## Calcite-Aragonite Equilibrium

Abstract. Calcite-aragonite equilibrium, determined with an oscillating Griggs-Kennedy squeezer over the range 100° to 575°C, is given by  $P = 5500 (\pm 500) + 12.6 (\pm 1.5) T$ where pressure is in bars and temperature is in degrees Celsius. Our new determination agrees with earlier hightemperature work but is significantly different from previous low-temperature work. The equilibrium curve obtained can be used to interpret formation of aragonite during metamorphism.

MacDonald (1) used a simple squeezer to determine the calcitearagonite equilibrium pressure over the range 300° to 600°C, though the curve was reversed only from 400° to 600°C. The only work reported at lower temperature is that of Jamieson (2) for the range 29° to 77°C based on the measurement of electrical conductivity of aqueous solutions in equilibrium with calcite and aragonite. Clark (3), with a hydrostatic gas apparatus, determined a reversed point at 575°C. Because the work at low temperature was based on an indirect method, it was

Table 1. Results of  $CaCO_3$  runs; C, calcite; A, aragonite; parentheses denote minor phase, about 5 percent.

Pressure (kb)	Temperature (°C)	Starting material	Products	Time (hr)
11.5	400	С	A+(C)	7
12.2	400	C+(A)	A+(C)	6
10.6	400	A+(C)	C+(A)	11
10.0	400	A+(C)	C+(A)	6
9.0	400	A+(C)	С	6
4.0	100	A+(C)	C+(A)	12
9.0	100	C+(A)	Α	12
6.5	100	C+(A)	C+(A)	6
6.5	13	C+(A)	C+(A)	6
6.5	100	A+(C)	С	12
8.5	100	Α	A+(C)	11
7.5	100	A+(C)	A+(C)	5
7.5	100	С	A+(C)	12
6.5	100	A+(C)	A+(C)	12
5.5	100	A+ C	C+(A)	6
4.0	100	C+(A)	C+(A)	6
11.0	300	Α	A+(C)	6
9.0	300	Α	C+(A)	6
10.0	300	С	C+(A)	12
10.0	300	Α	A+(C)	6
13.2	575	С	A+(C)	1⁄2
12.7	575	Α	c	1⁄2

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desired to determine the equilibrium curve by more direct means.

Dachille and Roy (4) took advantage of the oscillation of one anvil with respect to the other anvil in the Griggs-Kennedy squeezer to study phase equilibria at relatively low temperatures. The general concordance of results from the "oscillating squeezer" with those of hydrostatic devices was discussed by Dachille and Roy; additional theoretical and experimental work by us supports their findings. Their success with several rather refractory materials, similar work by us on coesite-quartz equilibrium at 250°C, and Bell's (5) work on the polymorphs of Al<sub>2</sub>SiO<sub>5</sub> suggested use of the modified apparatus to determine the calcitearagonite equilibrium at relatively low pressures and temperatures. Our numerical results for the calcite-aragonite transition are given in Table 1 and in the curve of Fig. 1. The data of Clark and the curves by MacDonald and Jamieson are also shown in Fig. 1.

Starting material was Baker's "reagent grade" 99.0 percent CaCO<sub>3</sub> which x-ray examination showed to be the calcite form. Aragonite was prepared in two ways: (i) by mixing Na<sub>2</sub>CO<sub>3</sub> and CaCl<sub>2</sub> in water at 100°C and (ii) by placing the CaCO<sub>3</sub> directly in the squeezer and raising the pressure several kilobars into the aragonite field at the desired temperature. X-ray examination of the starting aragonite usually showed some calcite in material made by the first method but very little or none in material made by the second method. Both Clark and MacDonald noted that aragonite made by the first method was transformed, on standing, to calcite. The ease of transformation here is probably due to the very small grain size; the aragonite which has persisted (metastably) in natural environments for geologic times is of larger grain size.

The effect of grain size is dramatically shown in the measurement of the velocity of elastic waves in limestones as a function of pressure. Very finegrained material, such as Solenhofen limestone, exhibits as the pressure is raised, a reversible decrease in velocity of both compressional and shear waves, beginning at about 5 kb; only small hysteresis effects are noted (6). Coarser limestones show the usual small increase of velocity with pressure. This behavior is attributed to the reversible calcite-aragonite reaction in the very fine-grained limestones.

Our results agree with those of Clark, and our data agree with the extrapolation of a point at 800°C and approximately 16 kb by Goldsmith (7). The slope  $(12.6 \pm 1.5 \text{ bars/deg C})$  is somewhat less than either MacDonald's value (16 bars/deg C) or Jamieson's value (16.86 kg/cm<sup>2</sup> deg C). Because Sclar *et al.* (8) used the calcitearagonite equilibrium curve as an aid in the calibration of pressure in their belt-type apparatus, it seems best not to use their results as supporting evidence for the equilibrium conditions.

Runs were made in the squeezer at  $575^{\circ}$ C in order to make direct comparison with Clark's data; the results were identical. This fact suggests that the pressures determined in the oscillating squeezer can be correlated with those measured in a hydrostatic gas apparatus calibrated against the freezing point of mercury, at least for CaCO<sub>3</sub>.

The change in entropy, calculated by the Clapeyron equation with a density value for calcite of  $2.710 \text{ g/cm}^3$ 



Fig. 1. Calcite-aragonite equilibrium. Runs in which the reaction product was mainly aragonite are shown by squares, calcite by circles. The crosses are data obtained by Clark; the first letter shows starting material, the second the end product. J, Jamieson's curve; M, MacDonald's curve. and a density value for aragonite of 2.944 g/cm<sup>3</sup> (9), is 0.88  $\pm$  0.11 cal/mole deg C. This value is in fair agreement with the values of 0.74 and  $1.0 \pm 0.5$  given by Backstrom and Anderson, respectively (1).

The chief geological application of the calcite-aragonite equilibrium curve is in the interpretation of aragonite formed during metamorphism. Occurrences have been reported in the glaucophane schists of California, both in the Ward Creek area and throughout 140 square miles of Franciscan rocks of the Pacheco Pass area, and in New Zealand along the contact between ultramafic rocks and Permian sedimentary and volcanic rocks (10). Revision of the curve to higher pressures implies a somewhat greater depth of burial for the formation of aragonite. A minimum depth of about 18 km is indicated by our data for the stable formation of aragonite rather than calcite, both of pure CaCO3. Because the solubility of MgCO<sub>3</sub> (and probably other related components) in calcite is appreciable at high temperatures (7), the equilibrium curve for solid-solution calcite will be somewhat lower than our present curve (11)

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## **Deuterated Water Effects on Acid Ionization Constants**

Abstract. Linear relations of the form

$$\Delta pK = pK^{\rm D} - pK^{\rm H} = a + b \ pK^{\rm H}$$

relating ionization constants of acids in light and heavy water must have the same slope b for any kind of acid unless the previously unconsidered charge type is important or this equation is not valid.

The difference between the logarithms of acid-ionization constants in normal and heavy water at comparable ionic strengths and temperature has been represented (1, 2) by a linear equation of the form

$$\Delta pK = pK^{\mathrm{D}} - pK^{\mathrm{H}} = a + b \ pK^{\mathrm{H}}.$$
(1)

Such an equation has been applied (2)to carboxylic acids and ammonium ions with different values of b for each kind of acid group. In this report it is shown that such a result is internally inconsistent when the requirements of ionizations from a dibasic acid are considered.

Consider the general case of a dibasic acid with any kind of acid groups and of any type of charge which ionizes by two paths



If the charge on species HAH is x, the charge on species HA and AH is (x-1)and the charge on A is (x-2). The last subscript on k refers to the group from which a hydrogen is being removed.

By titration of a dibasic acid the two acid ionization macroconstants determined are by definition

$$K_1 = (H^+)[(HA) + (AH)]/(HAH)$$
  
 $K_2 = (H^+)(A)/[(HA) + (AH)]$ 

Four ionization microconstants, one for each of the four depicted equilibria. may also be defined,  $k_1 = (H^+)(HA)/$ (HAH), and so forth. The two macroconstants are related to the four microconstants by

$$K_{1} = k_{1} + k_{2}$$

$$K_{2}^{-1} = k_{12}^{-1} + k_{21}^{-1}$$

$$K_{1}K_{2} = k_{1}k_{12} = k_{2}k_{21}$$
(2)

To determine all four microconstants one more item of information in addition to the values of the two macroconstants is required (3) but this is not our concern here.

In logarithmic form Eq. 2 is

$$pK_1 + pK_2 = pk_1 + pk_{12} = pk_2 + pk_{21}$$
(3)

from which

$$pk_1 - pk_{21} = pk_2 - pk_{12} \tag{4}$$

These equations may be written for ordinary hydrogen or deuterated solvents. For the above dibasic acid the difference in sums of the logarithms of the ionization constants in deuterated and normal water is

$$\delta = pK_1^{D} + pK_2^{D} - (pK_1^{H} + pK_2^{H})$$
  
=  $pk_1^{D} + pk_{12}^{D} - (pk_1^{H} + pk_{12}^{H})$  (5)

$$= pk_{2}^{D} + pk_{21}^{D} - (pk_{2}^{H} + pk_{21}^{H})$$
 (6)

where the last two equalities follow from Eq. 3. No assumptions have been made so far; the two ionizing groups may be the same or quite different. For instance, HAH may represent a dicarboxylic acid, a diammonium ion, or an amino acid such as glycine where one acid group is a carboxylic acid and the other a substituted ammonium ion.

Assume that Eq. 1 is valid for an acid of any charge type. Apply Eq. 1 to each of the two ionizing groups in Eqs. 5 and 6 regardless of the net charge on the molecule to obtain

$$\delta = a_1 + b_1 p k_1^{\mathbf{H}} + a_2 + b_2 p k_{12}^{\mathbf{H}}$$
 (7)

$$= a_2 + b_2 p k_2^{\mathrm{H}} + a_1 + b_1 p k_{21}^{\mathrm{H}}$$
 (8)

When equated, the a terms of Eqs. 7 and 8 cancel, yielding

$$b_1 (pk_1^{\mathrm{H}} - pk_{21}^{\mathrm{H}}) = b_2 (pk_2^{\mathrm{H}} - pk_{12}^{\mathrm{H}}).$$

Substitution from Eq. 4 yields

 $b_1 = b_2$ 

We conclude that if the linear relation (Eq. 1) is valid for ionizations from acids of any charge type, the slopes are the same for any kind of acid group. Hence nonidentical slopes (2) obtained from equations of the form of Eq. 1 for carboxylic acid and ammonium ionizations of any type of charge are inconsistent. If we are not willing to accept identical slopes, either type of charge is important or the linear relation of Eq. 1 is not valid. Acid-charge type has not been explicitly considered before and it does seem to be a factor in determining  $\Delta pK$ . Any linear relation is of course approximate and deviations might be ascribed to aterms in Eq. 1 arising from unusual

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