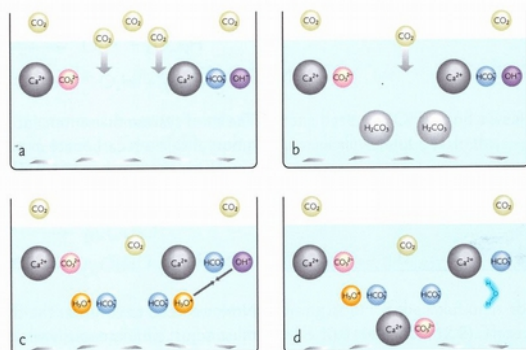


pressure of CO₂ over the solution, providing that a reservoir of excess calcium carbonate is offered (Fig. 12.13d). The reaction system can be summarized as in equation (12.14):



Fig. 12.13 Formation of a calcium hydrogen carbonate solution. (a) In a pure calcium carbonate solution, the ions of calcium (Ca²⁺), carbonate (CO₃²⁻), hydrogen carbonate (HCO₃⁻) and hydroxide (OH⁻) coexist. Undissolved calcium carbonate crystals (rectangular shapes) rest at the bottom of the vessel. Increasing the partial pressure of carbon dioxide above the solution surface enforces the gas to dissolve. (b) A part of the dissolved carbon dioxide is transformed to carbonic acid, H₂CO₃, here positioned at the bottom of the tray. (c) The two molecules of carbonic acid dissociate to form hydronium ions and hydrogen carbonate ions. One of the hydronium ions (right side) approaches the hydroxide ion to neutralize it. (d) The concentration of calcium ions is increased by the dissolution of solid calcium carbonate. One of the calcium carbonate crystals is removed from the bottom of the vessel.



Returning to the case we discussed above, where the atmospheric pressure of carbon dioxide over the solution is kept constant at 1 atm, producing a saturated solution of CO₂, the maximum amount of calcium carbonate that can be dissolved is 0.66 g/L, corresponding to 262 mg/L Ca²⁺, which results in a pH of 5.96 (Table 12.3). Reducing the concentration of calcium carbonate reduces the population of OH⁻, while the population of hydronium ions supplied by the carbonic acid remains unchanged. Therefore, the resulting solution pH must decrease with decreasing concentration of calcium carbonate dissolved (Fig. 12.14). Calcium hydrogen carbonate solutions are therefore invariably acidic.

In order to maintain the maximum concentration of dissolved calcium salt, the water must remain saturated with CO₂ gas at a partial pressure of 1 atm. If the partial pressure of CO₂ is kept at this constant value in a closed container, the system is in equilibrium. If the partial pressure of CO₂ is allowed to fall below 1 atm, the system will no longer be in equilibrium. As a result, calcium carbonate crystals must precipitate out of solution. In other words, if the pure atmosphere of CO₂ gas above the surface of the solution is replaced by air, the concentration of CO₂ in the solution will drop and, as a result, the

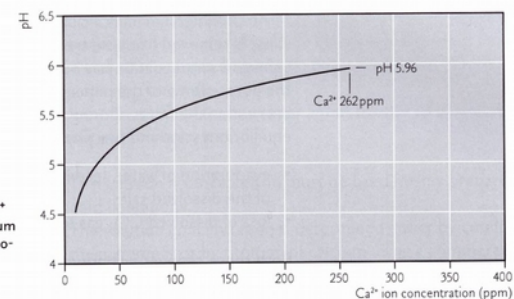


Fig. 12.14 Relationship between Ca²⁺ ion concentration and pH in a calcium hydrogen carbonate solution at atmospheric pressure of CO₂ (1 atm).

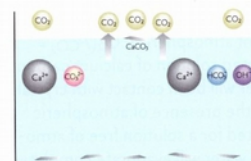


Fig. 12.15 Destabilization of the calcium hydrogen carbonate solution. When the pressure of carbon dioxide above the solution is lowered, dissolved carbon dioxide dissipates. Calcium carbonate must precipitate to equilibrate the system. The precipitate forms on the surface of the liquid (rectangular shape).

concentration of calcium salt in the solution will be diminished until it adjusts itself to a new equilibrium state (Fig. 12.15). Although the solution is unstable when it stands in an open vessel, the dissipation of CO₂ from the solution will to some extent be retarded by the fact that the gas is heavier than air and will tend to rest above the solution surface as long as it is not disturbed.

By increasing the partial pressure of carbon dioxide above 1 atm, one can achieve yet higher concentrations of dissolved calcium carbonate (Table 12.2). For instance, at a partial pressure of 2.5 atm the solubility of calcium carbonate, expressed as [Ca²⁺], lies at 8.97 mmol/L. Hydrogen carbonate solutions can be prepared in small quantities in pressurized vessels such as domestic soda siphons that use small bottles of compressed carbon dioxide, where the partial pressure of CO₂ is well above 1 atm (Huhsmann 2002). Large-scale systems consist of combined purification and enrichment, where the water is continuously saturated with CO₂. Here, the partial pressure of CO₂ is kept at 1 atm.

partial pressure of CO ₂ above solution	CaCO ₃		MgCO ₃ · 3H ₂ O	
	pH	[Ca ²⁺] (mmol/L)	pH	[Mg ²⁺] (mmol/L)
atm	10.04	0.067	10.7	1.54
absent	8.27	0.47	9.2	3.79
0.00035*	8.27	0.47	9.2	3.79
1.0	5.96	6.55	6.9	53.70
2.5	5.70	8.97	6.6	72.30

* partial pressure of atmospheric CO₂

Table 12.2 Solubility and pH of calcium carbonate and magnesium carbonate in water at different partial pressures of carbon dioxide above the solution