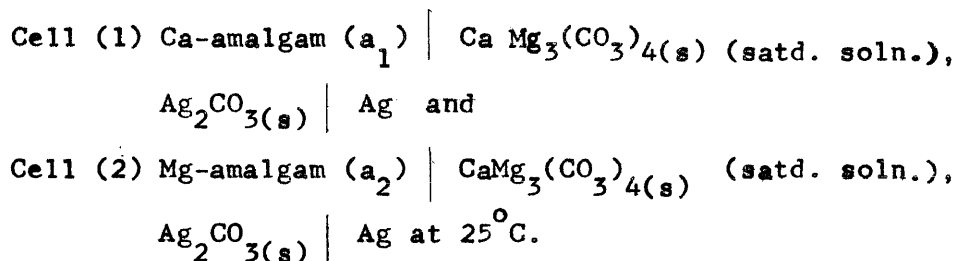
Free energy data are available for all those compounds concluded to be potentially stable in the compositional regions in question, i.e., MgO-MgCO₃-MgCO₃·3H₂O-Mg(OH)₂, CaO-MgO-Mg(OH)₂-Ca(OH)₂, and CaO-MgO-CO₂, at the temperature and pressure of interest in this study. But, as previously noted, because of the uncertainty in the accuracy in the free energy data for huntite and because the only other experimental data are geologic supposition, it is not possible to come to a conclusion regarding the potential stability of

this compound. Thus, prior to application of the calculation scheme as outlined above, reliable free energy data for huntite must be experimentally determined.

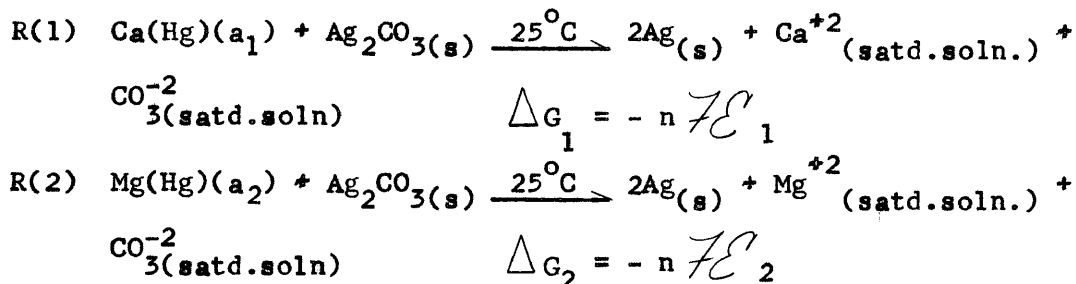
DETERMINATION OF THE FREE ENERGY OF FORMATION OF HUNTITEGeneral Procedure

The free energy of formation of huntite has been determined in this study by the reversible cell method. The approach was essentially that of Saegusa (1950), who devised an experimental technique for obtaining the free energy of formation of Na_2CO_3 by emf measurements of the following cell. Na-amalgam | $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(\text{s})$ (satd. soln.), $\text{Ag}_2\text{CO}_3(\text{s})$ | Ag.

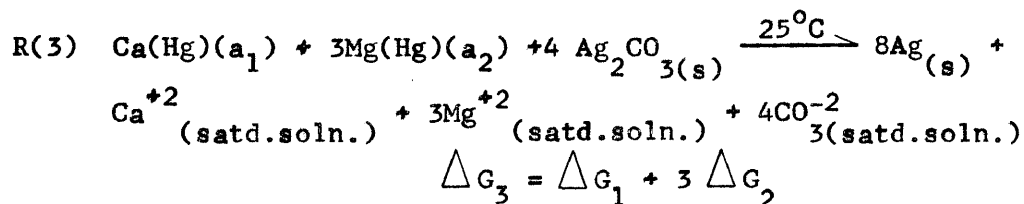
In order to obtain the free energy of formation of huntite by such a method, emf data for the following two cells were experimentally measured.



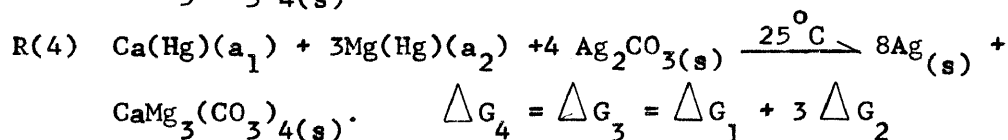
The net-cell reactions for these two cells are as follows.



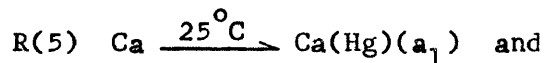
If one adds R(1) + 3R(2), the following reaction is obtained.



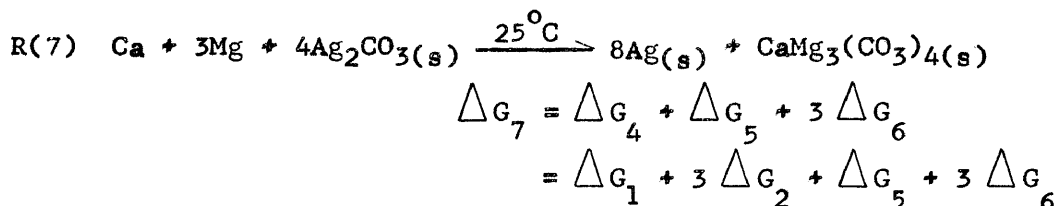
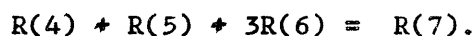
Since $\text{Ca}^{+2}(\text{satd.soln.}) + 3\text{Mg}^{+2}(\text{satd.soln.}) + 4\text{CO}_3^{-2}(\text{satd.soln.}) \rightleftharpoons \text{CaMg}_3(\text{CO}_3)_4(s)$, then



If free energy data were available for the reactions



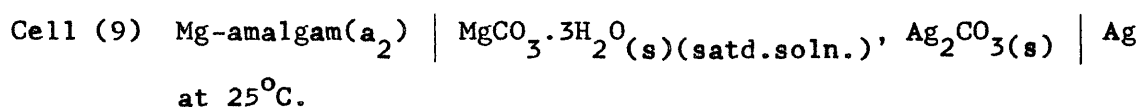
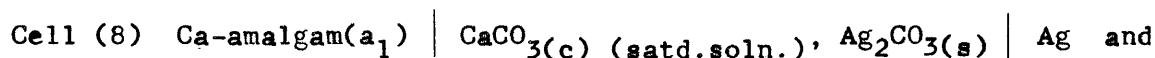
R(6) $\text{Mg} \xrightarrow{25^\circ\text{C}} \text{Mg(Hg)}(a_2)$, then the free energy of formation of huntite could be calculated by the following method.



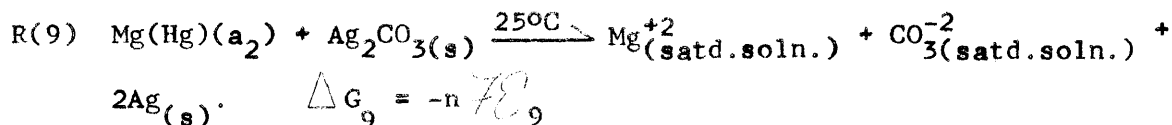
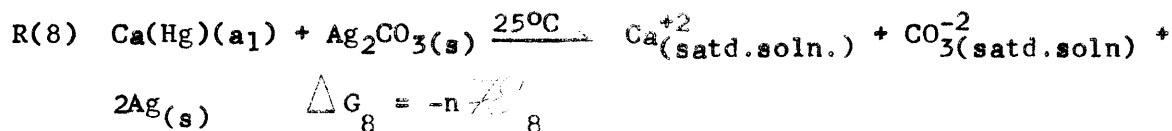
Since $\Delta G_7 = \Delta G_{f,25^\circ\text{C},\text{CaMg}_3(\text{CO}_3)_4}^\circ - 4 \Delta G_{f,25^\circ\text{C},\text{Ag}_2\text{CO}_3}^\circ$, then

$$\begin{aligned} \Delta G_{f,25^\circ\text{C},\text{CaMg}_3(\text{CO}_3)_4}^\circ &= \Delta G_1 + 3 \Delta G_2 + \Delta G_5 + 3 \Delta G_6 + \\ & 4 \Delta G_{f,25^\circ\text{C},\text{Ag}_2\text{CO}_3}^\circ. \end{aligned}$$

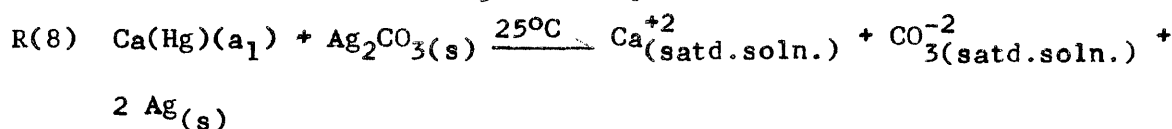
ΔG_5 and ΔG_6 were determined by emf measurements of the following two cells.



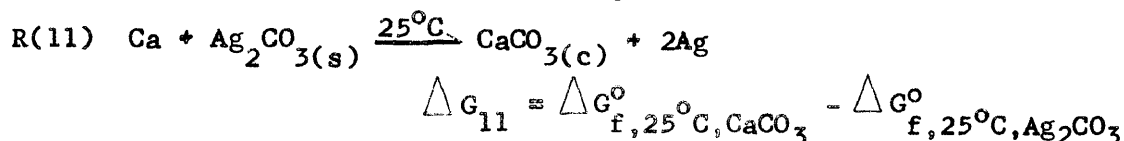
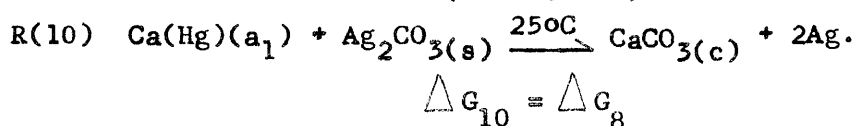
The net-cell reactions for these two cells are as follows.



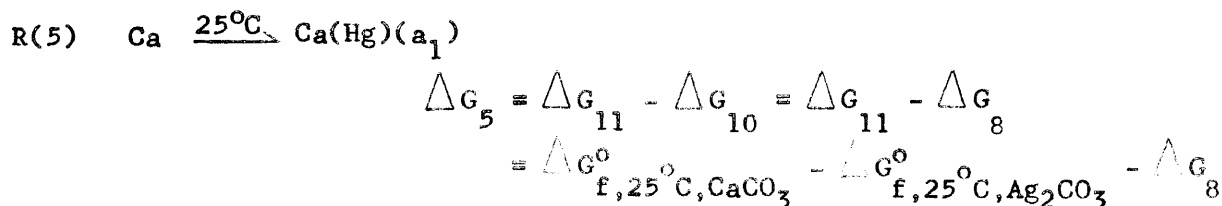
From R(8) and R(9) ΔG_5 and ΔG_6 can be calculated as follows.



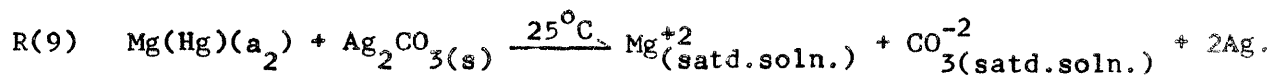
Since $\text{Ca}^{+2}(\text{satd. soln.}) + \text{CO}_3^{-2}(\text{satd. soln.}) \xrightarrow{25^\circ\text{C}} \text{CaCO}_3(c)$, then



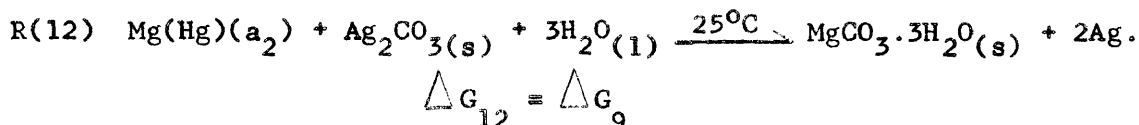
$$\text{R(11)} - \text{R(10)} = \text{R(5)}$$

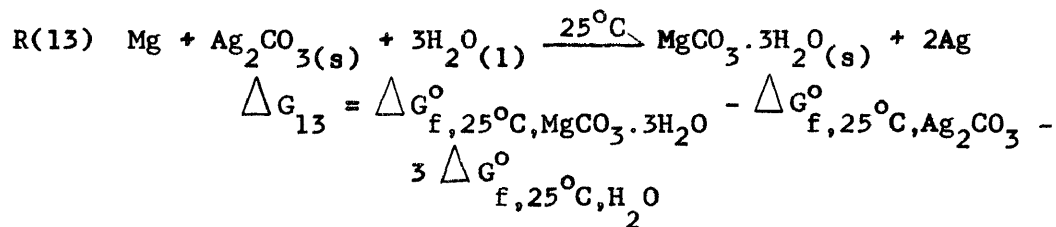


Also,

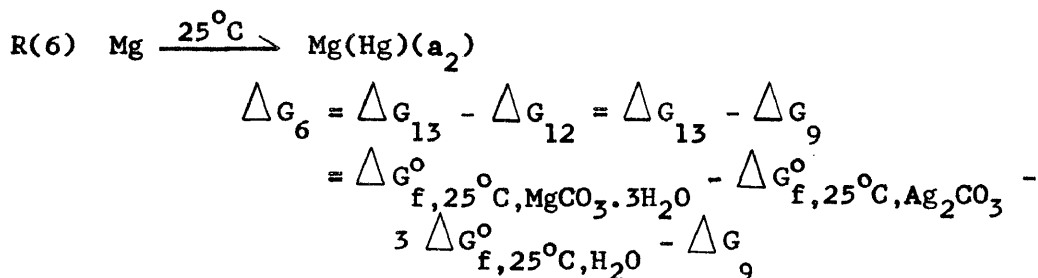


Since $\text{Mg}^{+2}(\text{satd. soln.}) + \text{CO}_3^{-2}(\text{satd. soln.}) + 3\text{H}_2\text{O}(l) \xrightarrow{25^\circ\text{C}} \text{MgCO}_3 \cdot 3\text{H}_2\text{O}(s)$, then



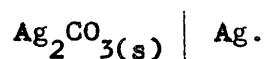
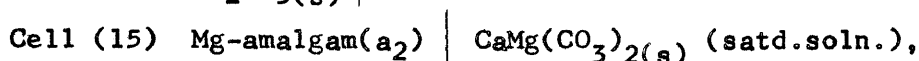
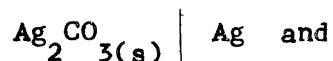
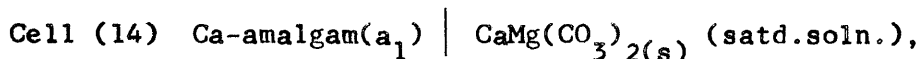


$$\text{R(13)} - \text{R(12)} = \text{R(6)}$$



$$\begin{aligned}
 \text{Thus, } \Delta G_{f,25^\circ\text{C},\text{CaMg}_3(\text{CO}_3)_4}^\circ &= \Delta G_1 + 3 \Delta G_2 - \Delta G_8 - 3 \Delta G_9 + \\
 \Delta G_{f,25^\circ\text{C},\text{CaCO}_3}^\circ &+ 3 \Delta G_{f,25^\circ\text{C},\text{MgCO}_3 \cdot 3\text{H}_2\text{O}}^\circ - 9 \Delta G_{f,25^\circ\text{C},\text{H}_2\text{O}}^\circ
 \end{aligned}$$

In order to verify this experimental procedure the free energy of formation of dolomite was obtained from emf measurements of the following two cells and then compared with values reported in the literature.



From the above experimental data the free energy of formation of dolomite was calculated.

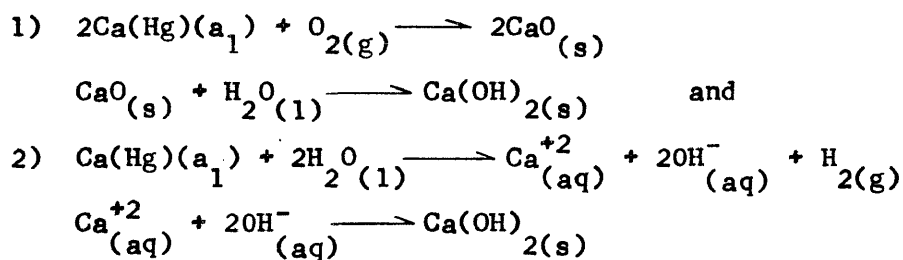
$$\begin{aligned}
 \Delta G_{f,25^\circ\text{C},\text{CaMg}(\text{CO}_3)_2}^\circ &= \Delta G_{14} + \Delta G_{15} - \Delta G_8 - \Delta G_9 + \Delta G_{f,25^\circ\text{C},\text{CaCO}_3}^\circ + \\
 &\quad \Delta G_{f,25^\circ\text{C},\text{MgCO}_3 \cdot 3\text{H}_2\text{O}}^\circ - 3 \Delta G_{f,25^\circ\text{C},\text{H}_2\text{O}}^\circ
 \end{aligned}$$

As outlined above, the free energies of formation of huntite and dolomite were experimentally obtained by emf measurements of the following

cells and from free energy data for $\text{CaCO}_3(\text{c})$, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s})$ and $\text{H}_2\text{O}(\text{l})$ found in the literature.

| | | | |
|-----------|---------------------|--|----|
| Cell (8) | Ca-amalgam(a_1) | $\text{CaCO}_3(\text{c})$ (satd.soln.), $\text{Ag}_2\text{CO}_3(\text{s})$ | Ag |
| Cell (14) | Ca-amalgam(a_1) | $\text{CaMg}(\text{CO}_3)_2(\text{d})$ (satd.soln.), $\text{Ag}_2\text{CO}_3(\text{s})$ | Ag |
| Cell (1) | Ca-amalgam(a_1) | $\text{CaMg}_3(\text{CO}_3)_4(\text{h})$ (satd.soln.), $\text{Ag}_2\text{CO}_3(\text{s})$ | Ag |
| Cell (9) | Mg-amalgam(a_2) | $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s})$ (satd.soln.), $\text{Ag}_2\text{CO}_3(\text{s})$ | Ag |
| Cell (15) | Mg-amalgam(a_2) | $\text{CaMg}(\text{CO}_3)_2(\text{d})$ (satd.soln.), $\text{Ag}_2\text{CO}_3(\text{s})$ | Ag |
| Cell (2) | Mg-amalgam(a_2) | $\text{CaMg}_3(\text{CO}_3)_4(\text{h})$ (satd.soln.), $\text{Ag}_2\text{CO}_3(\text{s})$ | Ag |

An experimental difficulty for obtaining emf measurements of such cells is the rapid oxidation of the Mg-amalgam electrode. For example Muller (1923) reported that he was unable to measure the emf of cells containing Mg-amalgam electrodes in aqueous solutions because of the rapid oxidation of the Mg. Also, in preparation of the Ca- and Mg-amalgams, the present writer observed rapid oxidation of the Ca and Mg in the amalgam when either exposed to the atmosphere or within the presence of aqueous solutions. Two processes describing this observation are the following.



Process one can be prevented from proceeding to the right by removing the reactant $\text{O}_2(\text{g})$ from the system. But $P_{\text{H}_2}(\text{eq})$ at 25°C for the second process is approximately 10^{74} atm, which makes preventing this process most

difficult. Saegusa (1950) devised a galvanic cell in which the amalgam was continuously mixed with the aqueous solution. This procedure successfully circumvented the problem of preventing the second process, as evidenced by agreement of his experimental data with that in the literature.

The construction of the cell is illustrated in Figure 6. A is the reservoir for the amalgam. The amalgam attains the temperature of the water bath, i.e., 25°C, as it flows through the capillary spiral B. C is the Pt contact with the amalgam, the anode in this cell, and E is the point of contact of the amalgam and the aqueous solution saturated with respect to $\text{Ag}_2\text{CO}_3(\text{s})$ and the appropriate Ca- and/or Mg-carbonate. The saturated aqueous solution in container F is forced by $\text{N}_2(\text{g})$ pressure through the Ag- Ag_2CO_3 cathode, G, to the point of contact E with the amalgam.

Experimental Procedure

Preparation of the Ca- and Mg-Amalgam Electrodes

The mercury used in preparation of the electrodes was cleaned by first being vigorously shaken in 3N HNO_3 and then in distilled $\text{H}_2\text{O}(1)$ and finally by being triply distilled under vacuum. Approximately 15 g of solid Mg and 15 g of solid Ca were washed in dilute HCl, immediately dried with acetone, and quickly inserted into individual 500 ml boiling flasks, each of which contained about 250 ml of cleaned mercury under $\text{N}_2(\text{g})$. The $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ had been previously removed by bubbling the $\text{N}_2(\text{g})$ through an aqueous solution of Cr^{+2} , then through concentrated $\text{H}_2\text{SO}_4(1)$, and

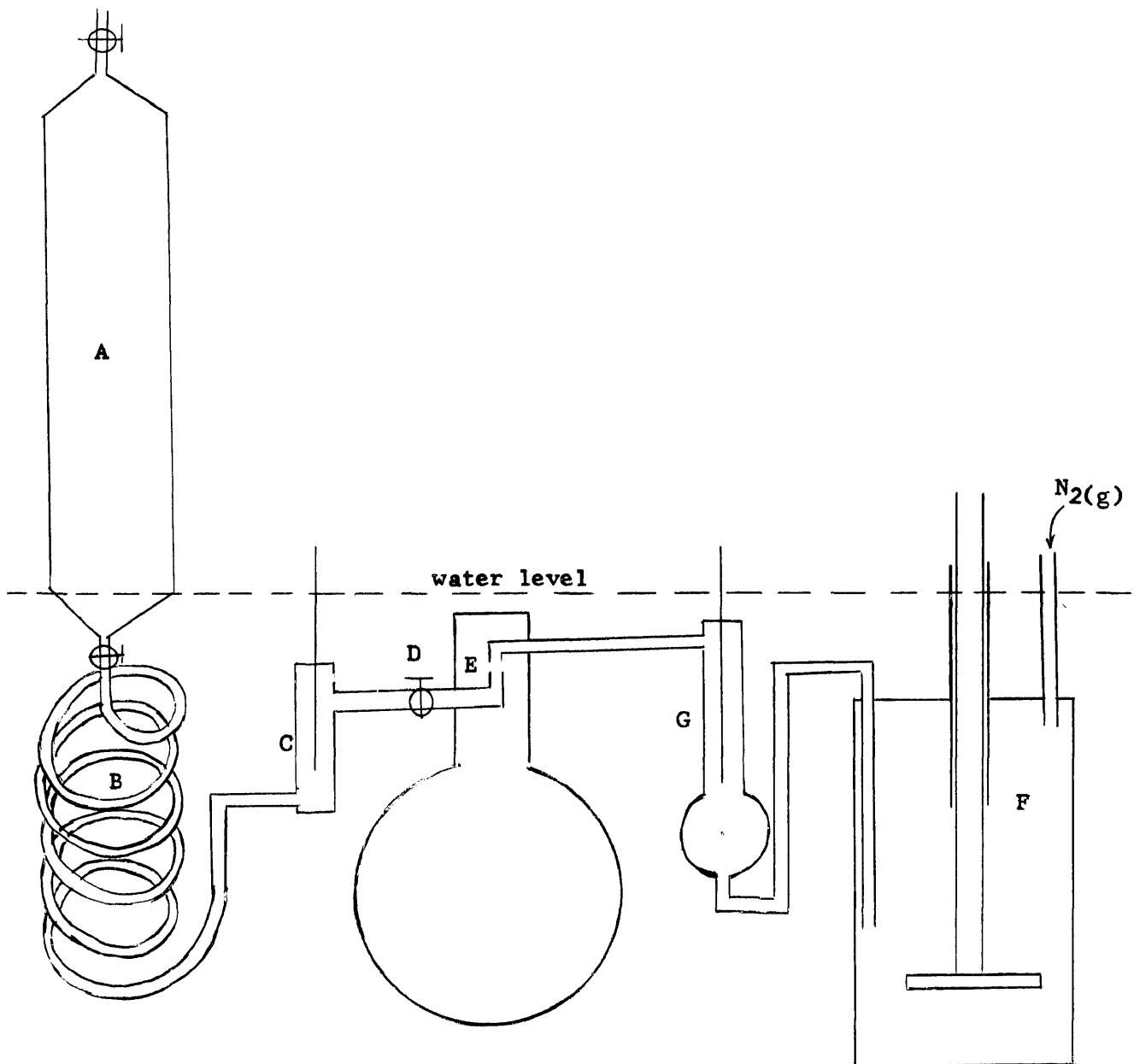


Figure 6. - Carbonate Cell: (A) amalgam reservoir; (B) capillary spiral; (C) Pt contact with amalgam; (E) point of contact of amalgam and aqueous solution; (F) aqueous solution reservoir; (G) Ag-Ag₂CO₃ electrode.

finally through $\text{KOH}_{(s)}$. The mercury was refluxed under $\text{N}_{2(g)}$ at approximately atmospheric pressure for several days. A small sample of each solution was then exposed to the atmosphere, and an immediate oxidation of the Ca or Mg was observed, which indicated that solution had taken place. Since the same Ca-amalgam was used for the electrodes in the cells, 1, 8, and 14, and the same Mg-amalgam was used for the cells, 2, 9, and 15, the concentrations of Ca and Mg in the amalgams were not determined.

Prior to the transfer of the amalgams to the reservoir A, Figure 6, containers A and C and the capillary B were evacuated and then flushed with purified $\text{N}_{2(g)}$ several times. The amalgam was then transferred to A via a short section of neoprene tubing from the boiling flask to the inlet valve on A. The amalgam was then allowed to flow through the capillary and fill the cell up to stopcock D.

Preparation of the $\text{Ag-Ag}_2\text{CO}_3$ Electrode

The Ag_2CO_3 for the $\text{Ag-Ag}_2\text{CO}_3$ electrode was prepared by the method proposed by Walker, Bray, and Johnston (1927). A solution of approximately 0.15M NH_4OH is added slowly to 0.3M AgNO_3 until all the $\text{Ag}_2\text{O}_{(s)}$ has gone back into solution. $\text{CO}_{2(g)}$ is then slowly passed through this solution of $\text{Ag}(\text{NH}_3)_2^+$ producing yellow crystals of $\text{Ag}_2\text{CO}_{3(s)}$, which are then washed with distilled water and stored in the dark.

Some of the $\text{Ag}(\text{NH}_3)_2^+$ solution prepared above was electrolyzed to deposit a silver plate on a Pt coil. The $\text{Ag}_2\text{CO}_{3(s)}$ and the Ag coated Pt wire were then placed into the glass container G (Figure 6), the outside

of which had previously been blackened to prevent decomposition of the Ag_2CO_3 by light.

Preparation of the Saturated Aqueous Solutions

The carbonates used in preparation of the saturated aqueous solutions are described as follows. The calcite used was reagent grade CaCO_3 . Dolomite was US Bureau of Standards Standard Sample No. 88. The huntite was supplied by the US National Museum and the original source was a natural deposit at Tea Tree Gully, South Australia, as described by Skinner (1958). The $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s})$ was prepared by adding a dilute solution of NH_4OH to a solution of KHCO_3 and MgCl_2 and allowing the mixture to stand for a few days with continual stirring. The $\text{Ag}_2\text{CO}_3(\text{s})$ was prepared as previously outlined.

Approximately 5 g of the Ca and/or Mg carbonates were added to individual 1-liter flasks, each of which contained about 900 ml of distilled water and 0.5 g of $\text{Ag}_2\text{CO}_3(\text{s})$. The outside of each flask had been previously blackened. The solutions were kept in a constant temperature bath at 25°C for several weeks with continual stirring. The $\text{Ca}^{+2}(\text{aq})$ and $\text{Mg}^{+2}(\text{aq})$ concentrations were then determined every week by titration with EDTA, as outlined by Bisque (1961). The solutions were assumed to be saturated with respect to the Ca and/or Mg carbonates, and with respect to Ag_2CO_3 , when the concentrations were observed to be constant within the experimental precision, (Table 3). After the emf of the cells had been measured, the presence of each Ca and/or Mg carbonate was verified by X-ray analysis, Figure 7.

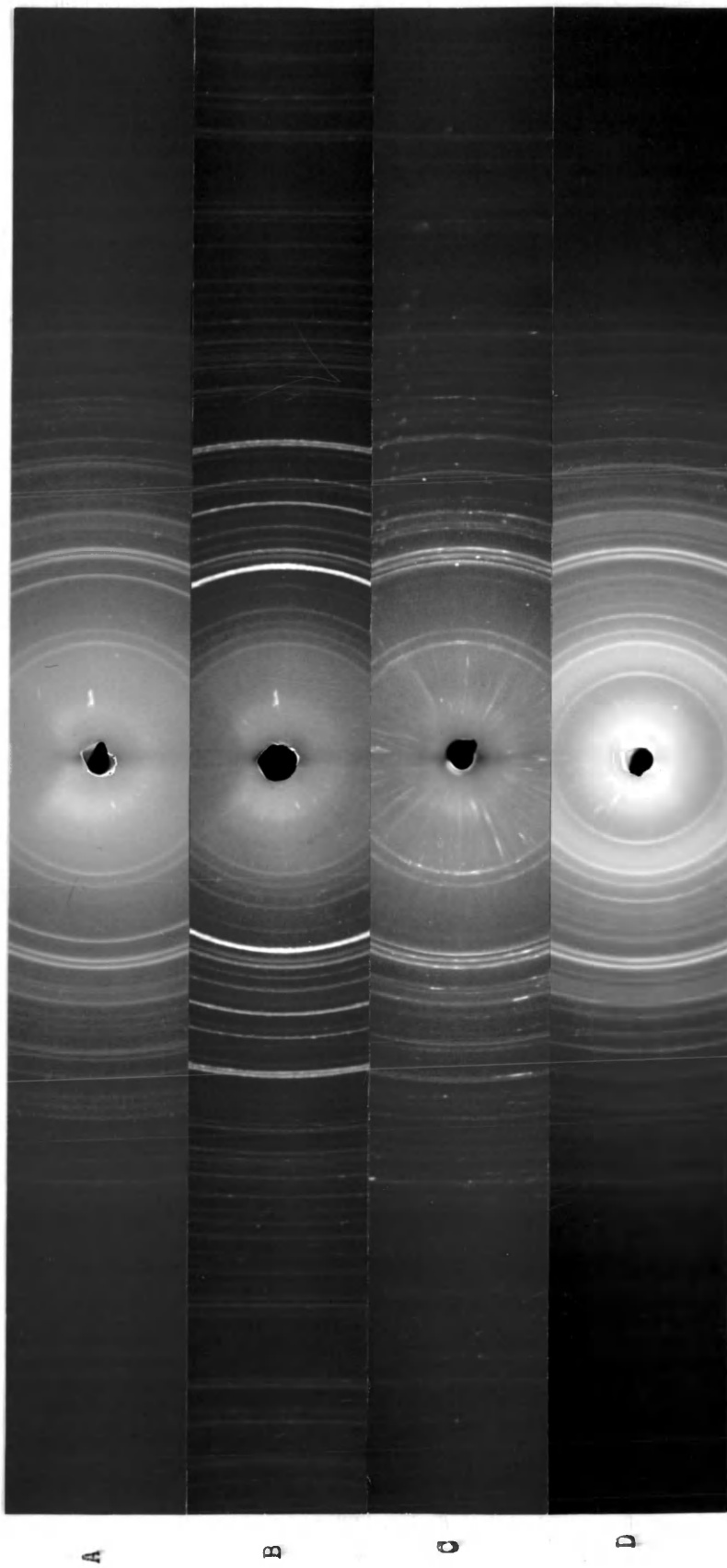


Figure 7. X-ray Diffraction Patterns: The above patterns represent mixtures of Ag_2CO_3 and (A) $\text{CaCO}_3(\text{c})$; (B) $\text{CaMg}(\text{CO}_3)_2(\text{d})$; (C) $\text{CaMg}_3(\text{CO}_3)_4(\text{h})$; (D) $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$

TABLE 3Concentrations of Ca^{+2} and/or Mg^{+2} in Aqueous Solutions

| | |
|--|--|
| $[\text{Mg}^{+2}]_{\text{MgCO}_3 \cdot 3\text{H}_2\text{O}}$ | $([\text{Ca}^{+2}] + [\text{Mg}^{+2}])_{\text{CaMg}(\text{CO}_3)_2}$ |
| $(2.208 \pm .009) \times 10^{-3}$ | $(0.982 \pm .008) \times 10^{-4}$ |
| $(2.210 \pm .010) \times 10^{-3}$ | $(0.980 \pm .010) \times 10^{-4}$ |
| $(2.198 \pm .006) \times 10^{-3}$ | |
| $[\text{Ca}^{+2}]_{\text{CaCO}_3}$ | $([\text{Ca}^{+2}] + [\text{Mg}^{+2}])_{\text{CaMg}_3(\text{CO}_3)_4}$ |
| $(.452 \pm .007) \times 10^{-4}$ | $(.615 \pm .005) \times 10^{-4}$ |
| $(.460 \pm .009) \times 10^{-4}$ | $(.605 \pm .006) \times 10^{-4}$ |

Procedure for Determining Cell Emf's

With the Ca-amalgam as one of the anode electrodes, the container F which contained the saturated solution of $\text{CaCO}_3(\text{c})$ and $\text{Ag}_2\text{CO}_3(\text{s})$ was attached to the Ag-Ag₂CO₃ electrode. This aqueous solution was slowly forced through the Ag-Ag₂CO₃ electrode and allowed to flow to E, the point of contact with the Ca-amalgam. (Figure 6). The rate of flow of amalgam was such that a fresh surface was continually in contact with the aqueous solution. The emf was measured by a Leeds and Northrup Type K-3 Universal Potentiometer in conjunction with a Leeds and Northrup 2430 D-C Galvanometer of sensitivity $7 \times 10^{-3} \mu\text{A}/\text{mm}$.

After a set of emf data had been obtained for the above cell, the Ag-Ag₂CO₃ electrode was flushed with distilled water. Then the container containing the solution saturated with respect to $\text{CaMg}(\text{CO}_3)_2(\text{d})$ and $\text{Ag}_2\text{CO}_3(\text{s})$ was attached and the electrode was flushed with this solution prior to making contact with the Ca-amalgam, and obtaining emf measurements. The same procedure was followed for the solution saturated with

respect to $\text{CaMg}_3(\text{CO}_3)_4(\text{h})$ and $\text{Ag}_2\text{CO}_3(\text{s})$.

Prior to obtaining data for the remaining three cells the containers A and C, and capillary tube B were dismantled and cleaned with dilute HNO_3 to remove any trace of the Ca-amalgam. The Mg-amalgam was then transferred to reservoir A and the emf for these remaining three cells was measured as outlined above.

Experimental Results

Emf Data

Five emf measurements at 25°C for each of the six cells and the computed averages and precisions are noted in Tables 4 and 5. The cell numbers in these tables refer to the following cells.

| | | | | | | | |
|-----------|---------------------|--|---|---------------|------------------------------------|--|----|
| Cell (8) | Ca-amalgam(a_1) | | $\text{CaCO}_3(\text{c})$ | (satd.soln.), | $\text{Ag}_2\text{CO}_3(\text{s})$ | | Ag |
| Cell (14) | Ca-amalgam(a_1) | | $\text{CaMg}(\text{CO}_3)_2(\text{s})$ | (satd.soln.), | $\text{Ag}_2\text{CO}_3(\text{s})$ | | Ag |
| Cell (1) | Ca-amalgam(a_1) | | $\text{CaMg}_3(\text{CO}_3)_4(\text{s})$ | (satd.soln.), | $\text{Ag}_2\text{CO}_3(\text{s})$ | | Ag |
| Cell (9) | Mg-amalgam(a_2) | | $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s})$ | (satd.soln.), | $\text{Ag}_2\text{CO}_3(\text{s})$ | | Ag |
| Cell (15) | Mg-amalgam(a_2) | | $\text{CaMg}(\text{CO}_3)_2(\text{s})$ | (satd.soln.), | $\text{Ag}_2\text{CO}_3(\text{s})$ | | Ag |
| Cell (2) | Mg-amalgam(a_2) | | $\text{CaMg}_3(\text{CO}_3)_4(\text{s})$ | (satd.soln.), | $\text{Ag}_2\text{CO}_3(\text{s})$ | | Ag |

TABLE 4

Emf Data for the Cells Containing Mg-amalgam

| CELL(9) | (v) | CELL(15) | (v) | CELL(2) | (v) |
|--------------------------|-----|-----------------------|-----|------------------------|-----|
| 0.01259 | | 0.01997 | | 0.03824 | |
| 0.01256 | | 0.01984 | | 0.03758 | |
| 0.01276 | | 0.01964 | | 0.03748 | |
| 0.01240 | | 0.02042 | | 0.03875 | |
| 0.01249 | | 0.02137 | | 0.03763 | |
| Avg=0.01256 \pm .00009 | | Avg=0.0203 \pm .005 | | Avg=0.0379 \pm .0004 | |

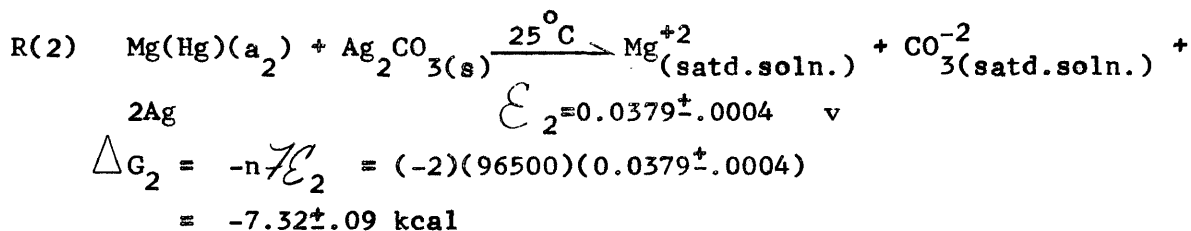
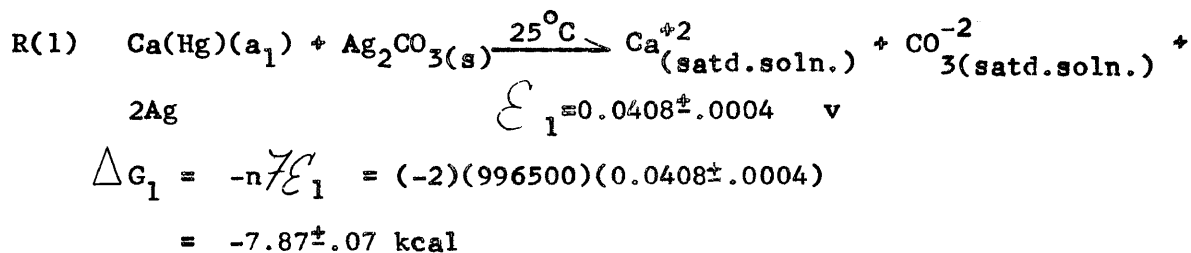
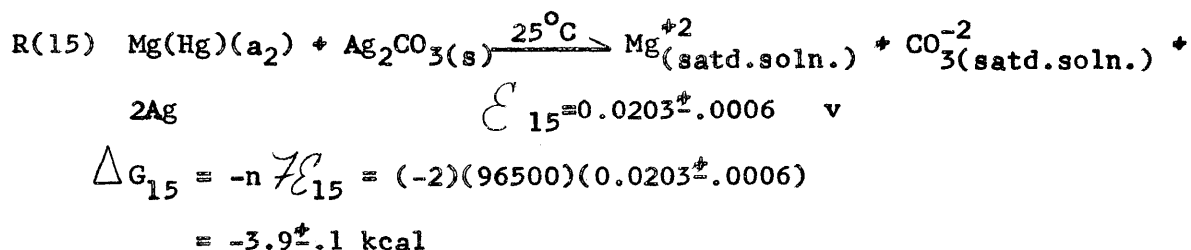
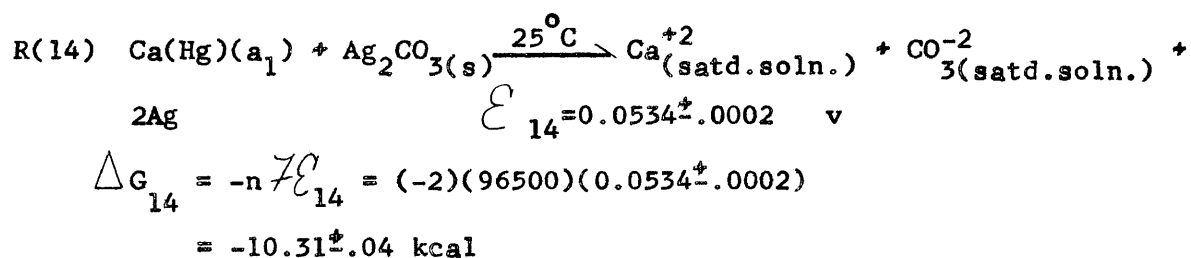
TABLE 5

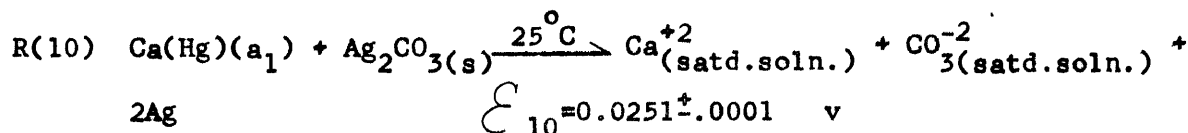
Emf Data for the Cells Containing Ca-amalgam

| CELL(8) (v) | CELL(14) (v) | CELL(1) (v) |
|------------------------|------------------------|------------------------|
| 0.02532 | 0.05318 | 0.04095 |
| 0.02506 | 0.05362 | 0.03985 |
| 0.02526 | 0.05372 | 0.04114 |
| 0.02518 | 0.05356 | 0.04103 |
| 0.02495 | 0.05312 | 0.04085 |
| Avg=0.0251 \pm .0001 | Avg=0.0534 \pm .0002 | Avg=0.0408 \pm .0004 |

Changes of Free Energy for Cell Reactions

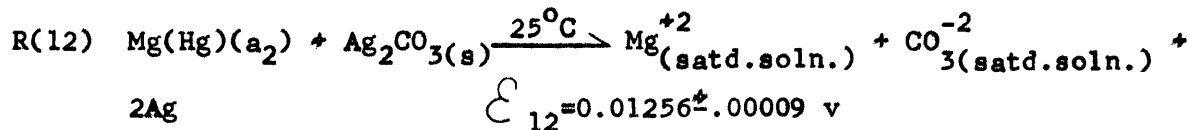
The changes of free energy for the following cell reactions are computed below and the results presented in Table 6.





$$\Delta G_{10} = -n F \mathcal{E}_{10} = (-2)(96500)(0.0251 \pm 0.0001)$$

$$= -4.85 \pm 0.02 \text{ kcal}$$



$$\Delta G_{12} = -n F \mathcal{E}_{12} = (-2)(96500)(0.01256 \pm 0.00009)$$

$$= -2.42 \pm 0.02 \text{ kcal}$$

TABLE 6

Changes of Free Energy for Cell Reactions

| Reaction | ΔG (kcal) |
|----------|-------------------|
| R(14) | -10.31 \pm 0.09 |
| R(15) | - 3.9 \pm 0.1 |
| R(1) | - 7.87 \pm 0.07 |
| R(2) | - 7.32 \pm 0.09 |
| R(10) | - 4.85 \pm 0.02 |
| R(12) | - 2.42 \pm 0.02 |

Free Energy of Formation of Dolomite

On the basis of the above experimental data and the free energy data for $\text{CaCO}_3(c)$, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(s)$, and $\text{H}_2\text{O}(l)$, Table 1, the free energy of formation of dolomite can be computed as follows.

$$\Delta G_{f, 25^\circ\text{C}, \text{CaMg}(\text{CO}_3)_2}^\circ = \Delta G_{14} + \Delta G_{15} - \Delta G_{10} - \Delta G_{12} + \Delta G_{f, 25^\circ\text{C}, \text{CaCO}_3}^\circ + \Delta G_{f, 25^\circ\text{C}, \text{MgCO}_3 \cdot 3\text{H}_2\text{O}}^\circ - 3 \Delta G_{f, 25^\circ\text{C}, \text{H}_2\text{O}}^\circ$$

$$= -519 \pm 1 \text{ kcal/mole}$$

This value agrees, within the experimental precision, with those values reported by Stout and Robie (1963), -518637 ± 664 cal/mole, Garrels, Thompson, and Siever (1960), -520410 cal/mole, and Halla (1949),

-518855 cal/mole, but does not agree with the value reported by Langmuir (1964), -516600 ± 500 cal/mole.

Free Energy of Formation of Huntite

The following computation is based on the experimental emf data and literature data for $\text{CaCO}_3(\text{c})$, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s})$, and $\text{H}_2\text{O}(\text{l})$.

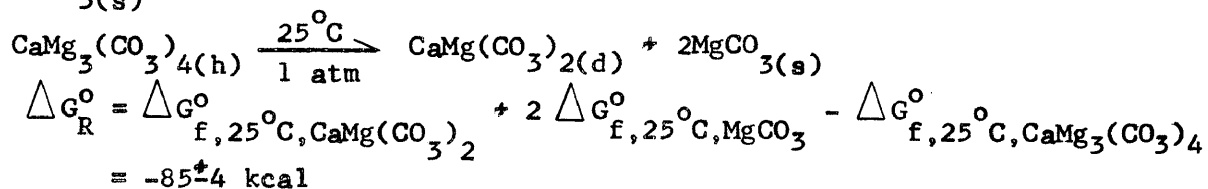
$$\begin{aligned} \Delta G_{f, 25^\circ\text{C}, \text{CaMg}_3(\text{CO}_3)_4}^\circ &= \Delta G_1 + 3 \Delta G_2 - \Delta G_{10} - 3 \Delta G_{12} + \\ \Delta G_{f, 25^\circ\text{C}, \text{CaCO}_3}^\circ + 3 \Delta G_{f, 25^\circ\text{C}, \text{MgCO}_3 \cdot 3\text{H}_2\text{O}}^\circ - 9 \Delta G_{f, 25^\circ\text{C}, \text{H}_2\text{O}}^\circ & \\ = -915 \pm 3 \text{ kcal/mole} & \end{aligned}$$

This value does not agree with that reported by Garrels, Thompson, and Siever (1960), i.e., -1007000 cal/mole. It should be noted that those authors expressed considerable doubt concerning the accuracy of their reported value.

CONCLUSIONSPotential Stability of Huntite

As previously outlined, one of the objectives of this study was to ascertain the potential stability of huntite at 25°C, $P_{\text{total}} = 1 \text{ atm}$, $P_{\text{CO}_2} = 10^{-3} \text{ atm}$, and $P_{\text{H}_2\text{O}} > P_{\text{H}_2\text{O}(\text{eq})}$. This can now be accomplished by using the above experimentally determined value for the free energy of formation of huntite.

If this compound is potentially stable at these conditions, then it can not decompose to the potentially stable phases $\text{CaMg}(\text{CO}_3)_2(\text{d})$ and $\text{MgCO}_3(\text{s})$.



Since the above reaction is spontaneous to the right, this means that huntite is not potentially stable at 25°C and $P_{\text{total}} = 1 \text{ atm}$.

It is interesting to note that if the value reported by Garrels, Thompson, and Siever (1960) for $\Delta G_{\text{f}, 25^\circ\text{C}, \text{CaMg}_3(\text{CO}_3)_4}^{\circ}$ is used in the above calculation, ΔG for the reaction is equal to +6.2 kcal. This

would mean that huntite is potentially stable at these conditions. Also, if this writer's $\Delta G_{f,25^\circ\text{C},\text{CaMg}(\text{CO}_3)_2}^\circ = -519 \pm 1$ kcal/mole is used in the above calculation, the result is that huntite is determined to be not potentially stable when $\Delta G_{f,25^\circ\text{C},\text{CaMg}_3(\text{CO}_3)_4}^\circ$ is that value determined in this study and to be potentially stable when $\Delta G_{f,25^\circ\text{C},\text{CaMg}_3(\text{CO}_3)_4}^\circ$ is that of Garrels, Thompson, and Siever (1960).

Application of the Calculation Scheme

The other objective of this study was to contribute to the understanding of the applicability of free energy data to complex systems. As noted above, this will be accomplished by application of the calculation scheme, which was introduced in this study, to the problem of determining the stable states for the following compositional regions: CaO-MgO-CO₂, MgO-MgCO₃-MgCO₃·3H₂O-Mg(OH)₂, and CaO-MgO-Mg(OH)₂-Ca(OH)₂ at 25°C, $P_{\text{total}} = 1$ atm, $P_{\text{CO}_2} = 10^{-3}$ atm, and $P_{\text{H}_2\text{O}} \geq P_{\text{H}_2\text{O}(\text{eq})}$.

Stable States for the CaO-MgO-CO₂ Region

As previously outlined, this calculation scheme consists of the application of three rules for the determination of the stable phases and the calculation of their respective amounts for any specified bulk composition in multicomponent systems. The required experimental data are a list of the potentially stable phases and their free energies of formation.

The potentially stable phases in this region at 25°C, $P_{\text{total}} = 1$ atm, $P_{\text{CO}_2} = 10^{-3}$ atm are the components, CaO_(s), MgO_(s), and CO_{2(g)}, and the compounds CaCO_{3(c)}, MgCO_{3(c)}, and CaMg(CO₃)_{2(d)}. Since each of these phases is potentially stable, all combinations of these components and compounds

must be initially considered as possible stable states. The maximum number of coexistent phases is three as determined by the phase rule. From this list of all possible combinations of components and compounds (Table 7) one can select the stable state for a specific bulk composition by sequentially applying the three rules of this calculation scheme.

By considering the list of potentially stable compounds, the first rule can be applied to reject those combinations which can not be possible stable states for any bulk composition in this system at these conditions. (Table 8). Any combination containing CaO-CO_2 , MgO-CO_2 , or $\text{CaCO}_3\text{-MgCO}_3$ can not be a possible stable state, since these constituents will spontaneously react to produce $\text{CaCO}_3(\text{c})$, $\text{MgCO}_3(\text{s})$, and $\text{CaMg}(\text{CO}_3)_2(\text{d})$, respectively, and further lower the free energy of the system.

The application of the second rule can be accomplished by deriving a series of test equations for each combination which, according to the first rule, is a possible stable state, and then, by testing to see which assemblage of phases can be produced from a specific bulk composition. The selected bulk composition is the following.

$$T_{\text{CaO}} = 43 \text{ moles,}$$

$$T_{\text{MgO}} = 10 \text{ moles,}$$

$$T_{\text{CO}_2} = 47 \text{ moles.}$$

For example, the test equations for the combination $\text{MgO-CaCO}_3(\text{c})\text{-CaMg}(\text{CO}_3)_2(\text{d})$ are derived as follows. Since CO_2 and CaO do not appear in the combination, then

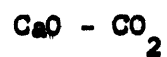
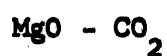
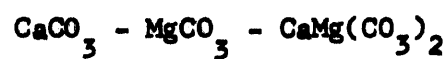
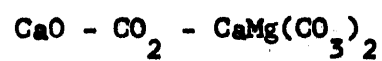
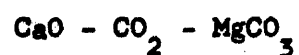
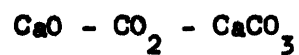
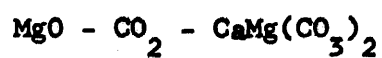
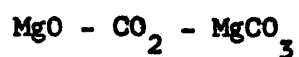
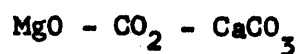
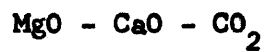
$$T_{\text{CO}_2} = (\text{CAL}) + 2(\text{DOL})$$

and

$$T_{\text{CaO}} = (\text{CAL}) + (\text{DOL}),$$

TABLE 8

List of Combinations Rejected as Possible Stable States



where (CAL) and (DOL) are the moles of $\text{CaCO}_3(\text{c})$ and $\text{CaMg}(\text{CO}_3)_2(\text{d})$, respectively, in the combination. Solving these two equations for the two unknowns, (CAL) and (DOL), one obtains

$$(\text{DOL}) = T_{\text{CO}_2} - T_{\text{CaO}}$$

and

$$(\text{CAL}) = 2T_{\text{CaO}} - T_{\text{CO}_2}.$$

Also, since MgO appears in the combination, then

$$(\text{MgO}) = T_{\text{MgO}} - (\text{DOL}) = T_{\text{MgO}} - T_{\text{CO}_2} + T_{\text{CaO}}.$$

where (MgO) is the moles of MgO in the combination. Since $(\text{DOL}) > 0$,

$(\text{CAL}) > 0$, and $(\text{MgO}) > 0$, the test equations are

$$T_{\text{CO}_2} - T_{\text{CaO}} > 0,$$

$$2T_{\text{CaO}} - T_{\text{CO}_2} > 0,$$

and

$$T_{\text{MgO}} - T_{\text{CO}_2} + T_{\text{CaO}} > 0.$$

For the selected bulk composition to have produced this combination, all three test equations must be satisfied.

Each combination that passed the first rule as a possible stable state was tested by the second rule (Table 9). The only two combinations that could be made from the specified bulk compositions are

$$\text{MgO}-\text{CaCO}_3(\text{c})-\text{CaMg}(\text{CO}_3)_2(\text{d}) \quad \left\{ \begin{array}{l} (\text{MgO})= 6 \text{ moles} \\ (\text{CAL})=39 \text{ moles} \\ (\text{DOL})= 4 \text{ moles} \end{array} \right.$$

and

$$\text{CaO}-\text{CaCO}_3(\text{c})-\text{CaMg}(\text{CO}_3)_2(\text{d}) \quad \left\{ \begin{array}{l} (\text{CaO})= 6 \text{ moles} \\ (\text{CAL})=27 \text{ moles} \\ (\text{DOL})=10 \text{ moles} \end{array} \right.$$

The third rule is now applied to these two combinations to determine the stable state, i.e., which combination results from those reactions producing the greatest decrease in the free energy of the system, Table 10.

TABLE 9

Application of Rule No. 2

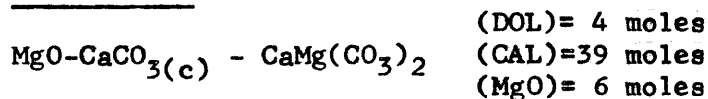
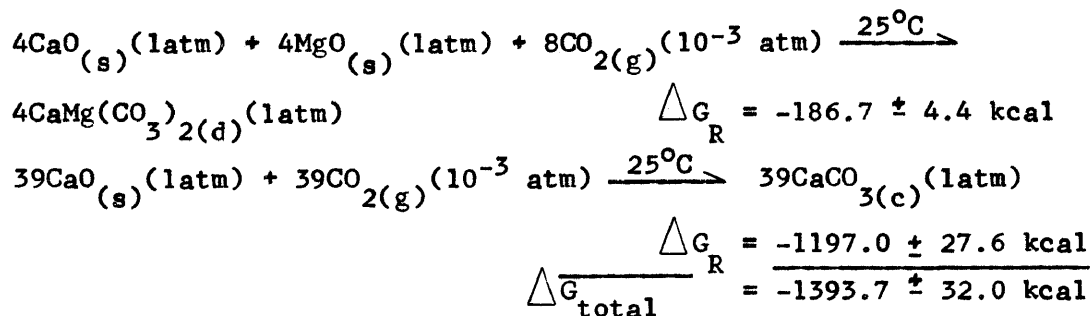
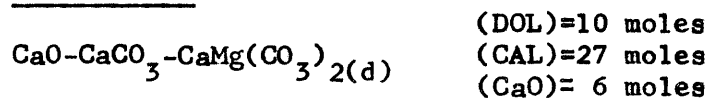
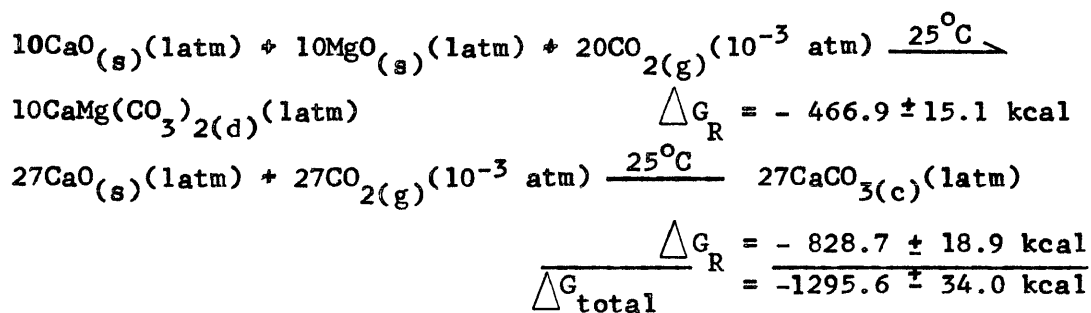
| <u>COMBINATIONS</u> | <u>TEST EQUATIONS</u> | <u>TEST</u> |
|----------------------------|---|---|
| MgO, CaO, CAL | $(CAL) = T_{CO_2} > 0$ $(CaO) = T_{CaO} - T_{CO_2} > 0$ $(MgO) = T_{MgO} > 0$ | $(CAL) = 47$ $(CaO) = -4$ $(MgO) = 10$ |
| MgO, CaO, MAG | $(MAG) = T_{CO_2} > 0$ $(MgO) = T_{MgO} - T_{CO_2} > 0$ $(CaO) = T_{MgO} > 0$ | $(MAG) = 47$ $(MgO) = -37$ $(CaO) = 43$ |
| MgO, CaO, DOL | $(DOL) = \frac{1}{2}T_{CO_2} > 0$ $(MgO) = T_{MgO} - \frac{1}{2}T_{CO_2} > 0$ $(CaO) = T_{CaO} - \frac{1}{2}T_{CO_2} > 0$ | $(DOL) = 23.5$ $(MgO) = -13.5$ $(CaO) = 19.5$ |
| MgO, CAL, DOL | $(MgO) = T_{MgO} - T_{CO_2} + T_{CaO} > 0$ $(CAL) = 2T_{CaO} - T_{CO_2} > 0$ $(DOL) = T_{CO_2} - T_{CaO} > 0$ | $(MgO) = 6$ $(CAL) = 39$ $(DOL) = 4$ |
| MgO, MAG, DOL | $(MgO) = T_{MgO} - T_{CO_2} + T_{CaO} > 0$ $(MAG) = T_{CO_2} - 2T_{CaO} > 0$ $(DOL) = T_{CaO} > 0$ | $(MgO) = 6$ $(MAG) = -39$ $(DOL) = 43$ |
| CaO, CAL, DOL | $(CaO) = T_{CaO} - T_{CO_2} + T_{MgO} > 0$ $(CAL) = T_{CO_2} - 2T_{MgO} > 0$ $(DOL) = T_{MgO} > 0$ | $(CaO) = 6$ $(CAL) = 27$ $(DOL) = 10$ |
| CaO, MAG, DOL | $(CaO) = T_{CaO} - T_{CO_2} + T_{MgO} > 0$ $(MAG) = 2T_{MgO} - T_{CO_2} > 0$ $(DOL) = T_{CO_2} - T_{MgO} > 0$ | $(CaO) = 6$ $(MAG) = -27$ $(DOL) = 37$ |
| CO ₂ , CAL, DOL | $(CO_2) = T_{CO_2} - T_{CaO} - T_{MgO} > 0$ $(CAL) = T_{CaO} - T_{MgO} > 0$ $(DOL) = T_{MgO} > 0$ | $(CO_2) = -6$ $(CAL) = 33$ $(DOL) = 10$ |
| CO ₂ , MAG, DOL | $(CO_2) = T_{CO_2} - T_{MgO} - T_{CaO} > 0$ $(MAG) = T_{MgO} - T_{CaO} > 0$ $(DOL) = T_{CaO} > 0$ | $(CO_2) = -6$ $(MAG) = -33$ $(DOL) = 43$ |
| MgO, CAL | $T_{CaO} - T_{CO_2} = 0$ $(CAL) = T_{CO_2} > 0$ $(MgO) = T_{MgO} > 0$ | $T_{CaO} - T_{CO_2} = -4$ |

| | | |
|-----------------------|--|-------------------------------------|
| MgO, DOL | $T_{CO_2} - 2T_{CaO} = 0$ $(DOL) = T_{CaO} > 0$ $(MgO) = T_{MgO} - T_{CaO} > 0$ | $T_{CO_2} - 2T_{CaO} = -39$ |
| CaO, MAG | $T_{MgO} - T_{CO_2} = 0$ $(MAG) = T_{CO_2} > 0$ $(CaO) = T_{CaO} > 0$ | $T_{MgO} - T_{CO_2} = -37$ |
| CaO, DOL | $T_{CO_2} - 2T_{MgO} = 0$ $(DOL) = T_{MgO} > 0$ $(CaO) = T_{CaO} - T_{MgO} > 0$ | $T_{CO_2} - 2T_{MgO} = 27$ |
| CO ₂ , DOL | $T_{CaO} - T_{MgO} = 0$ $(DOL) = T_{MgO} > 0$ $(CO_2) = T_{CO_2} - 2T_{CaO} > 0$ | $T_{CaO} - T_{MgO} = 33$ |
| CAL, DOL | $T_{CO_2} - T_{CaO} - T_{MgO} = 0$ $(CAL) = T_{CaO} - T_{MgO} > 0$ $(DOL) = T_{MgO} > 0$ | $T_{CO_2} - T_{CaO} - T_{MgO} = -6$ |
| MAG, DOL | $T_{CO_2} - T_{MgO} - T_{CaO} = 0$ $(MAG) = T_{MgO} - T_{CaO} > 0$ $(DOL) = T_{CaO} > 0$ | $T_{CO_2} - T_{MgO} - T_{CaO} = -6$ |
| DOL | $T_{CaO} - T_{MgO} = 0$ $T_{CaO} - \frac{1}{2}T_{CO_2} = 0$ $(DOL) = T_{CaO} > 0$ | $T_{CaO} - T_{MgO} = 33$ |
| MgO, CaO | $T_{CO_2} = 0$ $(CaO) = T_{CaO} > 0$ $(MgO) = T_{MgO} > 0$ | $T_{CO_2} = 47$ |
| MgO, MAG | $(MAG) = T_{CO_2} > 0$ $(MgO) = T_{MgO} - T_{CO_2} > 0$ $T_{CaO} = 0$ | $T_{CO_2} = 43$ |
| CaO, CAL | $(CAL) = T_{CO_2} > 0$ $(CaO) = T_{CaO} - T_{CO_2} > 0$ $(MgO) = T_{MgO} = 0$ | $T_{MgO} = 10$ |
| CO ₂ , CAL | $(CAL) = T_{CaO} > 0$ $(CO_2) = T_{CO_2} - T_{CaO} > 0$ $(MgO) = T_{MgO} = 0$ | $T_{MgO} = 10$ |

| | | | |
|-----------------------|---|-------------------------------|----|
| CO ₂ , MAG | $\begin{aligned} (\text{MAG}) &= T_{\text{MgO}} > 0 \\ (\text{CO}_2) &= T_{\text{CO}_2} - T_{\text{MgO}} > 0 \\ (\text{CaO}) &= T_{\text{CaO}} = 0 \end{aligned}$ | T _{CaO} = | 43 |
| MgO | $\begin{aligned} T_{\text{CaO}} &= 0 \\ T_{\text{CO}_2} &= 0 \\ (\text{MgO}) &= T_{\text{MgO}} > 0 \end{aligned}$ | T _{CO₂} = | 47 |
| CaO | $\begin{aligned} T_{\text{MgO}} &= 0 \\ T_{\text{CO}_2} &= 0 \\ (\text{CaO}) &= T_{\text{CaO}} > 0 \end{aligned}$ | T _{CO₂} = | 47 |
| CO ₂ | $\begin{aligned} T_{\text{CaO}} &= 0 \\ T_{\text{MgO}} &= 0 \\ (\text{CO}_2) &= T_{\text{CO}_2} > 0 \end{aligned}$ | T _{MgO} = | 10 |
| CAL | $\begin{aligned} T_{\text{MgO}} &= 0 \\ (\text{CAL}) &= T_{\text{CaO}} > 0 \\ T_{\text{CaO}} - T_{\text{CO}_2} &= 0 \end{aligned}$ | T _{MgO} = | 10 |
| MAG | $\begin{aligned} T_{\text{CaO}} &= 0 \\ (\text{MAG}) &= T_{\text{MgO}} > 0 \\ T_{\text{MgO}} - T_{\text{CO}_2} &= 0 \end{aligned}$ | T _{CaO} = | 43 |

TABLE 10

Application of Rule No. 3

COMBINATIONREACTIONS and FREE ENERGY CHANGESCOMBINATIONREACTIONS and FREE ENERGY CHANGES

Since 39 moles of $\text{CaCO}_3(\text{c})$, 4 moles of $\text{CaMg}(\text{CO}_3)_2(\text{d})$, and 6 moles of $\text{CaO}_{(\text{s})}$ have resulted from the reactions producing the greatest decrease in the free energy of the system, this combination is the stable state for bulk composition of 43 moles CaO , 10 moles MgO , and 47 moles CO_2 .

It should be noted that since the maximum number of coexistent phases in this system at constant temperature and pressure is three, this

information concerning the stable state for the selected bulk composition noted above is sufficient for one to determine the stable states for all other bulk compositions in this system as graphically illustrated in Figure 8.

Stable States for the MgO-MgCO₃-MgCO₃.3H₂O-Mg(OH)₂ Region

Since there are no potentially stable phases within this compositional region and since the maximum number of coexistent phases is three, then there are only two possible ways to draw the alkemade lines. This limits the possible combinations to MgO-MgCO₃-MgCO₃.3H₂O and MgO-MgCO₃-Mg(OH)₂, for the bulk composition of

10 moles H₂O

65 moles MgO

25 moles CO₂.

Thus, the first and second rules of the calculation scheme need not be applied and the third rule can be directly applied to determine which of these two combinations is the stable state for the above bulk composition (Table 11).

TABLE 11

Application of Rule No. 3

COMBINATION

MgO-MgCO₃-MgCO₃.3H₂O

(MgO)=40 moles

(MAG)=15 moles

(Mag.3H)=10 moles

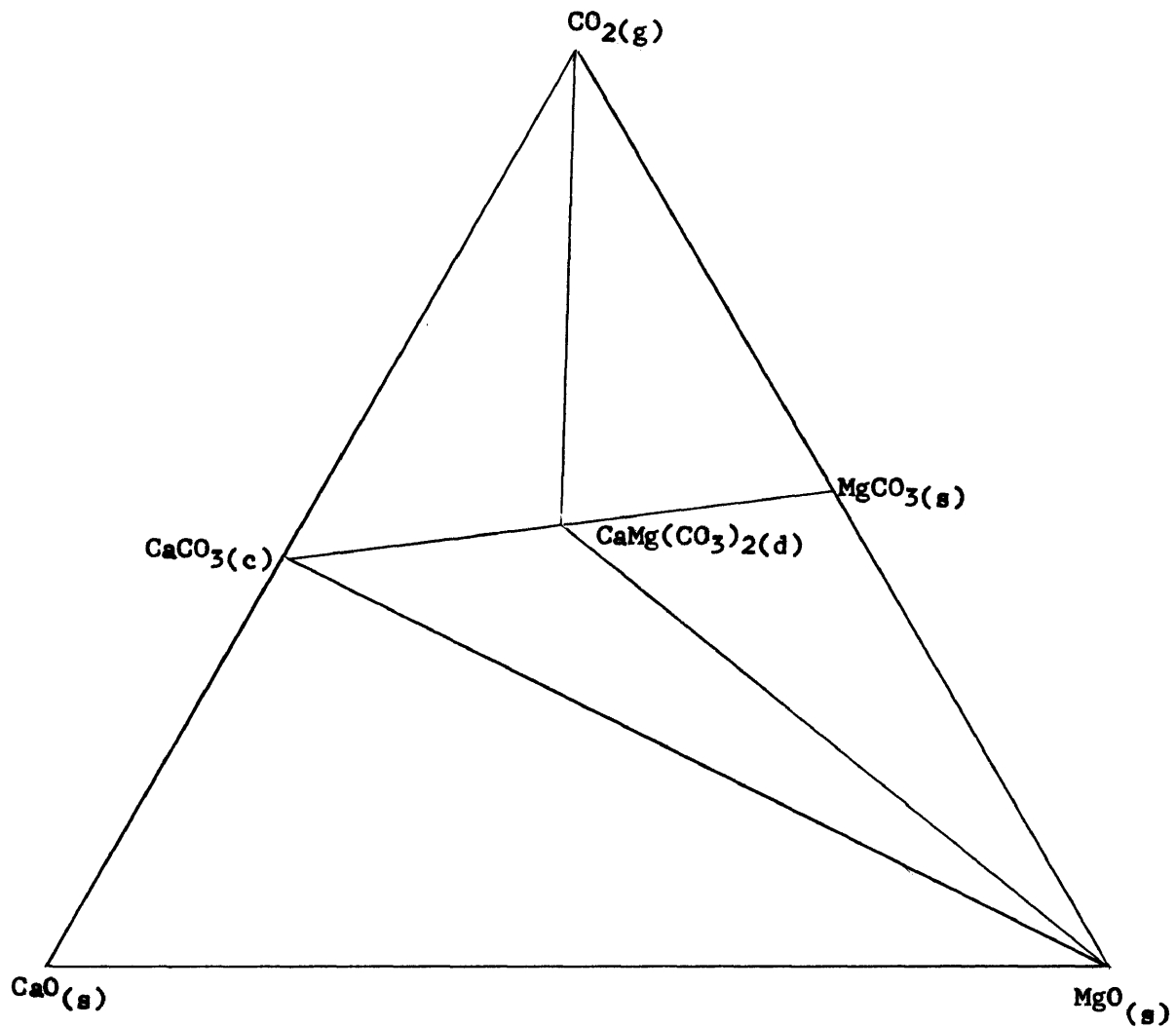
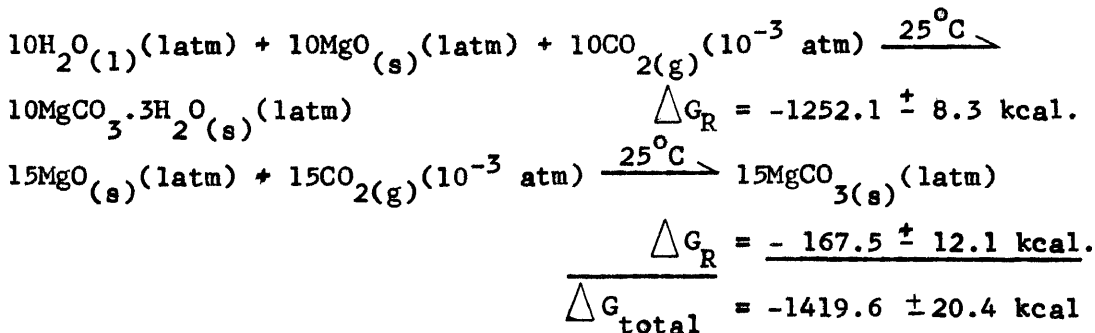
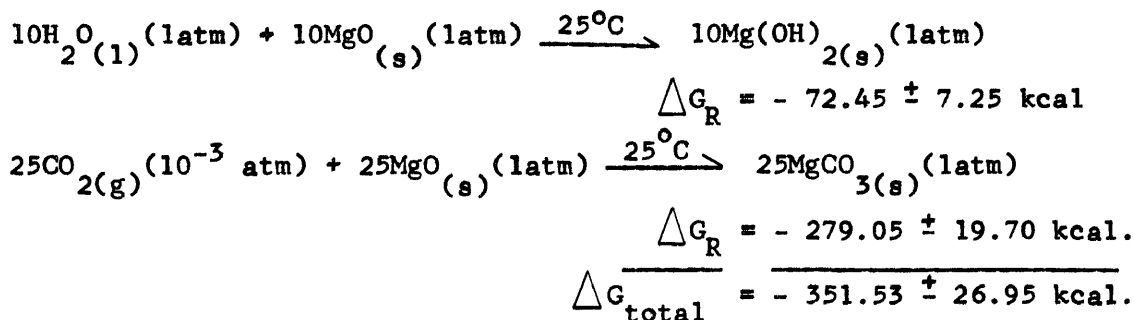


Figure 8. - CaO-MgO-CO₂ System (25 °C, $P_{\text{total}} = 1 \text{ atm}$, $P_{\text{CO}_2} = 10^{-3} \text{ atm}$)

REACTIONS and FREE ENERGY CHANGESCOMBINATIONREACTIONS and FREE ENERGY CHANGES

Thus, since the combination 40 moles MgO, 15 moles MgCO₃, and 10 moles MgCO₃·3H₂O has resulted from those reactions producing the greatest decrease in the free energy of the system, it is the stable state for the above bulk composition. This means that the alkemade line should be drawn between MgO and MgCO₃·3H₂O, as indicated by the dashed line in Figure 3.

Stable States for the CaO-MgO-Mg(OH)₂-Ca(OH)₂ Region

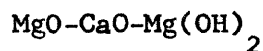
From arguments identical to those given for the MgO-MgCO₃-MgCO₃·3H₂O-Mg(OH)₂ region it is seen that the third rule of the calculation scheme can be applied to the two combinations MgO-CaO-Mg(OH)₂ and MgO-CaO-Ca(OH)₂

for the bulk composition 10 moles H_2O , 40 moles MgO , and 50 moles CaO (Table 12).

TABLE 12

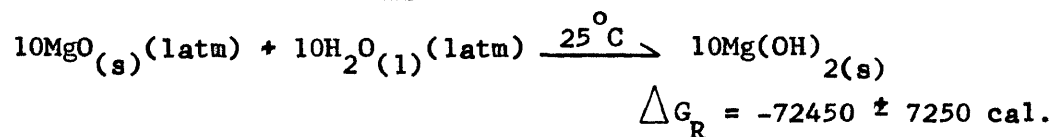
Application of Rule No. 3

COMBINATION

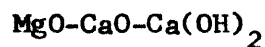


(MgO)=30 moles
(CaO)=50 moles
(MOH)=10 moles

REACTIONS and FREE ENERGY CHANGES

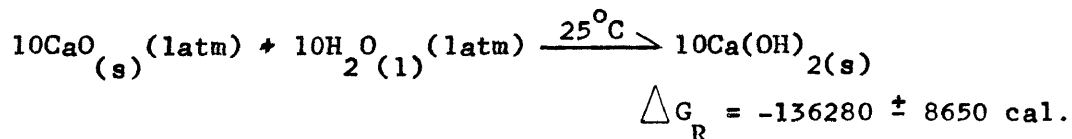


COMBINATION



(MgO)=40 moles
(CaO)=40 moles
(COH)=10 moles

REACTIONS and FREE ENERGY CHANGES



It is evident that the combination 40 moles MgO , 40 moles CaO , and 10 moles $Ca(OH)_2$ is the stable state for the above bulk composition. Therefore, the alkemade line should be drawn between MgO and $Ca(OH)_2$ as indicated by the dashed line in Figure 4.

Contribution to the Solution of the Geologic Problem

Any conclusion regarding the origin of a deposit of dolomite should obviously be based on all available geologic evidence, i.e., field and laboratory data. A geologist may be able to reach a conclusion on the basis of field data as to which one of the three general categories the origin of a specific dolomite deposit belongs, i.e., whether dissolution of solid phases, wet secondary origin, or wet primary origin. But the application of laboratory data to the problems of dolomite genesis enables the geologist to be more specific in his choice of a process. For example, Faust and Callaghan (1948) came to the conclusion on the basis of field data that the origin of the Carrant Creek, Nevada dolomite could be classified as a wet secondary origin. They cited laboratory data to substantiate the specific process of Mg^{+2} in ascending hydrothermal solutions replacing the Ca^{+2} in the calcite present in the porous tuff beds.

As evidenced by the above example, if the geologist attempts to select a process for the origin of a specific dolomite deposit, then he must consider thermodynamic and/or kinetic laboratory data. But before the appropriate questions can be asked of thermodynamics or kinetics the investigator must make an assumption regarding the chemical system to be considered. The questions to be asked of thermodynamics are as follows: (1) what is the range of temperature and pressure at which dolomite is potentially stable? (2) what are the bulk compositions within the appropriate chemical system which should produce dolomite as a stable phase? Kinetics answers such questions as to whether or not dolomite will be produced from such bulk

compositions in a reasonable amount of geologic time and what might be the probable mechanisms for producing dolomite within the appropriate chemical system.

This thesis has been limited to considering the questions asked of thermodynamics. The omission of kinetic considerations means only that kinetics is a separate question and not of secondary importance. Also, this thesis has been further restricted to considering the thermodynamic questions relating to the $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ system at 25°C , 1 atm total pressure and $P_{\text{CO}_2} = 10^{-3}$ atm. It is the writer's opinion that this system should be understood before attempting to consider the relatively more complex systems found in lakes, lagoons, sea-water, and hydrothermal solutions. But, these complex systems must be eventually understood in order for the geologist to have answers to the questions regarding the compositions of aqueous solutions which should produce dolomite as a stable phase.

These systems found in lakes, lagoons, sea-water, and hydrothermal solutions are more complex than those which have been investigated in the laboratory. The limitations on laboratory investigations are not only due to the tedious experimental work required for such multicomponent systems, but are also due to the difficulty in portraying the experimental results. For the unary, binary, and ternary systems, exact description of the stable states can be accomplished by graphical means. Various approximations must be introduced to represent the stable states for other multicomponent systems on a plane diagram. Thus research has been limited to the simple systems. This limitation is a real hinderance to the application of laboratory data to most mineral genesis problems. The calculation scheme introduced in

this study removes this limitation by eliminating the need for a graphical description. This is accomplished by presenting the results of experimental work on any system in the following form.

- 1) A list of those combinations of potentially stable phases which, according to the first rule, are possible stable states for any bulk composition.
- 2) A list of their respective test equations.
- 3) A list of the free energy changes as functions of temperature and pressure for those reactions producing the potentially stable phases from the components.

From these data it is possible to calculate the stable assemblage of phases at the temperature and pressure of interest for any bulk composition.

Another advantage gained by this calculation scheme is to circumvent the experimental difficulty in determining the stable states. In the CaO-MgO-CO₂ system at 25° C, this difficulty is due to the slow rate of the reactions producing dolomite or huntite.

Before the calculation scheme can be applied to the CaO-MgO-CO₂-H₂O system the following data must be determined.

- 1) Free-energy data of sufficient precision to determine the potential stability of MgCO₃.3H₂O, MgCO₃.Mg(OH)₂.3H₂O, and 3MgCO₃.Mg(OH)₂.3H₂O.
- 2) The existence of quaternary compounds.
- 3) Free energy as a function of temperature, pressure, and composition for the solution phases.

Once these data have been determined, the calculation scheme can be applied

to the $\text{CaO-MgO-H}_2\text{O-CO}_2$ system. Then it becomes reasonable to consider the application of the calculation scheme to the next most complicated case, i.e., the $\text{X-CaO-MgO-CO}_2\text{-H}_2\text{O}$ system, where X is the fifth component. Then the addition of the sixth component, then the seventh, etc., may be considered until one understands the systems complex enough to represent lakes, lagoons, sea-water, and hydrothermal solutions. When all this has been accomplished, the geologist will have the answer to the thermodynamic question, what are the bulk compositions within these natural complex systems which should produce dolomite as a stable phase?

APPENDIX

Symbols

- a: thermodynamic activity
- \mathcal{E} : electrical potential difference
- \mathcal{F} : faraday
- G: Gibbs free energy
- γ : activity coefficient
- K: thermodynamic equilibrium constant
- μ : ionic strength
- n: number of electrons transferred in the balanced chemical reaction

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