Thermodynamics of Calcium-Isotope-Exchange Reactions. 1. Exchange between **Isotopic Calcium Carbonates and Aqueous Calcium Ions**

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This paper reports our results for the direct experimental determination of the equilibrium constant for the calcium-isotope-exchange reaction ${}^{40}CaCO_3(s) + {}^{44}CaCl_2(aq) \rightleftharpoons {}^{44}CaCO_3(s) + {}^{40}CaCl_2(aq)$. The reaction was studied in electrochemical double cells without liquid junction of the type shown in eq 2. The experimental value of the equilibrium constant at 295 ± 2 K is $K = 1.08 \pm 0.02$. The experimental value for K is compared with the values of K calculated for various model reactions according to the statistical thermodynamic theory of isotope effects. The isotopic solid carbonates were modeled according to both the Debye and Kieffer theories. No structured models of solvated isotopic aqueous calcium ions yield calculated equilibrium constants in agreement with our experimental results. This conclusion is in agreement with published molecular dynamics calculations which show that the aqueous solvation of $Ca^{2+}(aq)$ is essentially unstructured.

Introduction

The stable isotopes of calcium are ${}^{40}Ca$ (96.97%), ${}^{42}Ca$ (0.64), ⁴³Ca (0.145), ⁴⁴Ca (2.06), ⁴⁶Ca (0.0033), and ⁴⁸Ca (0.18). Because the upper limit to the magnitude of thermodynamic isotope effects goes very roughly as the square root of the mass ratio, calcium 48/40 thermodynamic isotope effects are potentially larger than for any other element except hydrogen. This paper reports the results of the first direct experimental determination of the equilibrium constant for a calcium-isotope-exchange reaction. We have investigated the exchange of ${}^{44}Ca^{2+}$ and ${}^{40}Ca^{2+}$ between the isotopic solid carbonates and the aqueous ions

$${}^{40}CaCO_3(s) + {}^{44}Ca^{2+}(aq) \rightleftharpoons {}^{44}CaCO_3(s) + {}^{40}Ca^{2+}(aq) \qquad (1)$$

We chose ${}^{44}Ca^{2+}$ rather than ${}^{48}Ca^{2+}$ because the former isotope is much less expensive than the latter isotope. Reaction 1 was studied in electrochemical double cells without liquid junction of the type

 $Pb(Hg,2-phase)|PbCO_3(s),^{40}CaCO_3(s)|^{40}CaCl_2(aq,m)$ $|Hg_2Cl_2(s)|Hg(l)-Hg(l)|Hg_2Cl_2(s)|^{44}CaCl_2(aq,m)|^{44}CaCO_3(s),$ $PbCO_3(s)|Pb(Hg,2-phase)$ (2)

where Pb(Hg,2-phase) denotes a two-phase (~ 5 wt % Pb) lead amalgam. The Pb(Hg,2-phase)|PbCO₃(s),CaCO₃(s)|Ca²⁺(aq) electrode is an electrode of the third kind that is reversible to Ca²⁺(aq).¹ Our electrochemical measurements show that reaction 1 is the net cell reaction for cell 2. The experimental result for the equilibrium constant for reaction 1 is compared with theoretical values for K calculated by applying the statistical thermodynamic theory of isotope effects to various model reactions.

Experimental Section

Lead amalgam is sensitive to air oxidation, so the cells were set up under a flow of oxygen-free argon gas. Commercially available argon gas was first passed through a two-stage chromous bubbler to remove any traces of oxygen and then through a two-stage presaturator filled with $CaCl_2(aq)$ at the same concentration as the cell electrolyte solutions. The double-cell design is similar to that used to study lithium-isotope-exchange reactions.² A sample of ${}^{44}CaCO_3$ containing 98.55 ± 0.05 atom % ${}^{44}Ca$ was obtained from the Oak Ridge National Laboratory. Naturalabundance primary standard-grade CaCO₃ (96.97 atom % ⁴⁰Ca) was used for ${}^{40}CaCO_3(s)$. The CaCO₃(s) samples were conditioned by storing them under distilled water at 80 °C for several days to convert any contaminating polymorphs (aragonite or vaterite) to calcite. X-ray powder patterns of PbCO₃(s) + $CaCO_3(s)$ mixtures taken from the cells showed no evidence of

any solid phases other than calcite and PbCO₃. In particular, there was no evidence of hydroxycarbonates of lead under our cell conditions.

The lead amalgam was prepared as follows. A 190-g sample of triply distilled Hg(l) (Ballard Bros.) was placed in a beaker and covered with dilute (~ 0.005 M) HNO₃(aq). A 10-g sample of granular lead (analytical reagent grade) was added and dissolved in the Hg by gentle heating. The resulting amalgam was washed several times with dilute HNO₃(aq) while the amalgam was agitated with argon gas. As long as both lead amalgam phases are present in the anode and cathode compartments of a double cell, it is not necessary to know the exact overall concentration of lead in the amalgam because a two-phase, two-component system at fixed temperature and pressure is thermodynamically invariant; that is, the activity of lead in the equilibrium two-phase system is fixed.

Aqueous solutions of ⁴⁰CaCl₂ and ⁴⁴CaCl₂ with the same molality were prepared as follows. Two 2.0-mL samples of 0.10 M HCl(aq) were pipetted into 10.0-mL volumetric flasks and weighed to ± 0.2 mg on an analytical balance. Weighed samples of ⁴⁰CaCO₃(s) and ⁴⁴CaCO₃(s) in about 3% stoichiometric excess were added separately to the flasks. The resulting solutions were dried at 160 °C for 2 days. The volumetric flasks were then evacuated and filled with dry argon gas. Appropriate amounts (about 10 g) of deionized, multiply distilled, deoxygenated water were added to both flasks. The amount of water added was checked by weighing and adjusted to give the same molalities, either by adding small drops of water or by evaporating small amounts of water from the solution by passing a stream of argon gas over its surface.

The cell vessels were constructed from Pyrex glass. The inner walls of the cells were silicone-coated³ to prevent creepage of the aqueous solutions between the electrodes and cell walls. The calomel electrodes were prepared according to the procedures recommended by Hills and Ives.³ After the $Hg(1)|Hg_2Cl_2(s)$ phases were placed in the cell, the cell was evacuated and then filled with argon gas. The ${}^{40}CaCl_2(aq)$ and ${}^{44}CaCl_2(aq)$ solutions then were added to the respective sides of the double cell. Argon from the presaturators was then bubbled through the cell solutions for 30 min. The two-phase lead amalgam was warmed until only one phase was present and then was added to the appropriate cell compartment under a stream of argon gas. Argon gas from the presaturators was again bubbled through the cell for 30 min, and then a mixture of the appropriate carbonates (50 mg of PbCO₃ plus 5 mg of ${}^{40}CaCO_3$ or ${}^{44}CaCO_3$) was placed on the surface of the two-phase lead amalgams in the two halves of the double cell.

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TABLE I: Results of Measurements at 295 ± 2 K on the Cell

Pb(Hg,2-phase)|PbCO₃(s),⁴⁰CaCO₃(s)|⁴⁰CaCl₂(aq,m) $|Hg_2Cl_2(s)|Hg(l)-Hg(l)|Hg_2Cl_2(s)|^{44}CaCl_2(aq,m)|^{44}CaCO_3(s),$ PbCO₃(s)|Pb(Hg,2-phase)

$m_{\rm CaCl_2}/{\rm mol}\cdot{\rm kg}^{-1}$	ϵ^a/mV	ϵ^b/mV
0.010	1.25 ± 0.20	1.17 ± 0.16
0.010	0.99 ± 0.12	0.77 ± 0.21
0.0050	1.25 ± 0.06	1.30 ± 0.07
0.015	0.74 ± 0.04	0.63 ± 0.17
0.0078	0.78 ± 0.18	0.71 ± 0.14

^aThe quoted uncertainties are the standard deviations of the readings taken at 1-h intervals over a 10-h period starting with the birth of the cell. ^bSame as ϵ^a except that the time interval is for the first 24 h of the cell life.

Finally, argon gas from the presaturators was bubbled through the cell for 15 min and the cells were sealed with ground-glass stoppers.

Voltages were measured with an NBS-traceable, certified, Leeds and Northrup type K-3 potentiometer. All cell measurements reported were made at 22 ± 2 °C. Temperatures were measured periodically while the voltage measurements were in progress.

Results

The electrode reactions in the double cell (2) are postulated to be

$$Pb(Hg) + {}^{40}CaCO_3(s) \rightleftharpoons PbCO_3(s) + {}^{40}Ca(aq,m_{40}) + 2e^-$$
$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq,2m_{40})$$
$$2Hg(l) + 2Cl^-(aq,2m_{44}) \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$

 $PbCO_3(s) + {}^{44}Ca^{2+}(aq, m_{44}) + 2e^- \Longrightarrow {}^{44}CaCO_3(s) + Pb(Hg)$

The sum of the four electrode reactions yields the net cell reaction

$${}^{40}CaCO_3(s) + {}^{44}CaCl_2(aq, m_{44}) \rightleftharpoons {}^{44}CaCO_3(s) + {}^{40}CaCl_2(aq, m_{40}) (1')$$

The results of measurements on double cells of the type (2) are given in Table I. Reversibility checks (cell voltage vs cell current) showed no evidence of hysteresis, which is strong evidence that the cells are reversible. A least-squares analysis of the side-cell voltages showed that the cells are Nernstian. The experimental value of the slope of a plot of the side cell emf values vs -ln- $(4m^3\gamma_{\pm}^3)$, using the published mean ionic activity coefficient data for CaCl₂(aq),⁴ is 12.90 \pm 0.10; the theoretical slope is 12.72 \pm 0.09. The Nernstian behavior of the two halves of the double cell provides very strong evidence that the overall cell reaction of the double cell is reaction 2.

Application of the Nernst equation to the net cell reaction 1', with the isotopic aqueous calcium chlorides treated as strong electrolytes, yields

$$\epsilon^{\circ} = \epsilon + \left(\frac{3RT}{2F}\right) \ln \left\{\frac{m_{40}\gamma_{\pm,40}}{m_{44}\gamma_{\pm,44}}\right\}$$
(3)

where ϵ° is the standard cell voltage and $\gamma_{\pm,40}$ and $\gamma_{\pm,44}$ are the mean ionic activity coefficients of ${}^{40}\text{CaCl}_2(\text{aq},m_{40})$ and ⁴⁴CaCl₂(aq, m_{44}), respectively. Because $m_{40} = m_{44}$ and the isotope effect on the activity coefficients is negligible,² we have $\gamma_{\pm,40} =$

 $\gamma_{\pm,44}$ for each of our cells, and therefore $\epsilon^{\circ} = \epsilon$. The average of the ϵ values in Table I for the first 10 h of the cell lives is 1.00 ± 0.24 mV = ϵ°_{av} , which yields an equilibrium constant for reaction 1' at 295 K of $K_1 = \exp(2\epsilon^{\circ}F/RT) = 1.08$ \pm 0.02. The average of the ϵ values in Table I for the first 24 h of the cell lives is 0.92 ± 0.30 mV, which yields $K_1 = 1.08 \pm$ 0.03 at 295 K.

The equilibrium constant determined for reaction 1' applies to the isotopic calcium chlorides treated as strong electrolytes; consequently reaction 1' can be rewritten as

$${}^{40}CaCO_3(s) + {}^{44}Ca^{2+}(aq) \rightleftharpoons {}^{44}CaCO_3(s) + {}^{40}Ca^{2+}(aq)$$
(4)

For convenience in the statistical thermodynamic analysis of various models for reaction 4, we formulate the equilibrium constant for reaction 4 as

$$K_4 = K_{\rm s} K_{\rm aq} \tag{5}$$

where K_s is given by

$$K_{\rm s} = q[{}^{44}{\rm CaCO}_3({\rm s})] / q[{}^{40}{\rm CaCO}_3({\rm s})]$$
(6)

and K_{aq} is given by

$$K_{\rm aq} = q[{}^{40}{\rm Ca}^{2+}({\rm aq})] / q[{}^{44}{\rm Ca}^{2+}({\rm aq})]$$
(7)

The symbol q[i] refers to the partition function of species *i* including zero-point energy terms.

Calculation of K_s . The calcite crystal is rhombohedral, space group D_{3d}^6 , with two formula units in the Bravais cell. One mole of $(CaCO_3)_2$ has $30N_A$ normal vibrations, of which $3N_A$ are acoustic vibrations and $27N_A$ are "optical" vibrations of the Bravais cell contents. Factor group analysis⁵ shows that the latter are distributed $A_{1g} + 2A_{1u} + 3A_{2g} + 3A_{2u} + 4E_g + 5E_u$. In what follows we shall consider the optic and acoustic modes separately.

Excellent single-crystal infrared and Raman data are available for natural-abundance calcite.⁶ The A_{2u} and E_u modes show substantial LO-TO splittings that can be reproduced reasonably well by polarizable-ion-model calculations.⁷ In addition, recent hyper-Raman studies⁸ have also located the (otherwise inactive) A_{1u} modes, which appeared at 1085 and 227 cm⁻¹. An inspection of either a pictorial representation of the normal modes⁶ or the calculated normal coordinates given by Plihal and Schaack9 shows that one A_{1u} , one A_{2u} , and three E_u modes have frequencies that are sensitive to Ca^{2+} substitution.

The frequency shifts for the A_{1u} and A_{2u} modes can be calculated most easily by constructing the pertinent symmetrized G matrices, denoted G_m , and then within each symmetry block applying the Teller-Redlich product rules in the form

$$\frac{\prod_{k}^{i} v_{k}}{\prod_{k}^{j} v_{k}} = \left\{ \frac{\det^{i} G_{m}}{\det^{j} G_{m}} \right\}^{1/2}$$
(8)

Here the superscripts i and j refer to two isotopes of Ca^{2+} , the frequency products extend over all k modes of the *m*th symmetry type, and the determinants of the G_m matrices are computed using the calcium isotopic masses i or j as indicated. For the A_{1u} symmetry block we find

$$\det G_{A_{1u}} = 2\mu_{Ca}\mu_O \tag{9}$$

where μ_x , as usual, designates the reciprocal of the mass of x. For the A_{2u} symmetry block we find

det
$$G_{A_{2u}} = 6\mu_0(3\mu_C + \mu_0)(\mu_{Ca} + \mu_{CO_3})$$
 (10)

Since only one of the A_{1u} and one of the A_{2u} modes involve displacements of the Ca^{2+} ion, only one factor need be retained in the extended products in eq 8 for these two symmetry blocks.

The E_u modes posed a more difficult problem. The observed (powder) spectrum has E_u-symmetry lines at 1484 cm⁻¹ (CO stretch) and 706 cm⁻¹ (OCO def), in addition to the isotopically sensitive lines at 320, 230, and 110 cm⁻¹. We first constructed

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TABLE II: Frequencies (cm⁻¹) of the Isotopically Sensitive Lattice Modes of Natural-Abundance and ⁴⁴Ca Calcites

			A_{2u}		F	Eu	
		$\mathbf{A}_{1\mathbf{u}}$	то	LO	ТО	LO	
	^{na} Ca	227	303	387	297	381	
					223	239	
					102	123	
	44Ca	216.76	294.88	376.63	293.35	376.32	
,					217.05	232.62	
					98.72	119.04	

the symmetrized 5 \times 5 G matrix for the E_u modes and then, although it is only approximately correct, used the high-frequency separation technique¹¹ to eliminate the 1484- and 706-cm⁻¹ vibrations, leaving a new 3×3 G matrix that focused on the modes of interest here. By trial and error we then found a diagonal 3 \times 3 F matrix that reproduced the remaining powder frequencies to within about 1 cm⁻¹. The isotope shifts of the three "computed" E_u vibrations were then calculated by conventional GF-matrix methods. In the thermodynamic calculations that followed, we assumed that each of the observed LO or TO frequencies of the E_u type shifted by the same factor as did its counterpart in the model calculations just described. Table II lists the frequencies of all the isotopically sensitive lattice vibrations of natural-abundance and ${}^{44}Ca^{2+}$ calcites that were used to calculate the contribution of the optical modes to the thermodynamics of the exchange reaction.

The acoustic modes of $(CaCO_3)_2$ were treated by both the classic Debye model and the somewhat more realistic model proposed recently by Kieffer.¹² These models differ in two fundamental respects. The Debye model uses a parabolic function with a sharp cutoff at ω_{max} for the spectral distribution of acoustic modes; that is

$$g(\omega) d\omega = A\omega^2 d\omega; \quad \int_0^{\omega_{\text{max}}} g(\omega) d\omega = 3$$
 (11)

where ω is the angular frequency, and it replaces the separate velocities of propagation of the three acoustic waves (one longitudinal and two transverse) with a "mean" velocity $\langle v \rangle$ calculated from the equation

$$\frac{3}{\langle v \rangle^3} = \frac{1}{v_1^3} + \frac{1}{v_t^3} + \frac{1}{v_t'^3}$$
(12)

For natural-abundance calcite the three propagation velocities are $v_1 = 6.53$, $v_1 = 3.70$, and $v_1' = 2.93$ km·s⁻¹, giving $\langle v \rangle = 3.62$ km·s⁻¹.^{12d} The Debye characteristic temperature θ_D is then calculated from

$$\theta_{\rm D} = \frac{h}{2\pi k} \left(\frac{6\pi^2 N_{\rm A}}{ZV} \right)^{1/3} \langle v \rangle \tag{13}$$

where h and k are the Planck and Boltzmann constants, respectively, and ZV is the molar volume of the crystal in question; i.e., V is the molar volume of CaCO₃ (36.933 cm³·mol⁻¹) and Z = 2. For natural-abundance calcite eq 13 yields $\theta_D = 216.79$ K.

Kieffer's model retains the separate identities of the three acoustic waves and for each of them uses the acoustic spectral distribution function

$$g(\omega,\omega_k) \, \mathrm{d}\omega = \frac{3(2/\pi)^3 [\sin^{-1}(\omega/\omega_k)]^2}{(\omega^2 - \omega_k^2)^{1/2}} \, \mathrm{d}\omega$$
$$\int_0^{\omega_k} g(\omega,\omega_k) \, \mathrm{d}\omega = 1 \tag{14}$$

TABLE III: Free-Energy Functions (cal-mol⁻¹) for Natural-Abundance Calcite

	$-(A^{\circ} - E_0^{\circ})_{acoust}$			-(A° -	$E_0^{\circ})_{\rm tot}$	tot		
T/K	Kieffer	Debye	$-(A^{\circ} - E_0^{\circ})_{opt}$	Kieffer	Debye	$-(G^{\circ} - H_0^{\circ})_{expt}$		
295	886.0	794.4	2152.4	3038.4	2946.8	3005		
200	434.3	375.5	855.0	1289.3	1230.5	1264		
150	241.4	202.6	398.4	639.8	601.0	627		
100	96.9	76.9	116.6	213.5	193.5	211		

which is rigorously correct for linear lattices. In eq 14 ω_k is the angular cutoff frequency of the kth acoustic branch $(1 \le k \le 3)$, calculated from the equations

$$(2\pi)^3 / V_{\rm L} = 4\pi K_{\rm max}^3 / 3 \tag{15}$$

and

$$\omega_k = 2K_{\max} v_k / \pi \tag{16}$$

In eq 15 the quantity $V_{\rm L}$ is the volume of the Bravais cell, which is 122.6×10^{-24} cm³ for $(CaCO_3)_2$.^{12d} The previously mentioned propagation velocities give Kieffer-model cutoff frequencies for natural-abundance $(CaCO_3)_2$ of 174, 99, and 78 cm^{-1.12d}

According to either model, the isotopic sensitivity of the contribution to K_s from the acoustic modes enters via the wavepropagation velocities. We presume that in all the acoustic modes the various Bravais cells move as rigid units. If isotopic substitution does not affect the unit cell volume or the elastic constants, then it follows from elasticity theory¹³ that the velocities of the transverse and acoustic waves will vary inversely as the square roots of the masses of the Bravais cells. In the Debye model θ_D changes by the factor $(i_{CaCO_3}/j_{CaCO_3})^{1/2}$ and in the Kieffer model each of the cutoff frequencies ω_k is multiplied by this same factor.

In an effort to assess the relative merits of the Debye and Kieffer models, we first calculated the temperature dependence of (A°) $-E_0^\circ$) for 1 mol of natural-abundance calcite on the basis of the two models and compared the results with the experimental values of $(G^{\circ} - H_0^{\circ})$ reported by Staveley and Linford.¹⁴ In either model, the 27 optical modes of $(CaCO_3)_2$ contribute an amount to $(A^{\circ} - E_0^{\circ})$ for 1 mol of CaCO₃ given by

$$\frac{1}{2}\sum_{i=1}^{27} RT \ln (1 - e^{-hcv_i/kT})$$
(17)

if the v_i 's are expressed in cm⁻¹. The Debye model for the acoustic modes makes a contribution to the molar value of $(A^{\circ} - E_0^{\circ})$ of

$$\frac{3}{2}RT\left\{\ln\left(1-e^{-\theta_{\rm D}/T}\right)-\frac{1}{3}D\left(\frac{T}{\theta_{\rm D}}\right)\right\}$$
(18)

where $D(T/\theta_{\rm D})$ is the Debye function,¹⁵ not the Debye heat-capacity function. The Kieffer-model result for the acoustic contribution is

$$\frac{1}{2}RT\sum_{k=1}^{3}\int_{0}^{\omega_{k}}\ln\left(1-e^{-\hbar\omega/2\pi kT}\right)g(\omega,\omega_{k}) \,\mathrm{d}\omega \qquad (19)$$

where $g(\omega, \omega_k) d\omega$ is the expression given in eq 14. All the integrals needed both here and later were evaluated by using a set of computer programs written in this laboratory. The results of these calculations are given in Table III. The frequencies used in the optical branch calculation were the observed frequencies reported by Denisov et al.⁸ (A_{1u}) and Yamamoto et al.,¹⁰ together with the values for the three unobserved A_{2g} modes calculated by the latter authors.

Over the temperature range covered here, the Kieffer model gives $-(A^{\circ} - E_0^{\circ})$ magnitudes that are too large by 1.1-2.1% vs

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TABLE IV: Contributions to the Molar Helmholtz Energy Difference of Isotopomeric Calcites

		acoustic contributions/cal				optical contributions/cal			
	-(A° -	$-E_0^{\circ})$	zero-poin	nt energy	-(A° -	- <i>E</i> ₀ °)	zero-poir	nt energy	
	Kieffer	Debye	Kieffer	Debye	TO	LO	ТО	LO	
naCa ⁴⁴ Ca	886.0 898.9	794.4 807.0	220.3 216.2	242.3 237.7	1140.2 1178.2	950.5 985.8	1268.0 1236.5	1501.0 1464.8	

TABLE V:	Tetrahedral and	Octahedral Solvation	Model Results for	$^{i}Ca(OH_{2})_{n}^{2+}$
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n	K _{Ca-O} ^a	H _{OCaO} ^b	V _{3,40} ^c	V _{4,40}	V _{3,44}	V4,44	K _{aq}	
4	0.539	0.165	289.96	96.00	284.44	94.96	0.8584	
4	0.352	0.086	233.31	69.55	228.96	68.77	0.8616	
6	0.539	0.165	319.00	100.32	311.30	99.33	0.8544	
6	0.352	0.086	256.18	72.82	250.12	72.07	0.8589	

^a Stretching force constant in mdyn-Å⁻¹. ^b Bending force constant in mdyn-Å-rad⁻². ^c All frequencies given in cm⁻¹.

experiment, with no systematic variation evident. The Debye model gives values that are too small by amounts that increase from 1.9% at 295 K to 8.3% at 100 K. On this basis, the Kieffer model seems to provide the better representation of the thermodynamic behavior of the acoustic modes of calcite.

The calculation of K_s proceeds straightforwardly from what has been presented to this point. All that is required are the Helmholtz energies of 1 mol of each of the two isotopomeric CaCO₃'s at 295 K, because to an excellent approximation

$$G^{\circ}(^{44}CaCO_3) - G^{\circ}(^{na}CaCO_3) = A^{\circ}(^{44}CaCO_3) - A^{\circ}(^{na}CaCO_3) = -RT \ln K_{\text{solid}} (20)$$

To calculate A° values for natural-abundance CaCO₃, one need only add the acoustic and optical zero-point energies to the (A°) $-E_0^{\circ}$) values already in hand. In the Debye model, the acoustic zero-point energy of 1 mol of calcite is $(1/2)(9R\theta_D/8)$. In the Kieffer model, the corresponding term (in angular frequency units) is

$$\frac{1}{4}\sum_{k=1}^{3}\int_{0}^{\omega_{k}}\omega g(\omega,\omega_{k}) d\omega$$

The optical branch zero-point energy (in erg-molecule⁻¹) is simply

$$\frac{1}{4}\sum_{i=1}^{27}hc\nu_{i}$$

These last two quantities clearly must then be transformed to energies in the units appropriate to the choice of R. It also should be evident that, from the standpoint of ΔA° in eq 20, only the eight terms involving the optical modes listed in Table II will appear in the final result.

For ⁴⁴CaCO₃, scaling the natural-abundance wave propagation velocities by the mass factor discussed above yields a Debye temperature of 212.71 K and Kieffer cutoff frequencies of 76.53, 96.16, and 169.75 cm⁻¹. Repeating the previous set of calculations using these parameters then gives the acoustic contributions to $(A^{\circ} - E_0^{\circ})$ and the zero-point energy of ⁴⁴CaCO₃. The optical branch contributions to these quantities follow from the frequencies listed in Table II.

Table IV lists termwise the acoustic and isotopically sensitive optical contributions to the Helmholtz energies per mole of natural-abundance and ⁴⁴Ca calcites. From these entries, considering only the TO modes, we obtained $\Delta A^{\circ} = -86.5$ cal (Kieffer) or -86.7 cal (Debye); $K_s = 1.159$ at 295 K in both cases. For the LO modes we find $\Delta A^{\circ} = -88.5$ cal (Kieffer) or -88.7cal (Debye); $K_s = 1.163$ at 295 K in both cases. We therefore conclude that $K_s = 1.161 \pm 0.002$ at 295 K.

Calculation of K_{aq} . Because of our incomplete knowledge of the detailed structure of aqueous salt solutions, a rigorous statistical thermodynamic calculation of K_{aq} is not possible. However, we can calculate K_{aq} for model reactions of the type

$${}^{40}CaCO_3(s) + {}^{44}Ca(OH_2)_n{}^{2+}(g) \rightleftharpoons {}^{44}CaCO_3(s) + {}^{40}Ca(OH_2)_n{}^{2+}(g) (21)$$

where n is an integer and the hydrated calcium ions are assumed

to have a fixed geometry. The use of the reaction 21 as a model for reaction 4 assumes that (a) the isotope effect on the Gibbs energy of the aquated calcium ion arises solely from the interactions between the calcium ion and the water molecules in the primary coordination sphere and (b) all other contributions to the Gibbs energies of the isotopic ions in equimolal solutions cancel because of the symmetric nature of reaction 21.

The simplest model for the isotopic calcium ions in solution is the unsolvated ion (n = 0) model

$${}^{40}CaCO_3(s) + {}^{44}Ca^{2+}(g) \rightleftharpoons {}^{44}CaCO_3(s) + {}^{40}Ca^{2+}(g)$$
 (22)

The value of K_{aq} for reaction 22 is given by

$$K_{\rm aq} = \left(\frac{m_{40}}{m_{44}}\right)^{3/2} = \left(\frac{39.96259}{43.95549}\right)^{3/2} = 0.866\,88 \quad (23)$$

If the aqueous calcium ion is solvated in a regular tetrahedral fashion, and if the waters of hydration can be modeled by mass 18.016 pseudoatoms, an inspection of either the pictorial normal coordinates or the G-matrix elements tabulated by Nakamoto¹⁶ shows that only a triply degenerate (F_2) stretch, v_3 , and a triply degenerate (F₂) bend, ν_4 , will have frequencies that are sensitive to the mass of the calcium ion.

If the solvation is octahedral, and if the pseudoatom approximation is also made, then again only a triply degenerate (F_{1n}) stretch, ν_3 , and a triply degenerate (F_{1u}) bend, ν_4 , will have frequencies that vary with the mass of Ca^{2+} .¹⁶

To proceed further, information about the $Ca^{2+}-O_w$ (where the subscript w denotes a water oxygen atom) distance and the pertinent force constants is required. X-ray and neutron diffraction studies of aqueous $CaCl_2$ solutions have obtained Ca^{2+} solvation numbers in the range 5.5–10 and $Ca^{2+}-O_w$ distances in the range 2.39-2.46 Å.¹⁷ To date, no spectral features have been detected that could be identified with vibrations of the hydrated Ca²⁺ entity in solution,¹⁸ but studies in this laboratory¹⁹ have found that in representative hydrated crystals the $Ca^{2+}-O_w$ stretch falls in the range 250-320 cm⁻¹, and the corresponding force constant ranges from 0.45 to 0.55 mdyn Å⁻¹. The O_w -Ca²⁺- O_w bending force constant is poorly known, but it could range reasonably from 0.05 to 0.20 mdyn-Å-rad⁻².

Guided by this information, we used the GF-matrix method to calculate plausible frequencies for the Ca²⁺-sensitive modes of tetrahedrally and octahedrally solvated ⁴⁰Ca²⁺ and ⁴⁴Ca²⁺. Nakamoto's¹⁶ G-matrix elements were used, with a $Ca^{2+}-O_w$ distance of 2.39 Å. The F matrices were diagonal, and the force constants were varied widely. Representative results of these

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force constants ^a		⁴⁰ Ca(0	⁴⁰ Ca(OH ₂) ₉ ^b		⁴⁴ Ca(OH ₂) ₉		
K _{Ca-O}	H _{O-Ca-O}	Ко-о	A2"	E'	A ₂ "	E'	K_{aq}
0.44	0.05	0.13	343.16	325.39	335.81	318.96	
••••			179.16	129.85	178.28	128.18	
			161.41		160.50		0.8463
0.30	0.05	0.10	286.36	271.04	280.46	265.92	
			159.04	113.21	158.62	111.62	
			142.16		140 58		0.8491

TABLE VI: Nonahedral Solvation Model Results

^a Stretching force constants in mdyn·Å⁻¹; bending force constant in mdyn·Å·rad⁻². ^b All frequencies given in cm⁻¹.

calculations are given in Table V. The values of K_{aq} in Table II were obtained from the equation

$$K_{aq} = \left(\frac{{}^{40}Ca + 18.016n}{{}^{44}Ca + 18.016n}\right)^{3/2} \prod_{i} \left\{\frac{\exp(-u_{i,40}/2)}{[1 - \exp(-u_{i,40})]}\right\} \times \left\{\frac{[1 - \exp(-u_{i,44})]}{\exp(-u_{i,44}/2)}\right\} (24)$$

In the tetrahedral and octahedral solvation models *n* is either 4 or 6, and the extended product has six factors—three involving v_3 and three involving v_4 . The quantity $u_i = hcv_i/kT$ if the v_i are expressed in cm⁻¹.

Prompted by the recent molecular dynamics studies of Probst, Heinzinger et al.^{17,20} we also considered nonahedral coordination for Ca²⁺(aq). The D_{3h} -symmetry structure that was adopted for the nonahydrate²⁰ resembles the calcium ion coordination in CaCl₂·6H₂O.²¹ Six of the coordinated water oxygens form a trigonal prism. The metal ion is centered on the threefold axis of the prism, and the three remaining water oxygens lie on twofold axes that exit through the centers of its rectangular faces. All Ca²⁺-O distances were fixed at 2.39 Å, and the altitude of the prism was adjusted so that the O–O distance in the (equilateral) triangular faces was equal to the distance from an O atom on one of the twofold axes to its four nearest neighboring oxygens, namely, 2.759 Å.

In the pseudoatom approximation this XY₉ species has 24 normal modes, distributed $3A_1' + A_1'' + A_2' + 3A_2'' + 5E' +$ 3E''. The vibrational problem was solved in mass-weighted Cartesian coordinates²² rather than in symmetry coordinates, using a force field with two stretching force constants (X-Y and Y-Y) and one bending force constant (Y-X-Y, with both Y's in the same triangular face of the prism). Only seven of the 24 modes (the three A_2'' and two of the E') showed significant X-atom isotope shifts, but to ensure compliance with the Teller-Redlich product rule, all the frequencies were included in the calculation of the K_{aq} values shown in Table VI.

Two trends are apparent in Tables V and VI. The value of K_{aq} decreases as the complexity of the solvation model increases, and for a given assumed solvation number the value of K_{aq} increases when the vibration frequencies decrease. The calculated values of K_{aq} lie in the range 0.85–0.86, and when these values are

combined with the calculated value of $K_s = 1.161$, we obtain K values for reaction 1 that are very close to unity. However, a value for K_{aq} of about 0.93 is required to produce agreement between the calculated and observed values of the equilibrium constant for the overall isotope-exchange reaction. This could only be achieved with frequencies that would be so low as to call into question the very existence of a structured solvation shell for $Ca^{2+}(aq)$. In this respect we are in essential agreement with Brooker,¹⁸ who concluded on the basis of a review of the spectroscopic studies of $Ca^{2+}(aq)$ solutions that $Ca^{2+}(aq)$ has an "ill-defined, dynamic coordination sphere ...". The molecular dynamics particle-density maps of Probst, Heinzinger et al.^{17,20} also support the same conclusion, in that they show the aqueous solvation of $Ca^{2+}(aq)$ is essentially unstructured. A molecular dynamics calculation of the ${}^{40}Ca^{2+}(aq) - {}^{44}Ca^{2+}(aq)$ Gibbs energy difference would be of considerable interest and might serve to resolve the discrepancy between the calculated and experimental values of the equilibrium constant for reaction 1.

There are two papers^{23,24} in the literature dealing with possible calcium isotope fractionation between calcite and aqueous calcium ions under laboratory conditions. In these studies, $CaCO_3(s)$ was precipitated slowly from an aqueous solution of the bicarbonate by removing $CO_2(g)$ with a cold trap. Periodically during the precipitation procedure samples of $CaCO_3(s)$ were withdrawn from the reaction flask and analyzed by mass spectrometry. No fractionation of the calcium isotope, as measured by the 48/40 ratio, was found during any stage of the precipitation procedure. From these results the authors²³ concluded that the equilibrium constant for reaction 25 is 1.000 ± 0.002 at 7 °C. Similar results

$${}^{40}CaCO_3(s) + {}^{48}Ca^{2+}(aq) \rightleftharpoons {}^{48}CaCO_3(s) + {}^{40}Ca^{2+}(aq)$$
(25)

were found in the second study,²⁴ which reported an elementary separation factor of less than 0.1% or 0.05% per mass unit for calcium 44/40 and 48/40 exchange between calcites and Ca²⁺(aq). These results are in disagreement with our measured value of 1.08 \pm 0.02 at 22 °C for the 44/40 exchange reaction. In our judgment this disagreement is a result of ⁴⁰CaCO₃ + ⁱCaCO₃ coprecipitation phenomena that overwhelm the relatively miniscule driving force arising from the isotopic exchange equilibrium. Once precipitated, the Ca²⁺ ions locked in the interiors of the crystals would exchange at an essentially zero rate on the time scale of the experiments.

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Registry No. CaCO₃, 471-34-1; CaCl₂, 10043-52-4; Ca, 7440-70-2.

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