

Table 3-1. Dissociation constants for acids at 25°C

Acid	Formula	pK _{a1}	pK _{a2}	pK _{a3}
Hydrochloric	HCl	~-3		
Sulfuric	H ₂ SO ₄	~-3	1.99	
Nitric	HNO ₃	0		
Oxalic	H ₂ C ₂ O ₄	1.2	4.2	
Phosphoric	H ₃ PO ₄	2.15	7.20	12.35
Hydrofluoric	HF	3.18		
Formic	HCOOH	3.75		
Acetic	CH ₃ COOH	4.76		
Carbonic	H ₂ CO ₃	6.35	10.33	
Hydrosulfuric	H ₂ S	7.03	>14	
Boric	H ₃ BO ₃	9.27	>14	
Silicic	H ₄ SiO ₄	9.83	13.17	

Table 3-2. Dissociation constants for bases at 25°C

Base (hydroxide)	Formula	pK _{b₁}	pK _{b₂}	pK _{b₃}
Methylamine	CH ₃ NH ₂	3.36		
Ammonium	NH ₄ (OH)	4.7		
Magnesium	Mg(OH) ₂	8.6	2.6	
Pyridine	C ₅ H ₅ N	8.8		
Manganese	Mn(OH) ₂	9.4	3.4	
Ferrous	Fe(OH) ₂	10.6	4.5	
Al, amorphous	Al(OH) ₃	12.3	10.3	9.0
Al, gibbsite	Al(OH) ₃	14.8	10.3	9.0
Ferric, amorphous	Fe(OH) ₃	16.5	10.5	11.8

Table 3-3. Dissociation constants (K_w) of water as a function of temperature

T (°C)	$-\log K_{eq}$	T (°C)	$-\log K_{eq}$
0	14.938	30	13.836
5	14.727	35	13.685
10	14.528	40	13.542
15	14.340	45	13.405
20	14.163	50	13.275
24	14.000	55	13.152
25	13.995	60	13.034

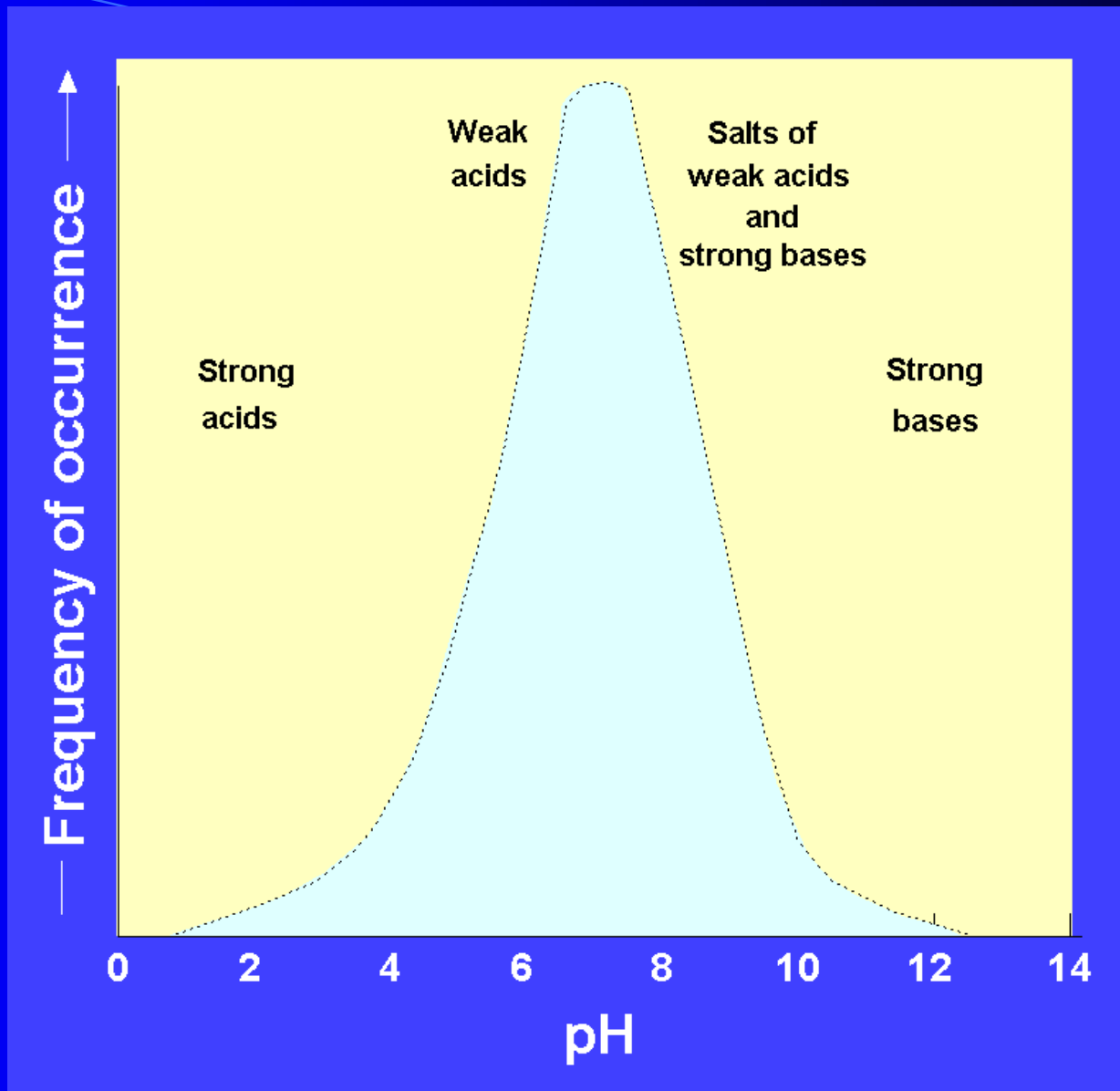


Figure 3-1. Schematic diagram showing the frequency of pH values in natural waters. The major controls for each pH range are indicated on the diagram. After Langmuir (1997).

Table 3-4. Equilibrium constants for the carbonate system

T (°C)	Dissociation constants		Solubility products	
	pK _{a1}	pK _{a2}	pK _{cal}	pK _{arg}
0	6.58	10.63	8.38	8.22
5	6.52	10.55	8.39	8.24
10	6.46	10.49	8.41	8.26
15	6.42	10.43	8.43	8.28
20	6.38	10.38	8.45	8.31
25	6.35	10.33	8.48	8.34
30	6.33	10.29	8.51	8.37
45	6.29	10.20	8.62	8.49
60	6.29	10.14	8.76	8.64

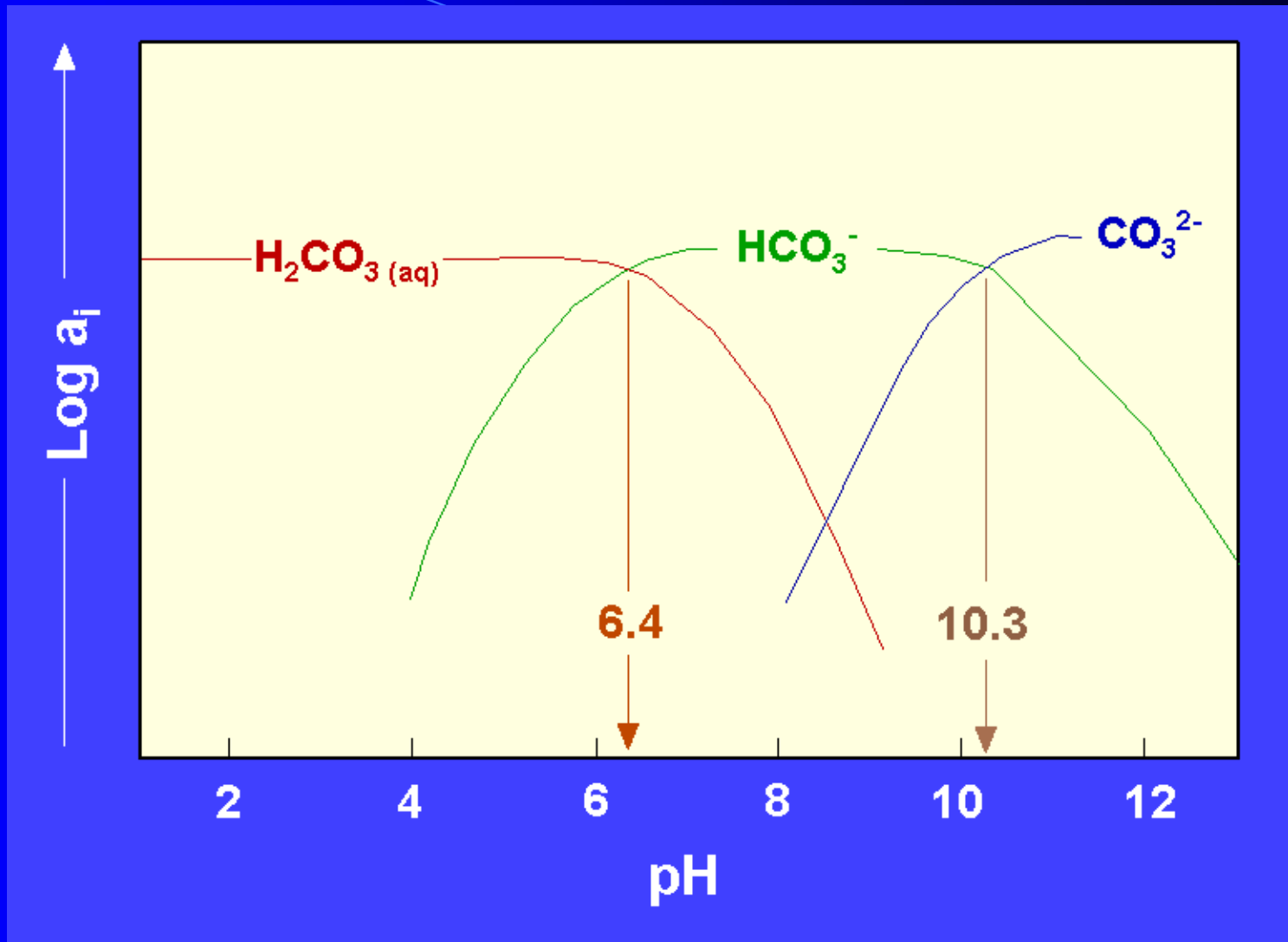


Figure 3-2. Relative activity of various carbonate species as a function of pH.

Table 3-5. Examples of processes that control the CO₂ content and pH of surface and ground waters

Process	Reaction	pH
Temperature change	Increase T, decrease solubility of CO ₂ (g)	Increases
	Decrease T, increase solubility of CO ₂ (g)	Decreases
Photosynthesis	$6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2(\text{g})$	Increases
Respiration	$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}$	Decreases
Anaerobic decay	$2\text{CH}_2\text{O} \rightarrow \text{CH}_4(\text{g}) + \text{CO}_2(\text{g})$	Decreases
Denitrification	$5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow 5\text{CO}_2(\text{g}) + 2\text{N}_2(\text{g}) + 7\text{H}_2\text{O}$	Increases
Dissolution of carbonate	$\text{CaCO}_3 \text{ calcite} + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2(\text{g})$	Increases
Precipitation of carbonate	$\text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3 \text{ calcite} + 2\text{H}^+$	Decreases
Weathering of Al-silicate minerals	$2\text{KAlSi}_3\text{O}_8 \text{ feldspar} + 2\text{CO}_2(\text{g}) + 11\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \text{ kaolinite} + 2\text{K}^+ + 2\text{HCO}_3^- + 4\text{H}_4\text{SiO}_4(\text{aq})$	Increases

Table 3-6. Equilibrium constants for amphoteric compounds

Hydroxide	Formula	-log K_A
Aluminum, amorphous	Al(OH)_3	-1.1
Aluminum, gibbsite	Al(OH)_3	1.4
Cadmium	Cd(OH)_2	5.3
Cobalt	Co(OH)_2	5.2
Copper	Cu(OH)_2	2.9
Ferrous	Fe(OH)_2	5.1
Ferric	Fe(OH)_3	4.4
Manganese	Mn(OH)_2	5.1
Nickel	Ni(OH)_2	4
Thorium, amorphous	Th(OH)_4	5.8
Uranium	$\text{UO}_2(\text{OH})_2$	3.6
Zinc, amorphous	Zn(OH)_2	1.9

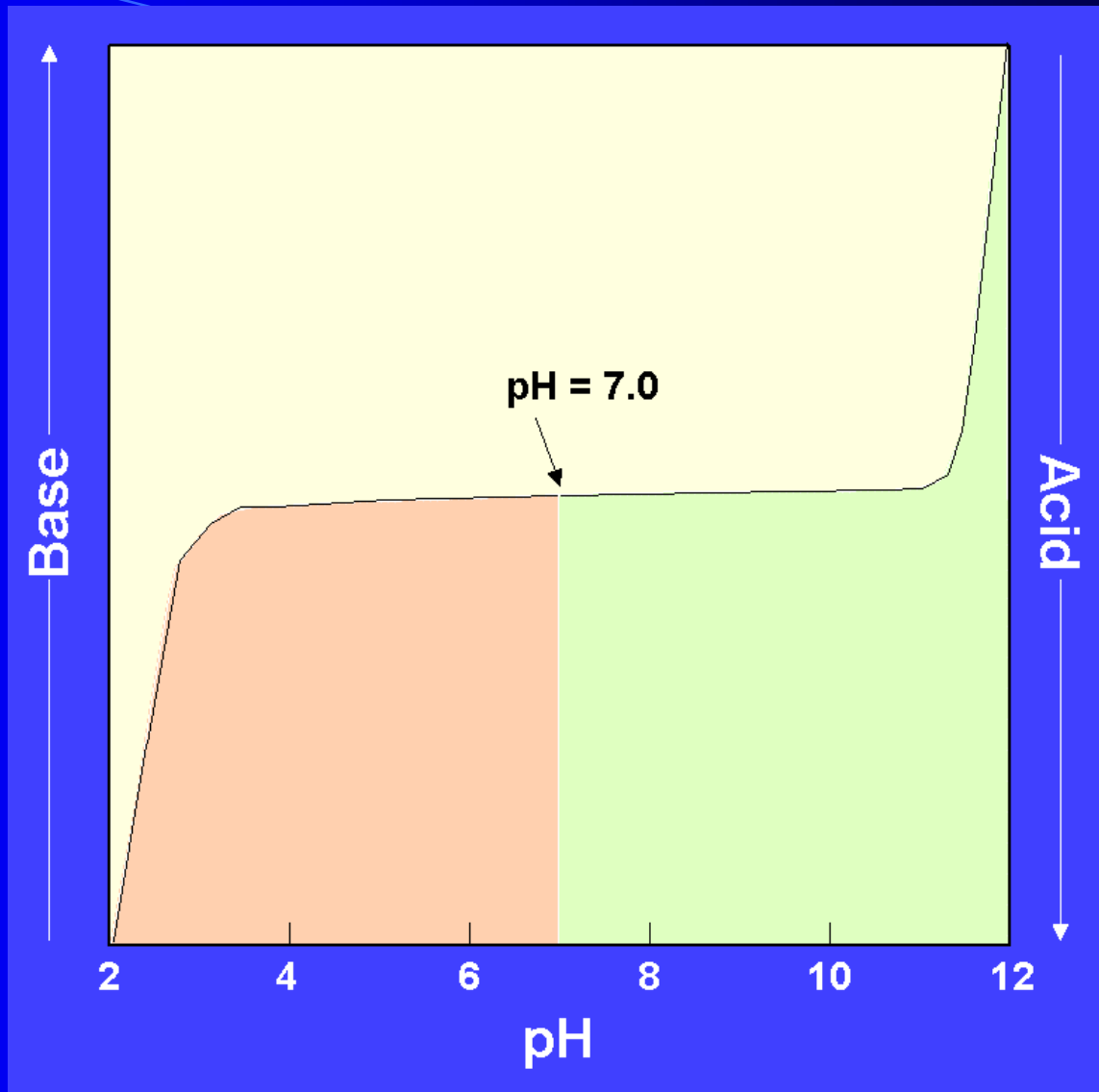


Figure 3-3. Schematic representation of an acid-base titration curve for a strong acid (base). The inflection point is at $\text{pH} = 7.0$, where all the excess H^+ (acid) or OH^- (base) has been consumed. Titrant is a base for an acidity determination; an acid for an alkalinity determination

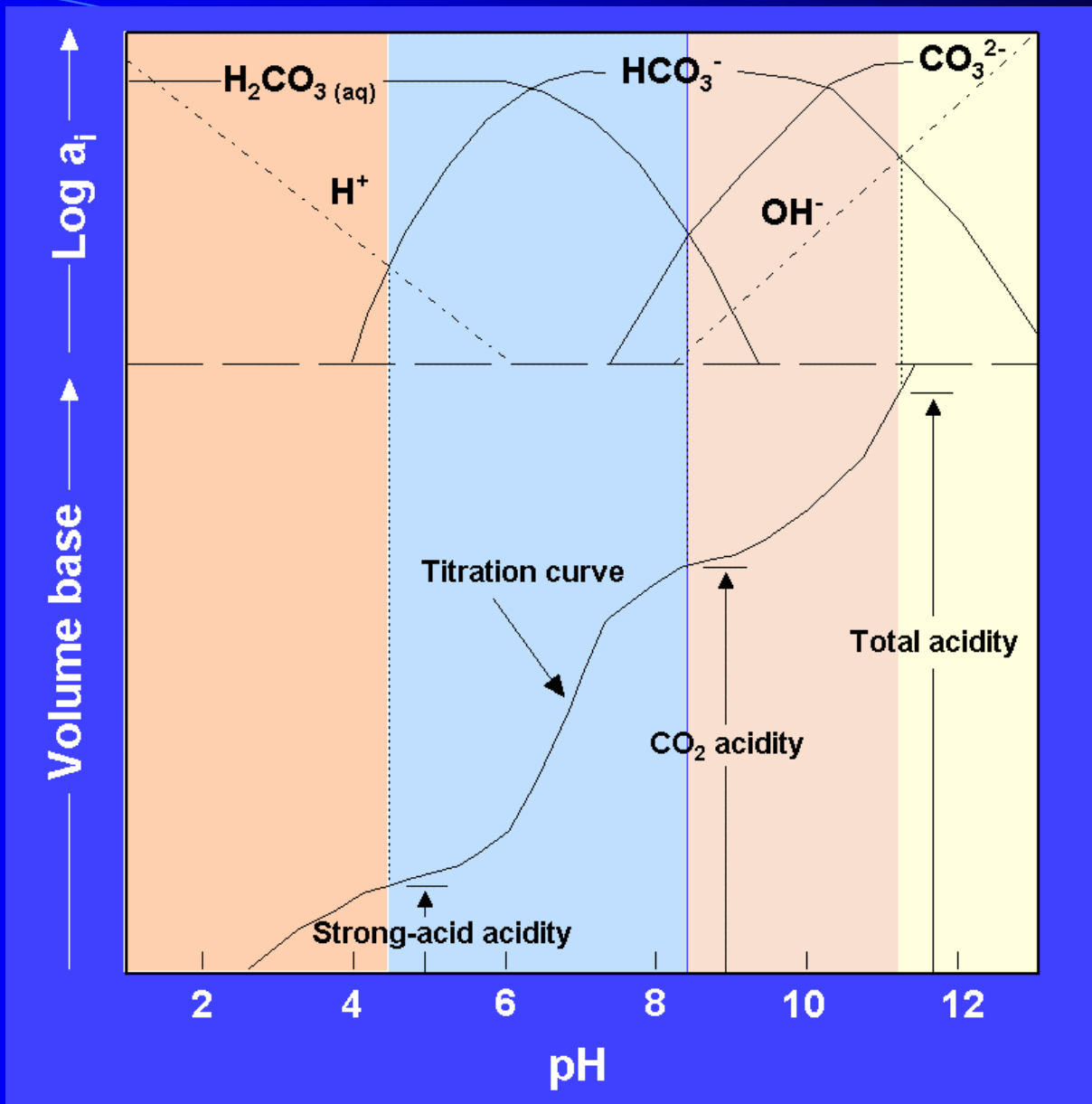


Figure 3-4. Schematic acidity titration curve for a solution that contains a strong acid and carbonic acid. See text for details.

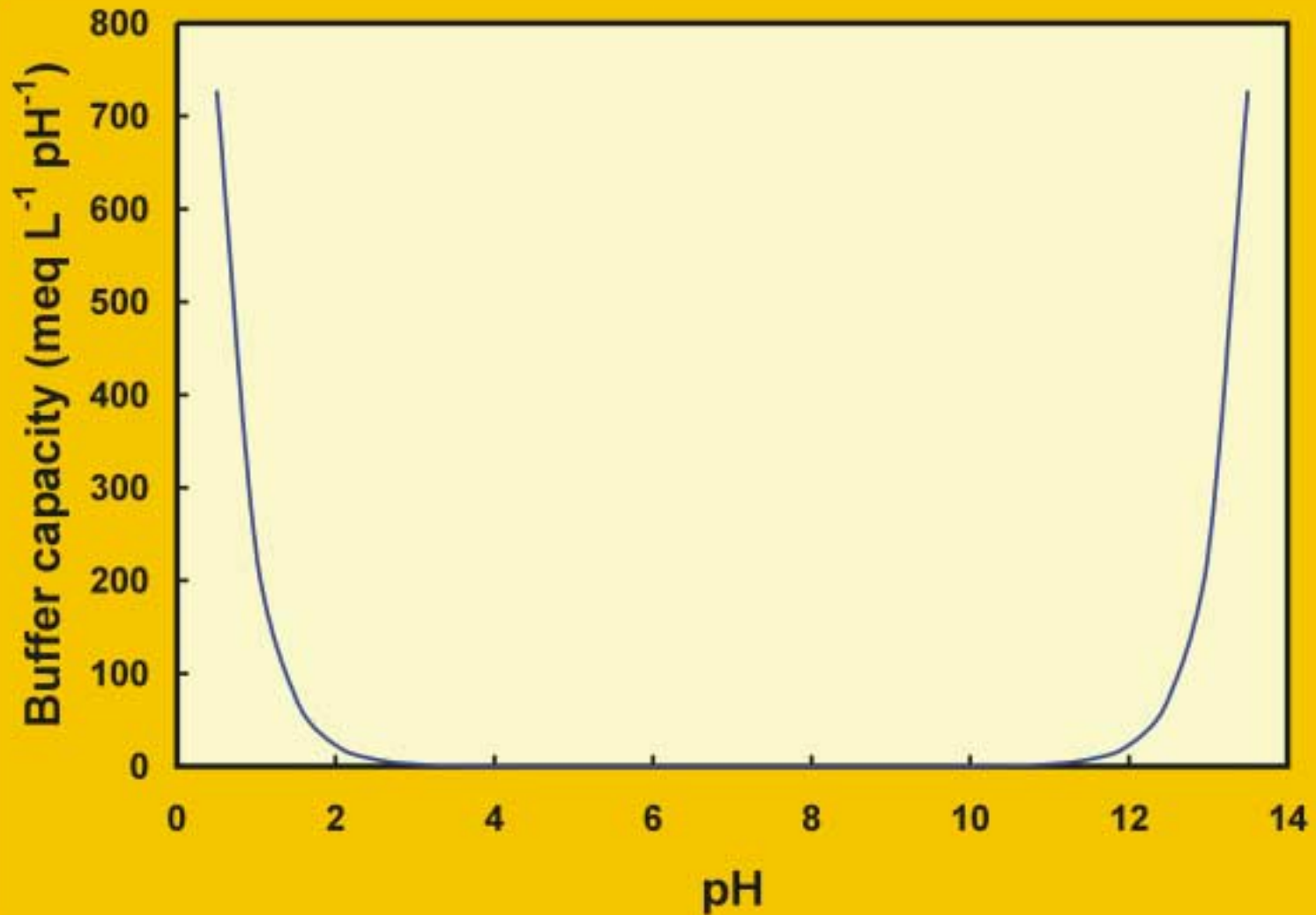


Figure 3-5. Variations in buffer capacity as a function of pH for water. Only at very low and very high pH values is water an important buffer.

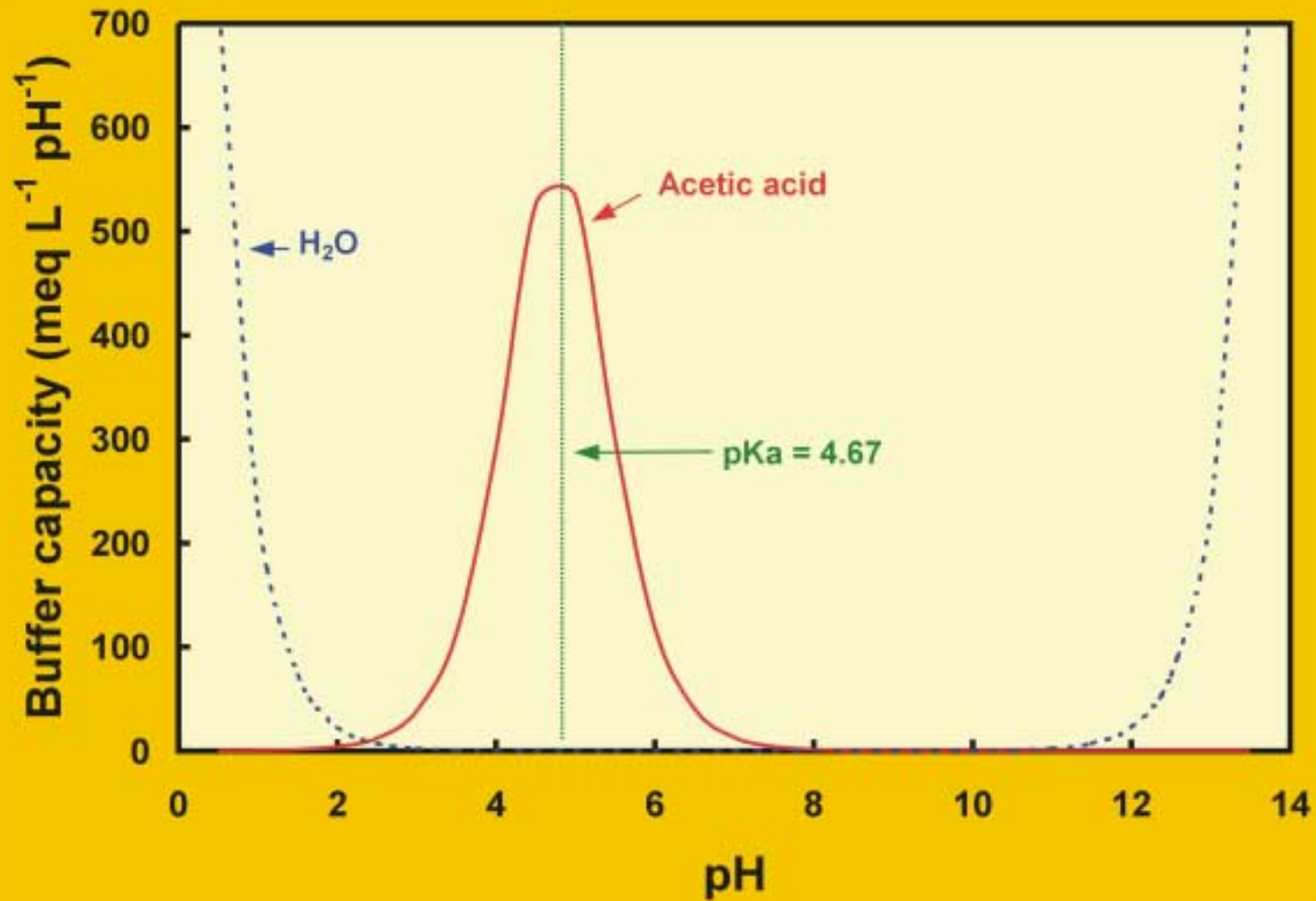


Figure 3-6. Variations in buffering capacity as a function of pH for water and acetic acid when $C_A = 1$ mol.

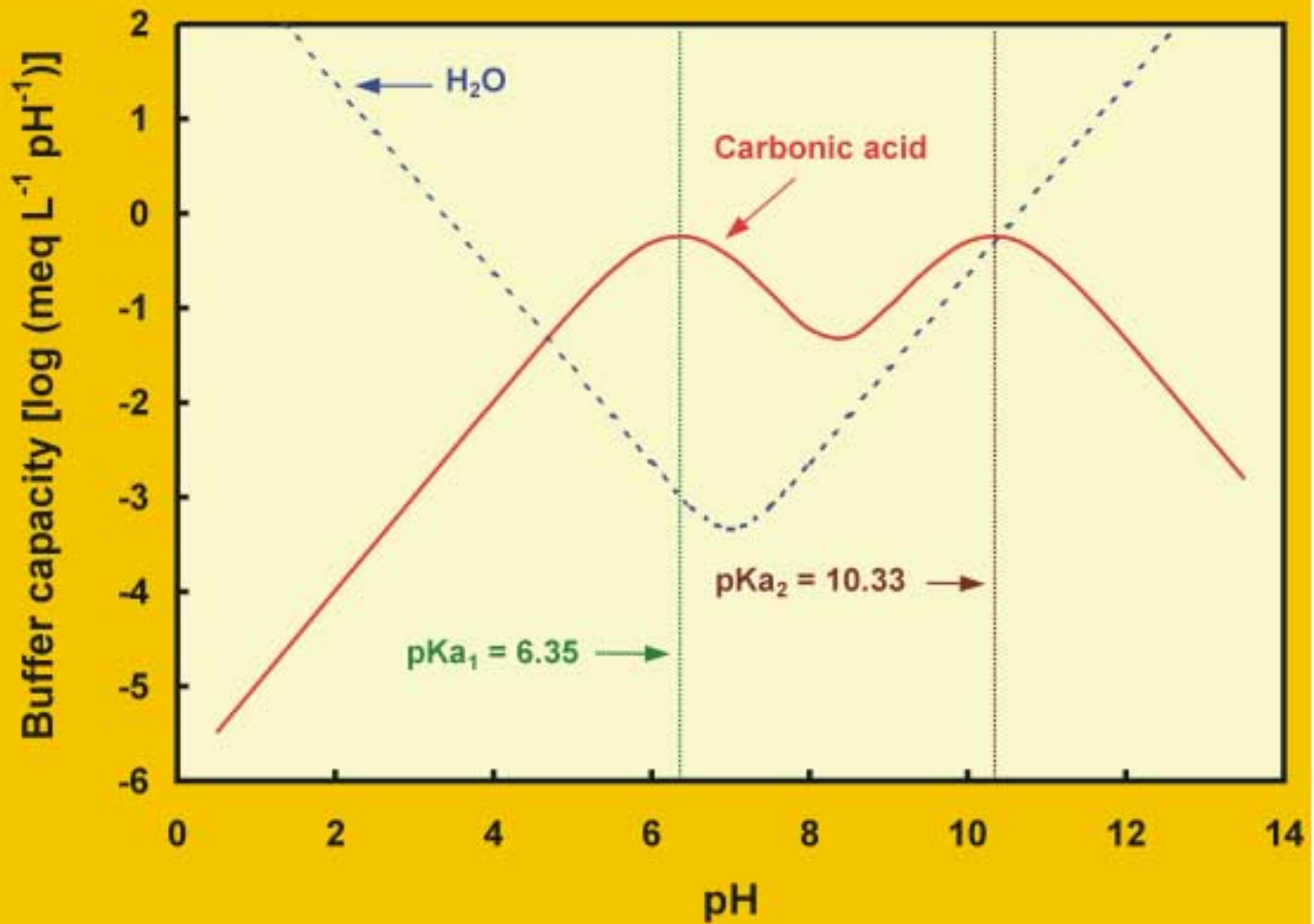


Figure 3-7. Variations in buffering capacity as a function of pH for the system carbonic acid-water when $C_A = 1 \times 10^{-3} \text{ mol L}^{-1}$.

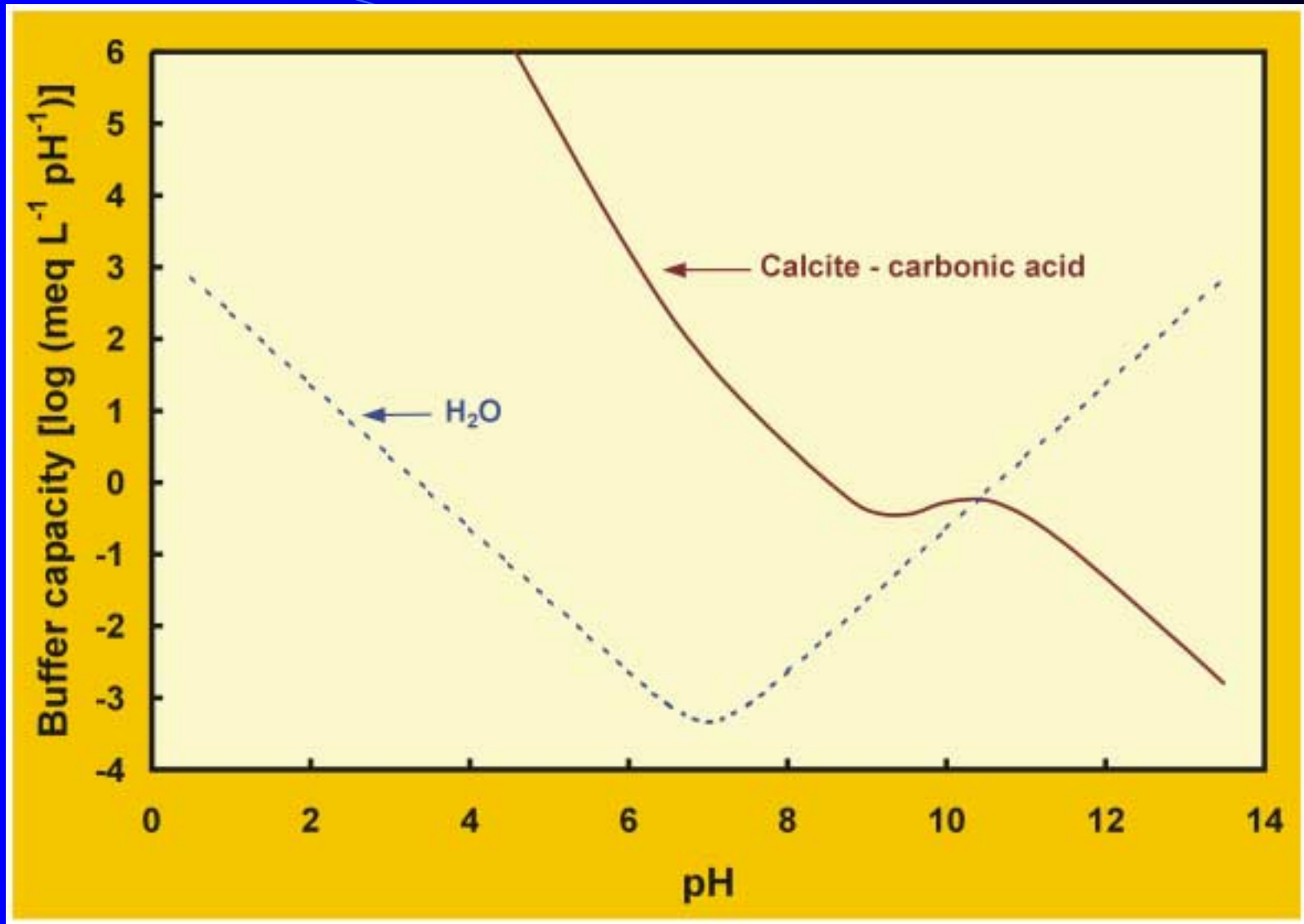


Figure 3-8. Variations in buffering capacity as a function of pH for the calcite-carbonic acid system. $C_T = 1 \times 10^{-3} \text{ mol L}^{-1}$.

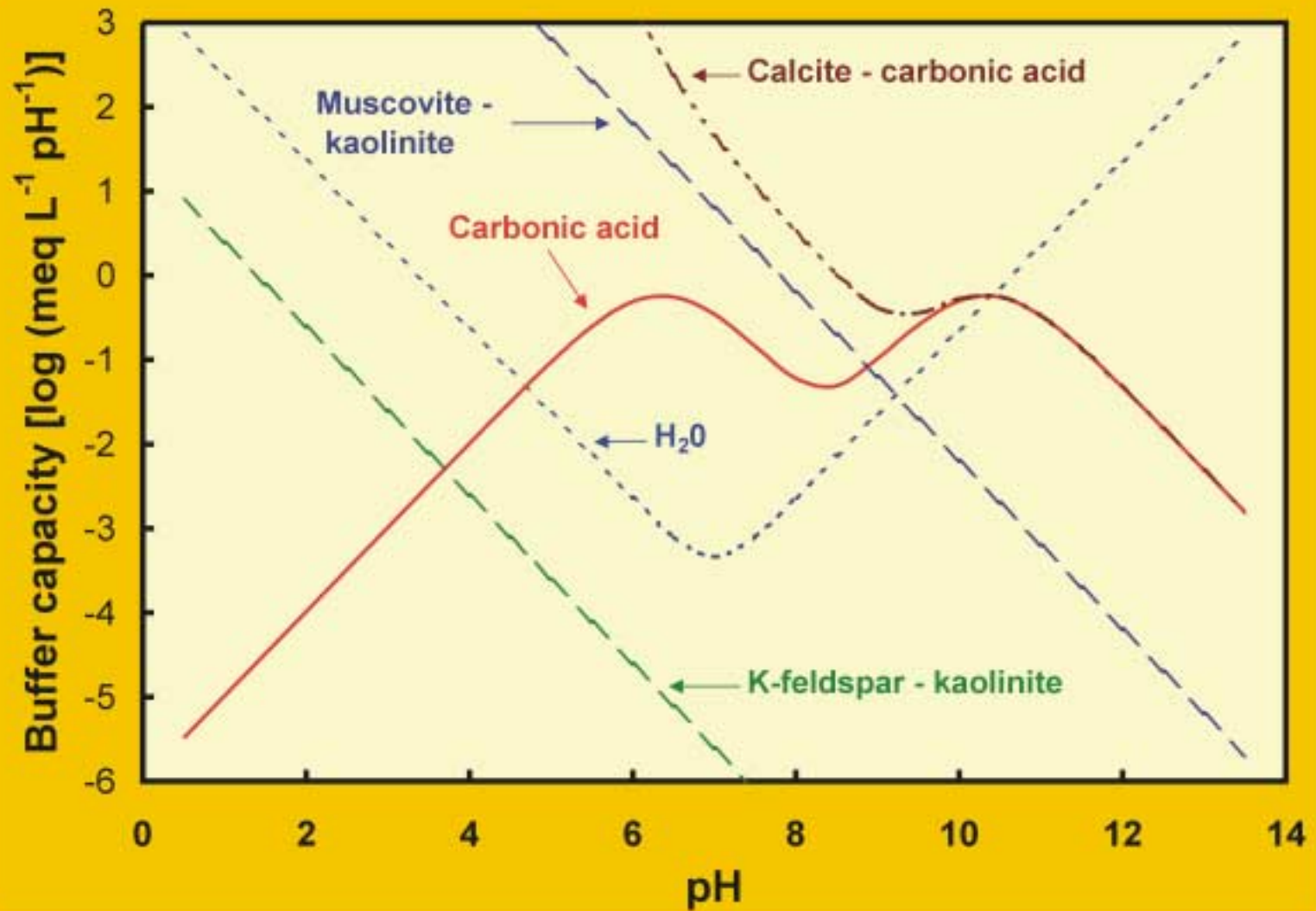


Figure 3-9. Summary of buffering reactions for natural waters containing carbonic acid and/or in contact with various minerals. Note the importance of the carbonate and clay minerals for buffering acid additions to natural waters.

Table 3-7. Relative reactivity of common minerals at pH = 5

Mineral group	Typical minerals	Relative reactivity at pH 5
Dissolving	Calcite, aragonite, dolomite, magnesite, brucite	1.00
Fast weathering	Anorthite, nepheline, forsterite, olivine, garnet, jadeite, leucite, spodumene, diopside, wollastonite	0.40
Intermediate weathering	Sorosilicates (epidote, zoisite), pyroxenes (enstatite, hypersthene, augite, hedenbergite), amphiboles (hornblende, glaucophane, tremolite, actinolite, astrophyllite), phyllosilicates (serpentine, chrysotile, talc, chlorite, biotite)	0.02
Slow weathering	Plagioclase feldspars (albite, oligoclase, labradorite), clays (vermiculite, montmorillonite)	0.01
Very slow weathering	K-feldspars (orthoclase, microcline), muscovite	0.01
Inert	Quartz, rutile, zircon	0.004

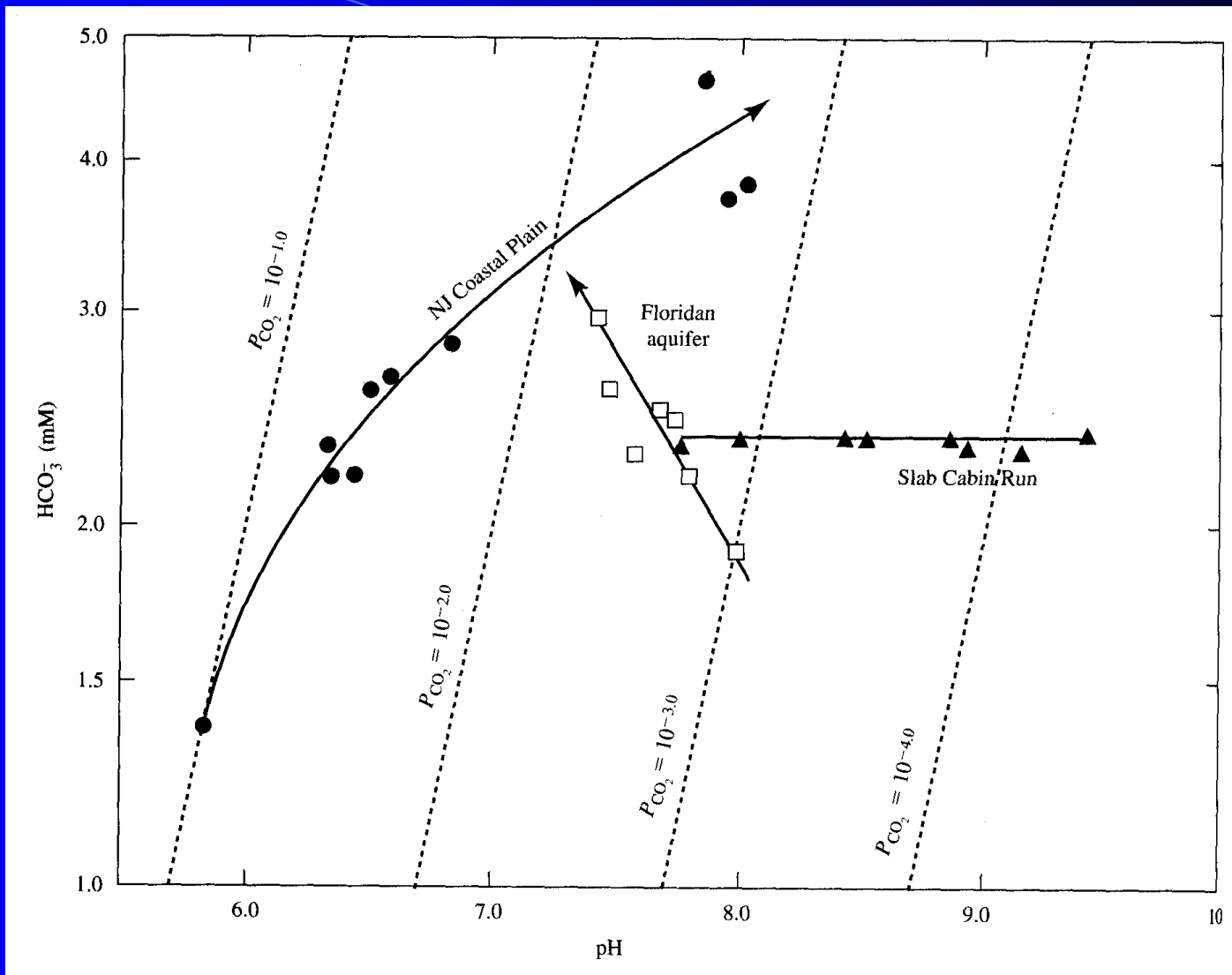
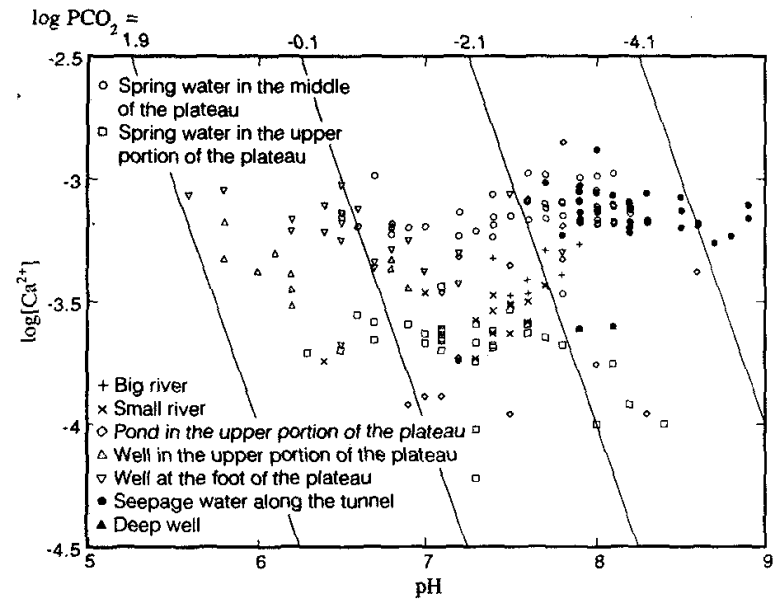
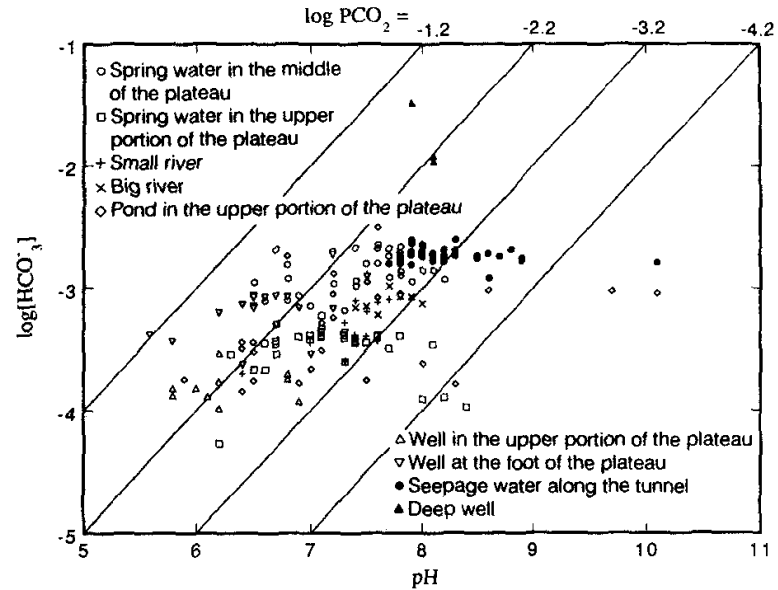


Figure 3-C1-1. Variations in pH, HCO_3^- , and P_{CO_2} for two groundwater and one stream system. Arrows indicate the direction of groundwater flow. From Langmuir (1997).

Figure 3-C2-1. The relationship between pH and $\log[\text{HCO}_3^-]$ and $\log[\text{Ca}^{2+}]$. From Li and Misawa (1994).



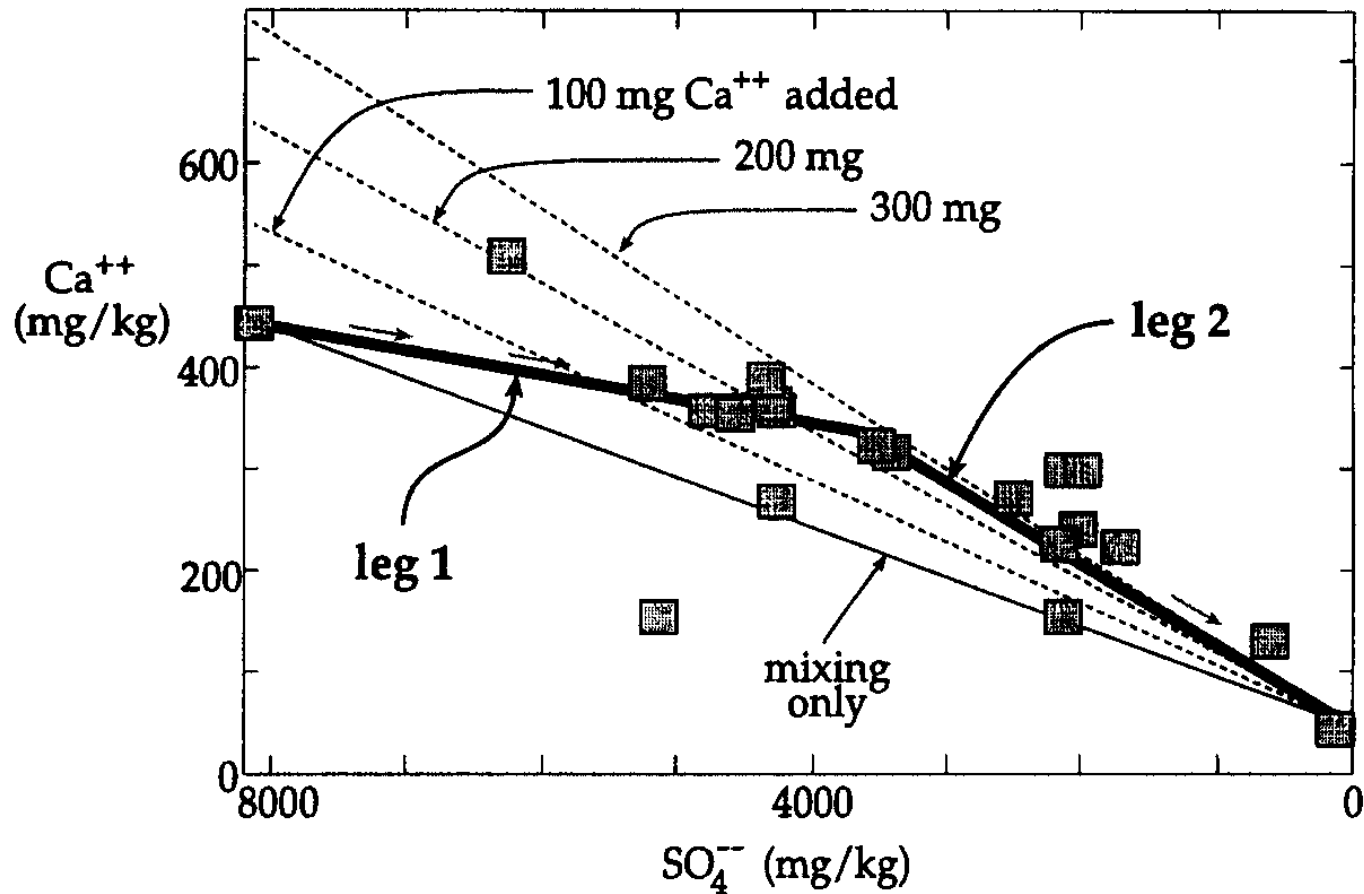


Figure 3-C3-1. Trend in Ca concentration predicted by the reaction path model. Dashed lines show simple mixing for fluids with different amounts of added Ca. Filled squares represent individual water samples. The reaction pathway is shown by the heavy line. In leg 1, Ca is added by dissolution of limestone. In leg 2, Ca concentrations change only by simple dilution. In leg 1, 2.5 kg of uncontaminated water and 250 mg of Ca are added to the solution. In leg 2, 12.5 kg of uncontaminated water is added. From Berger et al. (2000).

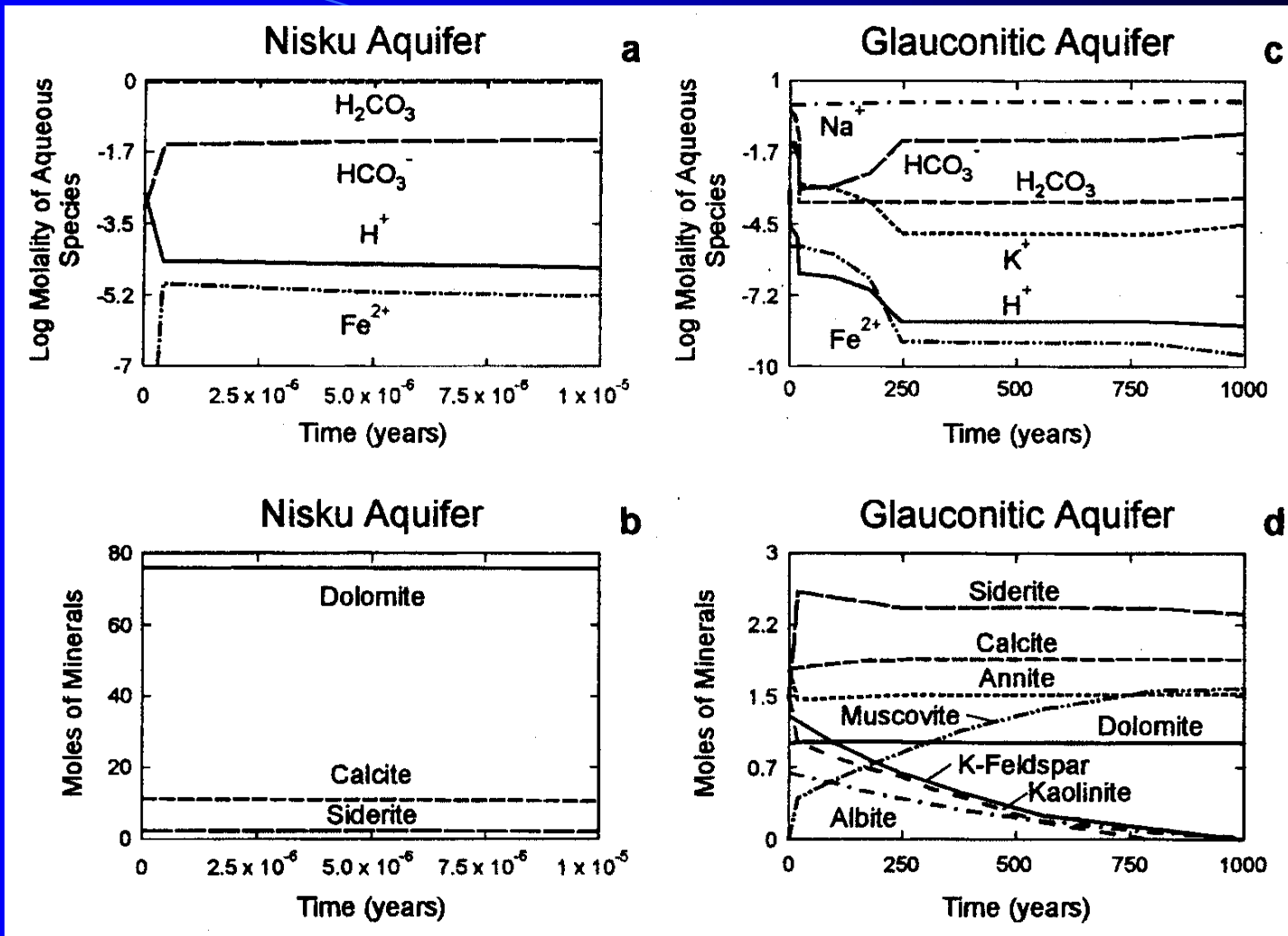


Figure 3-C4-1. Water-rock reactions as a function of time. Initial input is 1 mol of CO_2 into 1 kg of formation water. (a) Variation in amounts of aqueous species and (b) minerals for the Nisku carbonated aquifer. (c) Variation in amounts of aqueous species and (d) minerals for the Glaucconitic Sandstone aquifer. From Gunter et al. (2000).