

Calcium carbonate

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Calcium carbonate is a chemical compound, with the chemical formula CaCO₃. It is a common substance found as rock in all parts of the world, and is the main component of shells of marine organisms and snails. Calcium carbonate is the active ingredient in agricultural lime, and is usually the principal cause of hard water. It is commonly used medicinally as a calcium supplement or as an antacid.

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Occurrence

Calcium carbonate is found naturally as the following minerals and rocks:

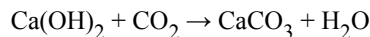
- Aragonite
- Calcite
- Vaterite or (μ-CaCO₃)
- Chalk
- Limestone
- Marble
- Travertine

Eggshells are composed of approximately 95% calcium carbonate.


To test whether a mineral or rock contains calcium carbonate, strong acids, such as hydrochloric acid, can be added to it. If the sample does contain calcium carbonate, it will fizz and produce carbon dioxide and water. Weak acids such as acetic acid will react, albeit less vigorously. All of the rocks/minerals mentioned above will react with acid.

Preparation

The vast majority of calcium carbonate used in industry is extracted by mining or quarrying. Pure calcium carbonate (e.g. for food or pharmaceutical use), can be produced from a pure quarried source (usually marble) or it can be prepared by passing carbon dioxide into a solution of calcium hydroxide: the calcium carbonate precipitates out, and this grade of product is referred to as a precipitate (abbreviated to PCC).



Chemical properties

Calcium carbonate	
	
General	
Systematic name	Calcium carbonate
Other names	Limestone, calcite, aragonite, chalk, marble
Molecular formula	CaCO ₃
Molar mass	100.087 g/mol
Appearance	White powder.
CAS number	[471-34-1]
Properties	
Density and phase	2.83 g/cm ³ , solid.
Solubility in water	Insoluble
Melting point	825°C (1098 K)
Boiling point	Decomposes
Acidity (p <i>K</i> _a)	?
Basicity (p <i>K</i> _b)	?
Thermochemistry	
Δ _f H ⁰ _{liquid}	-1154 kJ/mol
Δ _f H ⁰ _{solid}	-1207 kJ/mol
S ⁰ _{solid}	93 J/mol·K
Structure	
Molecular shape	Linear
Coordination geometry	Tetrahedral
Dipole moment	? D
Hazards	
MSDS	External MSDS
Main hazards	Not hazardous.
NFPA 704	
Flash point	Non-flammable.
R/S statement	R: R36 , R37 , R38 S: S26 , S36
RTECS number	?
Supplementary data page	
Structure and properties	<i>n</i> , ε _r , etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

See also: Carbonate

Calcium carbonate shares the typical properties of other carbonates.

Notably:

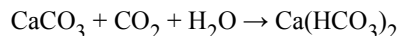
1. it reacts with strong acids, releasing carbon dioxide:

$$\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$$
2. it releases carbon dioxide on heating (to above 840 °C in the case of CaCO₃), to form calcium oxide, commonly called burnt lime:

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$$

Related compounds	
Other anions	Calcium bicarbonate Calcium sulfate
Other cations	Magnesium carbonate (dolomite) Strontium carbonate
Related compounds	Calcium oxide
Except where noted otherwise, data are given for materials in their standard state (at 25°C, 100 kPa) Infobox disclaimer and references	

Calcium carbonate will react with water that is saturated with carbon dioxide to form the soluble calcium bicarbonate.



This reaction is important in the erosion of carbonate rocks, forming caverns, and leads to hard water in many regions.

Uses

The main use of calcium carbonate is in the construction industry, either as a building material in its own right (e.g. marble) or limestone aggregate for roadbuilding or as an ingredient of cement or as the starting material for the preparation of builder's lime by burning in a kiln . A common contaminate is magnesium carbonate.

Calcium carbonate is widely used as an extender in paints, in particular matte emulsion paint where typically 30% by weight of the paint is either chalk or marble.

Calcium carbonate is also widely used as a filler in plastics. Some typical examples include around 15 to 20% loading of chalk in uPVC drain pipe, 5 to 15% loading of stearate coated chalk or marble in uPVC window profile. Fine ground calcium carbonate is an essential ingredient in the microporous film used in babies' diapers and some building films as the pores are nucleated around the calcium carbonate particles during the manufacture of the film by biaxial stretching.

Calcium carbonate is also used in a wide range of trade and DIY adhesives, sealants, and decorating fillers. Ceramic tile adhesives typically contain 70 to 80% limestone. Decorating crack fillers contain similar levels of marble or dolomite. It is also mixed with putty in setting Stained glass windows, and as a resist to prevent glass from sticking to kiln shelves when firing glazes and paints at high temperature.

Calcium carbonate is widely used medicinally as an inexpensive dietary calcium supplement, antacid, and/or phosphate binder. It is also used in the pharmaceutical industry as a base material for tablets of other pharmaceuticals.

Calcium carbonate is known as *whiting* in ceramics/glazing applications, where it is used as a common ingredient for many glazes in its white powdered form. When a glaze containing this material is fired in a kiln, the whiting acts as a flux material in the glaze.

Used in swimming pools as a pH corrector for maintaining alkalinity "buffer" to offset the acidic properties of the disinfectant agent.

It is commonly called chalk as it has been a major component of blackboard chalk. Chalk may consist of either calcium carbonate or gypsum, hydrated calcium sulfate CaSO₄·2H₂O.

In North America, calcium carbonate has begun to replace kaolin in the production of glossy paper. Europe has been practicing this as alkaline papermaking or acid-free papermaking for some decades. Carbonates are available in forms: ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC). The latter has a very fine and controlled particle size, on the order of 2 micron in diameter, useful in coatings for paper.

As a food additive, it is used in some soy milk products as a source of dietary calcium.

In 1989, a researcher introduced CaCO₃ into the Whetstone Brook in Massachusetts . His hope was that the calcium carbonate would counter the acid in the stream from acid rain and save the trout that had ceased to spawn. Although his experiment was a success, it did increase the amounts of aluminum ions in the area of the brook that was not treated with the limestone. This shows

that CaCO₃ can be added to neutralize the effects of acid rain in river ecosystems. Nowadays, calcium carbonate is used to neutralise acidic conditions in both soil and water.

Calcination Equilibrium

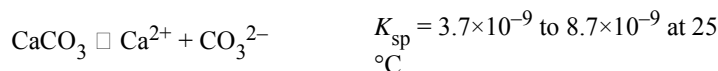
Calcination of limestone using charcoal fires to produce quicklime has been practiced since antiquity by cultures all over the world. The answer to the question, "how hot does the fire have to be?" is usually given as 825 °C, but stating an absolute threshold is misleading. Calcium carbonate exists in equilibrium with calcium oxide and carbon dioxide at any temperature. At each temperature there is a partial pressure of carbon dioxide that is in equilibrium with calcium carbonate. At room temperature the equilibrium overwhelmingly favors calcium carbonate, because the equilibrium CO₂ pressure is only a tiny fraction of the partial CO₂ pressure in air, which is about 0.035 kPa. At temperatures above 550 °C the equilibrium CO₂ pressure begins to exceed the CO₂ pressure in air. So above 550 °C, calcium carbonate begins to outgas CO₂ into air. But in a charcoal fired kiln, the concentration of CO₂ will be much higher than it is in air. Indeed if all the oxygen in the kiln is consumed in the fire, then the partial pressure of CO₂ in the kiln can be as high as 20 kPa. The table shows that this equilibrium pressure is not achieved until the temperature is nearly 800 °C. For the outgassing of CO₂ from calcium carbonate to happen at an economically useful rate, the equilibrium pressure must significantly exceed the ambient pressure of CO₂. And for it to happen rapidly, the equilibrium pressure must exceed total atmospheric pressure of 101 kPa, which happens at 898 °C.

550 °C	0.055 kPa
587 °C	0.13 kPa
605 °C	0.31 kPa
680 °C	1.80 kPa
727 °C	5.9 kPa
748 °C	9.3 kPa
777 °C	14 kPa
800 °C	24 kPa
830 °C	34 kPa
852 °C	51 kPa
871 °C	72 kPa
881 °C	80 kPa
891 °C	91 kPa
898 °C	101 kPa
937 °C	179 kPa
1082 °C	901 kPa
1241 °C	3961 kPa

Solubility of calcium carbonate in water

Solubility in pure water with varying CO₂ pressure

Calcium carbonate is poorly soluble in pure water. The equilibrium of its solution is given by the equation (with dissolved calcium carbonate on the right):



where the solubility product for [Ca²⁺][CO₃²⁻] is given as anywhere from $K_{\text{sp}} = 3.7 \times 10^{-9}$ to $K_{\text{sp}} = 8.7 \times 10^{-9}$ at 25 °C, depending upon the data source.^{[2][3]} What the equation means is that the product of molar concentration of calcium ions (moles of dissolved Ca²⁺ per liter of solution) with the molar concentration of dissolved CO₃²⁻ cannot exceed the value of K_{sp} . This seemingly simple solubility equation, however, must be taken along with the more complicated equilibrium of carbon dioxide with water (see carbonic acid). Some of the CO₃²⁻ combines with H⁺ in the solution according to:

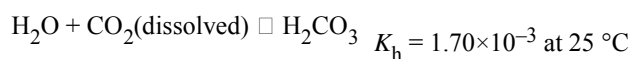


HCO₃⁻ is known as the bicarbonate ion. Calcium bicarbonate is many times more soluble in water than calcium carbonate -- indeed it exists *only* in solution.

Some of the HCO₃⁻ combines with H⁺ in solution according to:



Some of the H₂CO₃ breaks up into water and dissolved carbon dioxide according to:



And dissolved carbon dioxide is in equilibrium with atmospheric carbon dioxide according to:

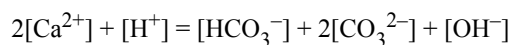
$$\frac{P_{\text{CO}_2}}{[\text{CO}_2]} = k_{\text{H}} \quad \text{where } k_{\text{H}} = 29.76 \text{ atm}/(\text{mol/L}) \text{ at } 25^\circ\text{C} \text{ (Henry constant), } P_{\text{CO}_2} \text{ being the } \text{CO}_2 \text{ partial pressure.}$$

For ambient air, P_{CO_2} is around 3.5×10^{-4} atmospheres (or equivalently 35 Pa). The last equation above fixes the concentration of dissolved CO_2 as a function of P_{CO_2} , independent of the concentration of dissolved CaCO_3 . At

atmospheric partial pressure of CO_2 , dissolved CO_2 concentration is 1.2×10^{-5} moles/liter. The equation before that fixes the concentration of H_2CO_3 as a function of $[\text{CO}_2]$. For $[\text{CO}_2] = 1.2 \times 10^{-5}$, it results in $[\text{H}_2\text{CO}_3] = 2.0 \times 10^{-8}$ moles per liter. When $[\text{H}_2\text{CO}_3]$ is known, the remaining three equations together with



(which is true for all aqueous solutions), and the fact that the solution must be electrically neutral,



make it possible to solve simultaneously for the remaining five unknown concentrations (note that the above form of the neutrality equation is valid only if calcium carbonate has been put in contact with **pure water** or with a neutral pH solution; in the case where the origin water solvent pH is not neutral, the equation is modified).

The table on the right shows the result for $[\text{Ca}^{2+}]$ and $[\text{H}^+]$ (in the form of pH) as a function of ambient partial pressure of CO_2 ($K_{\text{sp}} = 4.47 \times 10^{-9}$ has been taken for the calculation). At atmospheric levels of ambient CO_2 the table indicates the solution will be slightly alkaline. The trends the table shows are

- 1) As ambient CO_2 partial pressure is reduced below atmospheric levels, the solution becomes more and more alkaline. At extremely low P_{CO_2} , dissolved CO_2 , bicarbonate ion, and carbonate ion largely evaporate from the solution, leaving a highly alkaline solution of calcium hydroxide, which is more soluble than CaCO_3 .
- 2) As ambient CO_2 partial pressure increases to levels above atmospheric, pH drops, and much of the carbonate ion is converted to bicarbonate ion, which results in higher solubility of Ca^{2+} .

The effect of the latter is especially evident in day to day life of people who have hard water. Water in aquifers underground can be exposed to levels of CO_2 much higher than atmospheric. As such water percolates through calcium carbonate rock, the CaCO_3 dissolves according to the second trend. When that same water then emerges from the tap, in time it comes into equilibrium with CO_2 levels in the air by outgassing its excess CO_2 . The calcium carbonate becomes less soluble as a result and the excess precipitates as lime scale. This same process is responsible for the formation of stalactites and stalagmites in limestone caves.

Two hydrated phases of calcium carbonate, monohydrocalcite, $\text{CaCO}_3 \cdot \text{H}_2\text{O}$, and ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, may precipitate from water at ambient conditions and persist as metastable phases.

Solubility at atmospheric CO_2 pressure with varying pH

We now consider the problem of the maximum solubility of calcium carbonate in normal atmospheric conditions ($P_{\text{CO}_2} = 3.5 \times 10^{-4}$ atm) when the pH of the solution is adjusted. This is for example the case in a swimming pool where the pH is maintained

Calcium Ion Solubility as a function of CO_2 partial pressure at 25°C		
P_{CO_2} (atm)	pH	$[\text{Ca}^{2+}]$ (mol/L)
10^{-12}	12.0	5.19×10^{-3}
10^{-10}	11.3	1.12×10^{-3}
10^{-8}	10.7	2.55×10^{-4}
10^{-6}	9.83	1.20×10^{-4}
10^{-4}	8.62	3.16×10^{-4}
3.5×10^{-4}	8.27	4.70×10^{-4}
10^{-3}	7.96	6.62×10^{-4}
10^{-2}	7.30	1.42×10^{-3}
10^{-1}	6.63	3.05×10^{-3}
1	5.96	6.58×10^{-3}
10	5.30	1.42×10^{-2}

between 7 and 8 (by addition of NaHSO_4 to decrease the pH or of NaHCO_3 to increase it). From the above equations for the solubility product, the hydration reaction and the two acid reactions, the following expression for the maximum $[\text{Ca}^{2+}]$ can be easily deduced:

$$[\text{Ca}^{2+}]_{\text{max}} = \frac{K_{\text{sp}}k_{\text{H}}}{K_{\text{h}}K_{\text{a1}}K_{\text{a2}}P_{\text{CO}_2}} [\text{H}^+]^2$$

showing a quadratic dependence in $[\text{H}^+]$. The numerical application with the above values of the constants gives

pH	7.0	7.2	7.4	7.6	7.8	8.0	8.2	8.27	8.4
$[\text{Ca}^{2+}]_{\text{max}}$ (10^{-4} mol/L or °f)	1590	635	253	101	40.0	15.9	6.35	4.70	2.53
$[\text{Ca}^{2+}]_{\text{max}}$ (mg/L)	6390	2540	1010	403	160	63.9	25.4	18.9	10.1

Comments:

- decreasing the pH from 8 to 7 increases the maximum Ca^{2+} concentration by a factor 100
- note that the Ca^{2+} concentration of the previous table is recovered for $\text{pH} = 8.27$
- keeping the pH to 7.4 in a swimming pool (which gives optimum HClO/OCl^- ratio in the case of "chlorine" maintenance) results in a maximum Ca^{2+} concentration of 1010 mg/L. This means that successive cycles of water evaporation and partial renewing may result in a very hard water before CaCO_3 precipitates. Addition of a calcium sequestrant or complete renewing of the water will solve the problem.

References

- [^] *CRC Handbook of Chemistry and Physics* 44th ed., p2292
- [^] CSUDH
- [^] *CRC Handbook of Chemistry and Physics*, 44th ed.

See also

- Aragonite
- Calcite
- Limestone
- Ocean acidification
- Gesso
- Cuttlefish
- Cuttlebone

External links

- International Chemical Safety Card 1193
- CID 516889 from PubChem
- ATC codes: A02AC01 and A12AA04

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