

## SOME FREE ENERGY VALUES FROM GEOLOGIC RELATIONS

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### ABSTRACT

Mineral associations in earth surface environments have been used to obtain basic thermochemical data for reactions and compounds of geologic interest. From a study of weathering processes, standard free energies of formation from the elements at 25° C. and one atmosphere total pressure have been estimated for kaolinite (-883 kcal.), muscovite (-1298 kcal.), and K-feldspar (-856 kcal.). From relations in the zone of oxidation of ore deposits a correction has been made to the published value for hydrocerussite (from -409.1 kcal. to -406 kcal.) and a new value for malachite (-217 kcal.). It is suggested that the methods used can be applied to obtain useful free energy values for many other compounds.

### INTRODUCTION

Since 1952, when Latimer published the second edition of his classic "Oxidation Potentials," sufficient free energy data on compounds and ions have been easily available to calculate equilibrium relations for many low temperature-low pressure systems of geologic interest. Although these data are strictly applicable only at 25° C. and 1 atmosphere total pressure, the error in applying them to natural environments at or near the earth's surface is usually small.

Eh-pH diagrams utilizing such data were first used by Pourbaix (1949) as a convenient and provocative method of showing interrelation between solids and dissolved ionic species with special reference to problems of metallic corrosion. Since then, similar diagrams have been used to depict approximate equilibrium relations between minerals and the ions in equilibrium with them in aqueous solution, and the results have been compared to natural relations, especially in problems of atmospheric oxidation of ores, and those of primary chemical precipitation (cf. Garrels and Huber, 1953).

When such diagrams were first constructed, it was with hope that they would bear a faint resemblance to nature, and conceivably might be used like an "ideal gas" or "ideal solution"—as hypothetical models useful in showing how far complex natural relations departed from simple systems involving chemical compounds instead of minerals, and containing only those ions or other dissolved species for which thermochemical information happened to be available.

It has been a surprise to find that these naive chemical analogs of nature are directly useful in many instances. That is to say that numerous calculated solubilities fit those deduced from geologic relations, predicted assemblages of chemical compounds are reflected by identical assemblages of their nearest mineral analogs, and the environment of their

occurrence, expressed on a pH-potential grid, corresponds to that found in the field. In fact, natural systems reflect the diagrams much better than most experimental ones!

The reasons for this agreement seem to be: (1) There is sufficient time available for achievement of near-equilibrium in many natural low temperature aqueous environments. Even though the low temperature activation energies for transformations of silicate structures, for example, are high, and experimental work is well-nigh impossible, the months and years during which natural systems fluctuate through a small range of conditions permit a close approach to equilibrium. (2) The amount of interaction in natural systems is less than might be anticipated from their complexity. For example, the error in calculating the free energy of formation of calcite from solubility data on sea water is small if all the currently known interactions are considered. (3) The effect of biological activity is to add complexity on the one hand, and to catalyze reaction on the other. The net effect seems to be one of increasing reaction rates of well-established reactions, and hence of helping rather than hindering the investigator. (4) In a considerable number of instances, the difference in free energy between a pure synthetic compound and its mineral analog is not large (although the difference may be extremely important for some processes!)

Because of the close correspondence between natural relations and those calculated from free energy data—that is, from experiments carefully designed to approach equilibrium, the interesting possibility arose of obtaining free energy data directly from observations on natural systems. Numerous checks were made by calculating free energies of reaction or of formation for reactions or compounds for which complete free energy data already were available. The results were so encouraging that some values for free energy of formation of minerals hitherto unknown were attempted.

#### CHECK CALCULATIONS

To illustrate the methods used, and to show the degree to which there is quantitative agreement between free energy values calculated from natural relations and those determined by various experimental methods, a few examples are given here of calculation of free energy of formation of substances for which experimental values already have been published.



The argument has raged for years as to whether the low latitude oceans are saturated or supersaturated with calcium carbonate. Thus the system seems to be one that approaches equilibrium. According to

Sverdrup *et al.* (1942, p. 205) the average calcium content of the oceans is about 0.0102 mols per liter, the average  $\text{HCO}_3^-$  is about 0.0018 equivalents per liter, the average pH about 8.2, the ionic strength is 0.7, and the temperature in the vicinity of 25° C.

Assuming equilibrium, we can write:

$$\frac{a_{\text{Ca}^{++}} a_{\text{CO}_3^{--}}}{a_{\text{CaCO}_3\text{solid}}} = k_{\text{CaCO}_3} \quad (1)$$

$$\frac{a_{\text{H}^+} + a_{\text{CO}_3^{--}}}{a_{\text{HCO}_3^-}} = k_{\text{HCO}_3^-} \quad (2)$$

$$\Delta F^\circ_{\text{Reaction}} = RT \ln k = -1.364 \log k_{(25^\circ)} \quad (3)$$

$$\Delta F^\circ_{\text{Reaction}} = \Delta F^\circ_{\text{Ca}^{++}} + \Delta F^\circ_{\text{CO}_3^{--}} - \Delta F^\circ_{\text{CaCO}_3\text{solid}} \quad (4)$$

But  $a_{\text{CaCO}_3}$  solid at 25° C. and 1 atmosphere pressure is unity by convention, and  $a_{\text{Ca}^{++}} = \gamma_{\text{Ca}^{++}} m_{\text{Ca}^{++}}$ , and  $\gamma_{\text{HCO}_3^-} = a_{\text{HCO}_3^-} m_{\text{HCO}_3^-}$ , where  $m$  represents molality and  $\gamma$  the activity coefficient. From Garrels and Dreyer (1952, p. 234),  $\gamma_{\text{Ca}^{++}}$  in seawater is about 0.26, and  $\gamma_{\text{HCO}_3^-}$  about 0.36. At pH = 8.2,  $a_{\text{H}^+} = 10^{-8.2}$ .

Then, from No. 2:

$$a_{\text{CO}_3^{--}} = \frac{k_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-}}{a_{\text{H}^+}}$$

Substituting numerical values:

$$a_{\text{CO}_3^{--}} = \frac{10^{-10.34} 10^{-0.44} 10^{-2.75}}{10^{-8.2}} = 10^{-5.33} \quad (5)$$

Also:

$$a_{\text{Ca}^{++}} = m_{\text{Ca}^{++}} \gamma_{\text{Ca}^{++}}$$

Using the analyzed value of calcium for  $m_{\text{Ca}^{++}}$  (this assumes no important interactions of  $\text{Ca}^{++}$ ) and substituting a numerical value for  $\gamma_{\text{Ca}^{++}}$ :

$$a_{\text{Ca}^{++}} = 10^{-2.01} 10^{-0.59} = 10^{-2.60} \quad (6)$$

Substituting the values from No. 5 and No. 6 in No. 1:

$$\frac{10^{-2.60} 10^{-5.33}}{10^0} = k_{\text{CaCO}_3} = 10^{-7.93}$$

Then this value of  $k$  can be substituted in No. 3:

$$\Delta F^\circ_{\text{reaction}} = -1.364 \log 10^{-7.93}$$

$$\Delta F^\circ_{\text{reaction}} = 10.8 \text{ kcal.}$$

Finally, using this value, and values for  $\Delta F^\circ_{\text{Ca}^{++}}$  and  $\Delta F^\circ_{\text{CO}_3^{--}}$  from Latimer (1952) and substituting in No. 4:

$$10.8 = -132.18 - 126.2 - \Delta F^\circ_{\text{CaCO}_3\text{solid}}$$

$$\Delta F^\circ_{\text{CaCO}_3\text{solid}} = -269.2$$

This compares with the published value for calcite of  $-269.78$  and of aragonite of  $-269.53$  (Latimer, op. cit.).

The calcium carbonate-sea water system is an unusually complex one, owing to the high concentration of salts which makes it difficult to obtain reliable  $\gamma$  values for the ions involved. Yet the check is within one kilocalorie on the basis of a fairly crude calculation. Obviously no information has been obtained on calcite-aragonite relations, for which (Latimer, 1952):

$$\Delta F^\circ_{\text{calcite}} - \Delta F^\circ_{\text{aragonite}} = -0.27 \text{ kcal.}$$

$\Delta F^\circ_{\text{UO}_2\text{CO}_3}$

Another example is the calculation of  $\Delta F^\circ$  for  $\text{UO}_2\text{CO}_3$  (rutherfordine). The mineral is sometimes intimately associated with various uranyl oxide hydrates, or uranyl hydroxyhydrates. The stable hydrate in water is  $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$  (Bullwinkel, 1954, p. 7). From the reaction:



it is apparent that the existence of rutherfordine at equilibrium with  $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$  in nearly pure water at a fixed temperature can occur at a single value for the partial pressure of  $\text{CO}_2$ . Thus in the weathering environment, which is close to  $25^\circ \text{C}$ ., the coexistence of these two species suggests that the equilibrium partial pressure of  $\text{CO}_2$  is close to that of  $\text{CO}_2$  in the atmosphere ( $\cong 10^{-3.5}$  atmospheres). For those conditions the equilibrium constant for the reaction is:

$$k = \frac{1}{P_{\text{CO}_2}} = \frac{1}{10^{-3.5}}$$

The free energy is:

$$\Delta F^\circ_R = -1.364 \log 10^{-3.5} = 4.8 \text{ kcal.}$$

Using Bullwinkel's value of  $\Delta F^\circ$  for  $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$  (op. cit., p. 30) and Latimer's values for the others:

$$\Delta F^\circ_R = \Delta F^\circ_{\text{UO}_2\text{CO}_3} + 2\Delta F^\circ_{\text{H}_2\text{O}} - \Delta F^\circ_{\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}} - \Delta F^\circ_{\text{CO}_2(\text{gas})}$$

$$4.8 = \Delta F^\circ_{\text{UO}_2\text{CO}_3} - 113.4 + 391 + 94.3$$

$$\Delta F^\circ_{\text{UO}_2\text{CO}_3} = -377.1$$

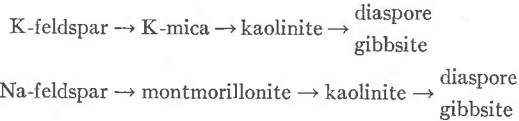
Bullwinkel's listed value is  $-377$ . Actually, his value and the one calculated here have to agree, because he found experimentally that the equilibrium partial pressure of  $\text{CO}_2$  was almost exactly that of the atmosphere, but this experimental determination does not destroy the validity of the preceding geologic reasoning.

These examples illustrate the *general* relation that geologic coexistence of two chemically precipitated phases usually indicates that the free energy of the reaction to form one from the other in their environment

is about 2 kilocalories or less. The phases in question may be compatible or incompatible pairs.

#### RELATIONS DEDUCED FROM WEATHERING PROCESSES

Students of weathering have worked out, from various lines of evidence, a general sequence of mineral stability as follows:



(c.f. Keller, 1957, Reiche, 1945, Goldich, 1938, Mohr and Van Baren, 1954).

In other words, in a system open to rain water, the rock-forming silicates tend to alter to last residue of aluminum oxide hydrates (and ferric oxide where ferric minerals originally are involved). In an idealized system, we can visualize a vertical soil profile under conditions of high rainfall and continuous downward drainage as a steady state condition with zones of stability of the minerals from unaltered silicates at the bottom to aluminous residue near the top.

We have fairly good information on the free energy of formation of gibbsite and boehmite (Deltombe and Pourbaix, 1956, p. 3), at one end of the reaction series, and at the other end only a value for  $\Delta H^\circ$  for orthoclase (Yoder and Eugster, 1955, p. 262). The plan here is to start with gibbsite, and attempt to calculate the free energies of formation of the intermediate products, using  $\Delta H^\circ$  for orthoclase as an approximate check-point at the other end of the series.

#### RELATIONS AMONG THE ALUMINUM OXIDE HYDRATES

Lateritic soils contain a variety of aluminum oxide hydrates. Among the chief minerals are diaspore ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), its dimorph boehmite; and gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). All three of these are found in important quantities, and are intimately associated. Boehmite is probably unstable relative to diaspore under geologic conditions (G. MacDonald, personal communication), but the free energy difference between these minerals is probably small, so that boehmite can form and persist. Recent work by Deltombe and Pourbaix (1956) indicates that gibbsite is stable relative to boehmite in aqueous solution at room temperature.

In summary, the geologic occurrence and thermochemical information are in harmony if it is assumed that gibbsite forms if equilibrium is attained in the presence of nearly pure liquid water, and diaspore and boehmite are the products of disequilibrium, or of heating, and drying. Gibbsite can be looked upon ideally as the product of wet leaching of

silicates; boehmite and diaspore as its dehydration products. Undoubtedly there is further important control by grain size and other complicating factors, but where soil leaching takes place in well drained soils in the presence of nearly pure water, gibbsite is the expected stable phase.

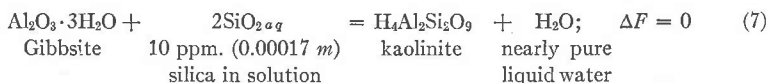
#### RELATION OF KAOLINITE TO ALUMINUM OXIDE HYDRATES

In the weathering of feldspar, kaolinite may or may not be an intermediate product in the formation of aluminum oxide hydrates. Goldman (1955) shows convincingly that feldspar altered directly to gibbsite in the Arkansas bauxite deposits. He further interprets that gibbsite altered to cliaichite (fine-grained aluminum oxide hydrates, probably chiefly monohydrate). This cliaichite is, in turn, selectively altered to kaolinite. Elsewhere, as in the alteration of shales to bauxite, kaolinite is a definite precursor of the aluminum oxide hydrates. Gordon and Tracey (1951, p. 32) tie in some of the resilication of bauxite in Arkansas with waters from overlying swamps.

Thus the reaction:



is clearly reversible under geologic conditions, going to the right when silica content of water is typical of that of swamp water, and to the left at some lower value. Furthermore, the monohydrates seem to be more easily kaolinized than the tri-hydrate, which follows from their relative stabilities in water, but both apparently can be resilicated. A reasonable estimate of the equilibrium condition would be kaolinization of gibbsite at a dissolved silica content of about 10 parts per million at 25° C. Tropical streams carry about three times this amount, average streams a little less (Clarke, 1927, Chap. III). From this the relation can be written:



According to Krauskopf (1956, p. 23) dissolved silica is saturated with respect to its amorphous polymers (silica glass) at a concentration of about 140 ppm. (0.0024 *m*) at 25° C. Thus:

$$\text{SiO}_2 \text{ glass} = \text{SiO}_2 \text{ aq (140 ppm)}; \quad \Delta F = 0$$

$$k = a_{\text{SiO}_2} = 0.0023 \quad (\text{assuming activity} = \text{molality for a molecular species in dilute solutions})$$

$$\Delta F^\circ_{\text{reaction}} = -1.364 \log 0.0023 = 3.5 \text{ kilocalories}$$

Therefore:

$$\Delta F^\circ_{\text{SiO}_2 \text{ aq}} - \Delta F^\circ_{\text{SiO}_2 \text{ glass}} = 3.5 \text{ kilocalories}$$

$$\Delta F^\circ_{\text{SiO}_2 \text{ aq}} = 3.5 + \Delta F^\circ_{\text{SiO}_2 \text{ glass}} = 3.5 - 190.9 = -187.4 \text{ kcal.}$$

For reaction No. 7, the equilibrium constant is:

$$k = \frac{1}{a^2_{\text{SiO}_2}} \frac{1}{(0.00017)^2} = 10^{7.54}$$

$$\Delta F^\circ_R = -1.364 \log 10^{7.54} = -10.3 \text{ kcal.}$$

From the standard free energy of the reaction, and the standard free energy of formation of the reactants and products, it is possible to solve for  $\Delta F^\circ$  of kaolinite.

$$\Delta F^\circ_R = \Delta F^\circ_{\text{kaol.}} + \Delta F^\circ_{\text{H}_2\text{O}} - \Delta F^\circ_{\text{gibbsite}} - 2\Delta F^\circ_{\text{SiO}_2, \text{aq}}$$

$$\Delta F^\circ_{\text{kaol.}} = \Delta F^\circ_R + \Delta F^\circ_{\text{gibbsite}} + 2\Delta F^\circ_{\text{SiO}_2, \text{aq}} - \Delta F^\circ_{\text{H}_2\text{O}}$$

$$\Delta F^\circ_{\text{kaol.}} = -10.3 - 554.6 - 374.8 + 56.7 = -883.0 \text{ kcal.}$$

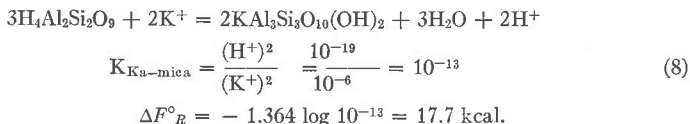
In passing it should be noted that  $\Delta F^\circ_{\text{kaolinite}}$  is not particularly sensitive to the value of soluble silica chosen—a tenfold larger or smaller value would change  $\Delta F^\circ_{\text{kaolinite}}$  by  $\pm 2.6$  kcal.

#### INTERRELATIONS OF KAOLINITE, MICA, AND K-FELDSPAR

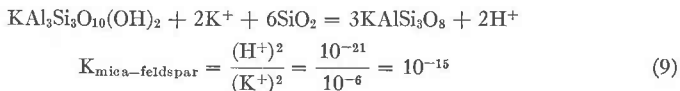
From the field evidence, kaolinization of feldspar seems to take place under almost any soil condition, even at pH values as high as 8 or 9, suggesting that such conditions are sufficient to convert feldspar into mica, and mica into kaolinite. If the feldspar-mica alteration is slow, and the mica-kaolin reaction fast, mica might not even be observed as an intermediate product; in fact it might not form at all as a crystalline material if conditions under which kaolinite is stable are superimposed on a feldspar grain. However, very careful work shows mica as an intermediary between feldspar and kaolin (Sand, 1956). The total evidence indicates that K-feldspar, quartz and K-mica are in equilibrium at a pH and  $\text{K}^+$  content of the system close to but higher than those at which K-mica and kaolin are stable.

Hydrolysis of mica yields maximum pH values of the order of 9.3 (Garrels and Howard) in solutions containing  $\text{K}^+$  ions at activity of about  $10^{-3.0}$  (about 40 ppm.). The reaction involved is a surface reaction transforming K-mica to H-mica, but should be a guide to the boundary between K-mica and kaolin. At any rate the K-mica-kaolin boundary will not be at lower pH at the same  $\text{K}^+$ . Tentatively we can place the K-mica-kaolin boundary at pH 9.5 at a  $\text{K}^+$  activity of  $10^{-3}$ , and the K-feldspar-K-mica boundary at pH 10.5 at the same activity of  $\text{K}^+$ . These values fit geologic relations fairly well; waters at the lower limit of the zone of soil formation must represent conditions very close to equilibrium with feldspar, or at least conditions under which reaction does not take place at a finite rate over long periods of time. Not many pH measurements have been made of waters percolating through at this boundary, but values of 9 to 10 are not uncommon.

Tentatively we can write:



and:



For (8):  $\Delta F^\circ_R = -1.364 \log 10^{-15} = 20.2 \text{ kcal.}$

$$\begin{aligned} \Delta F^\circ_R &= 2\Delta F^\circ_{\text{mica}} + 3\Delta F^\circ_{\text{H}_2\text{O}} + 2\Delta F^\circ_{\text{H}^+} - 3\Delta F^\circ_{\text{kaolin}} + 2\Delta F^\circ_{\text{K}^+} \\ 2\Delta F^\circ_{\text{mica}} &= -3\Delta F^\circ_{\text{H}_2\text{O}} - 2\Delta F^\circ_{\text{H}^+} + 3\Delta F^\circ_{\text{kaolin}} + 2\Delta F^\circ_{\text{H}^+} + \Delta F^\circ_R \\ 2\Delta F^\circ_{\text{mica}} &= +170.1 + 0 - 2649 - 134.9 + 17.7 \\ \Delta F^\circ_{\text{mica}} &= -1298 \text{ kcal.} \end{aligned}$$

For reaction No. 9, assuming first equilibrium with silica glass:

$$\begin{aligned} \Delta F^\circ_R &= 3\Delta F^\circ_{\text{OR}} + 2\Delta F^\circ_{\text{H}^+} - \Delta F^\circ_{\text{mica}} - 2\Delta F^\circ_{\text{K}^+} - 6\Delta F^\circ_{\text{SiO}_2(\text{glass})} \\ 3\Delta F^\circ_{\text{OR}} &= \Delta F^\circ_R - 2\Delta F^\circ_{\text{H}^+} + \Delta F^\circ_{\text{mica}} + 2\Delta F^\circ_{\text{K}^+} + 6\Delta F^\circ_{\text{SiO}_2(\text{glass})} \\ 3\Delta F^\circ_{\text{OR}} &= 20.2 - 0 - 1298 - 134.9 - 1145.4 \\ \Delta F^\circ_{\text{OR}} &= -853 \text{ kcal.} \end{aligned}$$

If it is assumed that equilibrium is with quartz instead of with silica glass:

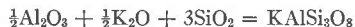
$$\Delta F^\circ_{\text{orthoclase}} = -856 \text{ kcal.}$$

As a check, a value of  $\Delta H^\circ$  for the formation of orthoclase from the oxides can be calculated, and compared with that cited by Yoder and Eugster (1955, p. 263). From the relation:

$$\Delta H^\circ = \Delta F^\circ + T\Delta S^\circ$$

the standard heat of formation can be obtained.

For the reaction to form orthoclase from the oxides:



the standard entropy of reaction is:

$$\Delta S^\circ_R = S^\circ_{\text{OR}} - \frac{1}{2}S^\circ_{\text{Al}_2\text{O}_3} - \frac{1}{2}S^\circ_{\text{K}_2\text{O}} - 3S^\circ_{\text{SiO}_2}$$

Using values of  $S^\circ$  for the oxides from Latimer, and that for orthoclase (adularia) from Kelley, et al (1955, p. 11)

$$\Delta S^\circ_R = 52.5 - 6.1 - 10.4 - 30 = 6 \text{ cal/mol.}$$

For the same reaction:

$$\begin{aligned} \Delta F^\circ_R &= \Delta F^\circ_{\text{OR}} - \frac{1}{2}\Delta F^\circ_{\text{Al}_2\text{O}_3} - \frac{1}{2}\Delta F^\circ_{\text{K}_2\text{O}} - 3\Delta F^\circ_{\text{SiO}_2} \\ \Delta F^\circ_R &= -856 + 188.3 + 38.1 + 577.2 = -52.4 \text{ kcal.} \end{aligned}$$



Then:

$$\Delta H^{\circ}_R = \Delta F^{\circ}_R + T\Delta S^{\circ}_R$$

$$\Delta H^{\circ}_R = -52.4 + (298 \times 0.006) = -50.6 \text{ kcal.}$$

The value cited by Yoder and Eugster (*op. cit.*) is  $-56.4$  kcal. The check, considering the length of the "bridge" used, the uncertainty in the value for gibbsite at one end of the bridge, and the uncertainty in the value for the heat of formation of orthoclase as cited by Yoder, as well as other possible sources of error, is good.

#### SUMMARY

In summary, the following values have been obtained for standard free energies of reactions and of formation of compounds:

TABLE 1. STANDARD FREE ENERGIES

	$\Delta F^{\circ}_{298.1}$ (kilocalories)	
<i>Reaction</i>		
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}_c + 2\text{SiO}_{2\text{aq}} = \text{H}_4\text{Al}_2\text{Si}_2\text{O}_{9c} + \text{H}_2\text{O}_{\text{liq}}$	- 10.3	All reaction values estimated plus or minus 2 kilocalories, with strong possibility of larger errors in values for minerals
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}_c + 2\text{SiO}_{(\text{glass})} = \text{H}_4\text{Al}_2\text{Si}_2\text{O}_{9c} + \text{H}_2\text{O}_{\text{liq}}$	- 17.3	
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}_c + 2\text{SiO}_{2\text{quartz}} = \text{H}_4\text{Al}_2\text{Si}_2\text{O}_{9c} + \text{H}_2\text{O}_{\text{liq}}$	- 20.5	
$3\text{H}_2\text{Al}_2\text{Si}_2\text{O}_{9c} + 2\text{K}_{\text{aq}}^+ = 2\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_{2c} + 3\text{H}_2\text{O}_{\text{liq}} + 3\text{H}_{\text{aq}}^+$	+ 18	
$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_{2c} + 2\text{K}_{\text{aq}}^+ + 6\text{SiO}_{2\text{quartz}} = 3\text{KAlSi}_3\text{O}_{8c} + 2\text{H}_{\text{aq}}^+$	+ 20	
<i>Mineral</i>	$\Delta F^{\circ}$	
Kaolinite	- 883	
K-mica	-1298	
K-feldspar	- 856	

The error on individual determinations is estimated at one or two kilocalories, but the possibility of cumulative errors across the "bridge" are considerable. There still is serious doubt concerning the value for gibbsite, which has been used as a base, because it is based in turn on the somewhat questionable value of  $\alpha\text{Al}_2\text{O}_3$ . But when a firmer value for  $\Delta F^{\circ}$  orthoclase becomes available as a check, it should be possible to fix mica and kaolinite within narrow absolute limits.

#### STANDARD FREE ENERGY OF FORMATION OF $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ AND $\text{Cu}_2(\text{OH})_2\text{CO}_3$

In addition to using natural occurrence to obtain  $\Delta F^{\circ}$  values for compounds for which values have not been obtained experimentally, it is

possible to use it to correct values already determined or to choose between data from conflicting sources.

### $Pb_3(OH)_2(CO_3)_2$

Latimer estimates a  $\Delta F^\circ$  value for  $Pb_3(OH)_2(CO_3)_2$  of  $-409.1$  kilocalories. This compound corresponds to the rare mineral hydrocerussite. In nature cerussite ( $PbCO_3$ ) is the major lead carbonate. If the reaction is written:



then the equilibrium constant, assuming that the groundwater is nearly pure water, is:

$$k = P_{CO_2}$$

$$\Delta F^\circ_R = \Delta F^\circ_{Pb_3(OH)_2(CO_3)_2} + \Delta F^\circ_{CO_2} - 3\Delta F^\circ_{PbCO_3} - F^\circ_{H_2O}$$

$$\Delta F^\circ_R = -409.1 - 94.26 + 449.1 + 56.7 = 2.4 \text{ kcal.}$$

Then:

$$2.4 = -1.364 \log k$$

$$k = 10^{-1.8}$$

Thus the equilibrium partial pressure, according to these relations, is  $10^{-1.8}$  atmospheres of  $CO_2$ . This clearly cannot be the case, for  $PbCO_3$  would be unknown at equilibrium at the earth's surface. Instead, because of its few occurrences, it is much more likely that it forms at a  $P_{CO_2}$  somewhat less than that commonly observed—perhaps at  $10^{-4}$  atmospheres. In this case:

$$k = 10^{-4}$$

$$\Delta F^\circ_R = -1.364 \log 10^{-4} = 5.5 \text{ kcal.}$$

Then, assuming that the correction should be made to  $Pb_3(OH)_2(CO_3)_2$ :

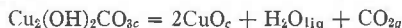
$$5.5 = \Delta F^\circ_{Pb_3(OH)_2(CO_3)_2} - 94.26 + 449.1 + 56.7$$

$$\Delta F^\circ_{Pb_3(OH)_2(CO_3)_2} = -406 \text{ kcal.}$$

This value, 3.1 kilocalories larger than that of Latimer, has been shown to be a minimum by a prettily reasoned application of the phase rule to similar equilibria by W. L. McIntire (unpublished manuscript), but the straightforward application of known mineral occurrence probably suffices.

### $Cu_2(OH)_2CO_3$

Basic copper carbonate, corresponding to the mineral malachite, occurs abundantly in the zone of weathering of copper deposits. In many instances it has been observed intimately intergrown with  $CuO$  (tenorite). From the relation:



it is apparent that in dilute aqueous solution the equilibrium constant contains only  $P_{\text{CO}_2}$ . From the prevalence of malachite occurring alone, but in apparent equilibrium with tenorite in some deposits, it can be concluded that the equilibrium  $P_{\text{CO}_2}$  is perhaps slightly less than that of the normal atmosphere. If so:

$$k = 10^{-3.7}$$

$$\Delta F^\circ_R = 1.364 \log 10^{-3.7} = 5.0 \text{ kcal.}$$

The value of  $\Delta F^\circ_{\text{Cu}_2(\text{OH})_2\text{CO}_3}$  is not available, but accepting those for the other species as given in Latimer:

$$\Delta F^\circ_R = 2\Delta F^\circ_{\text{CuO}} + \Delta F^\circ_{\text{H}_2\text{O}} + \Delta F^\circ_{\text{CO}_2} - \Delta F^\circ_{\text{Cu}_2(\text{OH})_2\text{CO}_3}$$

$$5.0 = -60.8 - 56.7 - 94.26 - \Delta F^\circ_{\text{Cu}_2(\text{OH})_2\text{CO}_3}$$

$$\Delta F^\circ_{\text{Cu}_2(\text{CO})_2\text{CO}_3} = -217 \text{ kcal.}$$

The method could obviously be used to determine  $\Delta F^\circ$  values for other basic copper salts, and work is in progress by P. Hostetler at Harvard University that will compare experimentally determined values with those deduced in this manner.

#### CONCLUSION

The examples given here of the use of natural mineral occurrence to obtain basic thermochemical data suggest that many useful estimates could be made to supplement current values derived almost entirely from laboratory experiment, and further that experimental values can be checked by knowledge of natural occurrence. Many geologists have gone to the laboratory to obtain data to use in explaining geologic phenomena; the possible contributions that might be made by reversing the process seem to be somewhat neglected.

#### ACKNOWLEDGMENTS

I want to express my gratitude to the members of the Geochemistry Seminar at Harvard University, who contributed largely to the development of the ideas presented here. I am especially indebted to P. B. Hostetler and to W. L. McIntire of that Seminar, to J. B. Thompson, and R. Siever, of the Division of Earth Sciences at Harvard, and to C. L. Christ, of the United States Geological Survey, who gave freely of their time in discussing many of the problems involved, and made many valuable suggestions.

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