

Reações químicas da água

Comportamento de ácido-base

- Água é anfotérica; Brønsted-Lowry:
$$\text{HCl (ácido)} + \text{H}_2\text{O (base)} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (ácido)} + \text{Cl}^- \text{ (base)}$$
$$\text{NH}_3 \text{ (base)} + \text{H}_2\text{O (acid)} \rightleftharpoons \text{NH}_4^+ \text{ (ácido)} + \text{OH}^- \text{ (base)}$$
- Água é base de Lewis e ácido de Lewis:
 - $\text{H}^+ \text{ (ácido)} + \text{H}_2\text{O (base)} \rightarrow \text{H}_3\text{O}^+$
 - $\text{Fe}^{3+} \text{ (ácido)} + \text{H}_2\text{O (base)} \rightarrow \text{Fe}(\text{H}_2\text{O})_6^{3+}$
 - $\text{Cl}^- \text{ (base)} + \text{H}_2\text{O (ácido)} \rightarrow \text{Cl}(\text{H}_2\text{O})_6^-$
- Duro ou mole?
 - Água é um ácido e base, duro(a) e fraco(a).

Reações de hidrólise



- Escreva pelo menos dez outros tipos de reações de hidrólise.

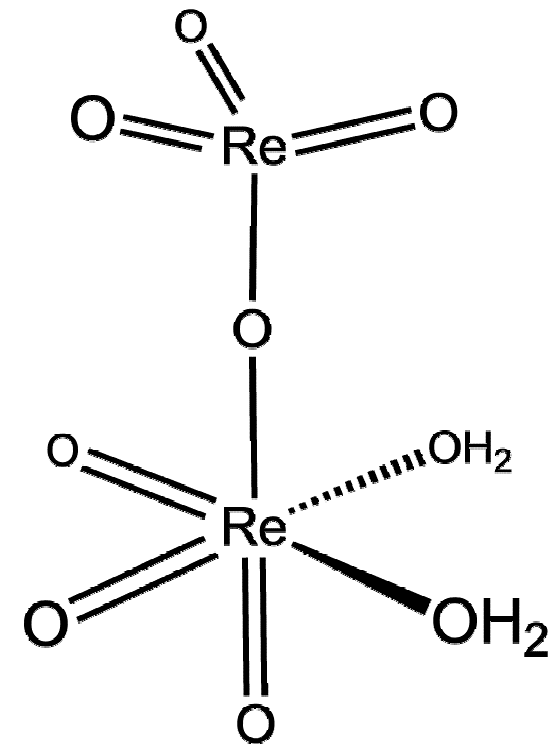
Reação de CO_2 e água com NaCl

- Cristais de cloreto de sódio expostos a água, água + CO_2 e água + HCl apresentam íons OH^- e HCO_3^- na superfície. Recristalizam, por aquecimento a 180°C ou superior.
- [doi:10.1016/0039-6028\(68\)90005-8](https://doi.org/10.1016/0039-6028(68)90005-8)

Água como ligante

- $\text{Fe}(\text{H}_2\text{O})_6^{3+}$
- Sólidos hidratados
 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
- Água de cristalização
Trona: $\text{Na}_3\text{HCO}_3\text{CO}_3 \cdot 2\text{H}_2\text{O}$
 $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ a 32°C transforma-se
em $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$.
 $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ acima de $37\text{--}38^\circ\text{C}$ forma
 $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

?



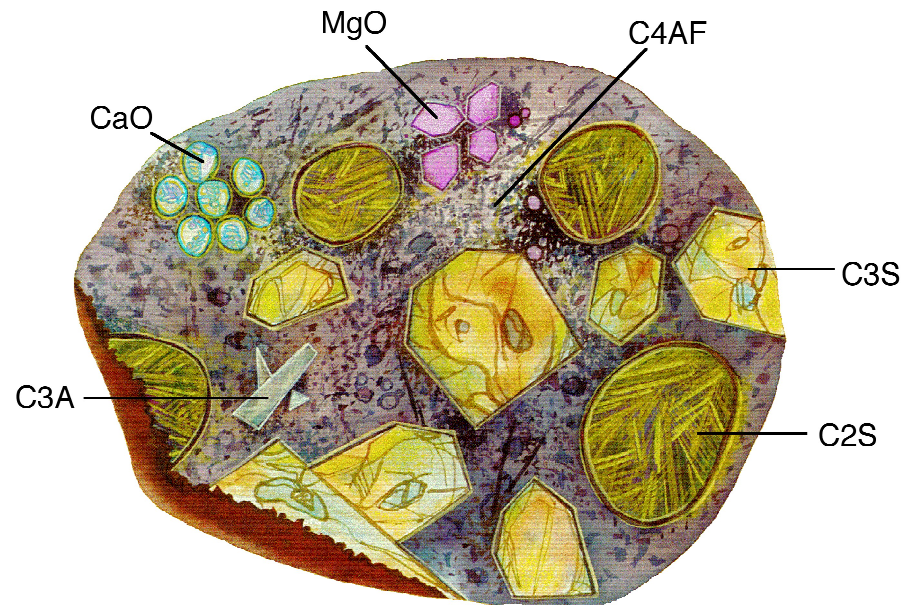
ácido perrênico

Cimento

- Clinker:

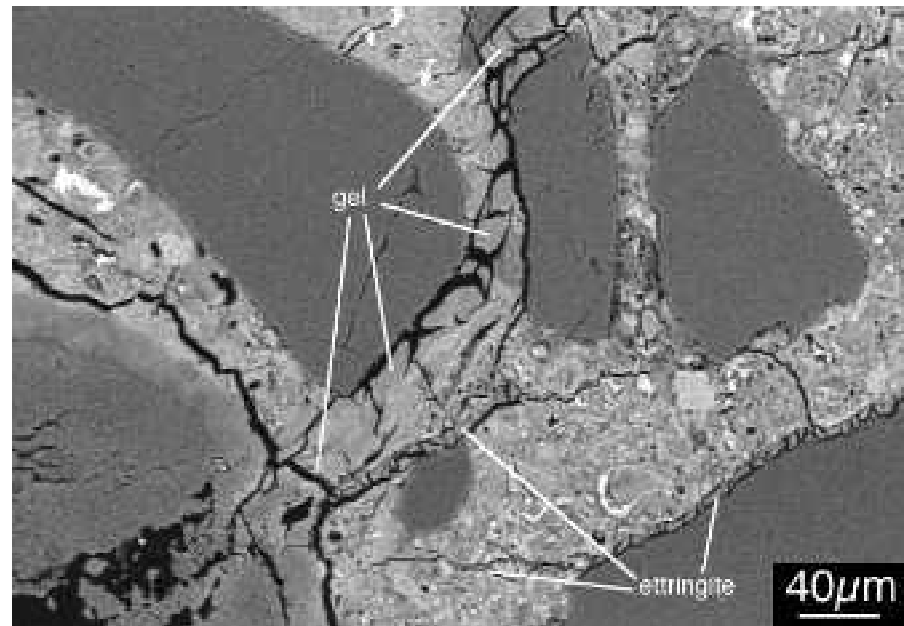
Cimento Portland tipo IV: 28% (C3S), 49% (C2S), 4% (C3A), 12% (C4AF), 1.8% MgO, 1.9% (SO₃), 0.9% de perda ao fogo e 0.8% CaO livre.

<http://www.understanding-cement.com/clinker.html>



Cimento

- Em presença de água, ocorrem muitas reações de hidratação e de carbonatação, que provocam a formação de um agregado de partículas sólidas, inter-travadas.



<http://www.whd.co.uk/Concrete/concretebysem.html>

Metasomatismo

- Substituição de mica, resultando em rochas cuja mineralogia foi completamente alterada por recristalização, formando-se minerais hidratados: clorita, muscovita, serpentina.



Orgânicas

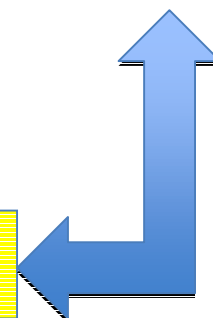
- Reação com carbocátions orgânicos
 - Hidratação de alcenos, formando álcoois
- Saponificação de óleos e gorduras
- Digestão de proteínas e polissacarídios
- Produto de reações de substituição S_N2 e de eliminação E2.
 - Desidratação
- Etanol \rightarrow eteno

Reações redox

- Água oxida substâncias que têm potencial de redução inferior ao do par H^+/H_2
 - Hidretos (NaH)
 - Metais alcalinos e alcalino-terrosos (menos Be)
 - $2 \text{Na} + 2 \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{H}_2$
 - Alumínio (reação é interrompida por passivação)
- Água pode ser oxidada a oxigênio
 - $4 \text{AgF}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{AgF} + 4 \text{HF} + \text{O}_2$
 - Poucos oxidantes atuam sobre a água na ausência de catalisadores

$\text{O}_2(g) + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229
$\text{MnO}_2(s) + 4\text{H}^+ + 2e^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$[\text{HXeO}_4]^- + 3\text{H}_2\text{O} + 6e^- \rightleftharpoons \text{Xe}(g) + 7\text{OH}^-$	+1.24
$\text{Tl}^{3+} + 2e^- \rightleftharpoons \text{Tl}^+$	+1.25
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33
$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$\text{CoO}_2(s) + 4\text{H}^+ + e^- \rightleftharpoons \text{Co}^{3+} + 2\text{H}_2\text{O}$	+1.42
$2\text{NH}_3\text{OH}^+ + \text{H}^+ + 2e^- \rightleftharpoons \text{N}_2\text{H}_5^+ + 2\text{H}_2\text{O}$	+1.42
$2\text{HIO}(aq) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{I}_2(s) + 2\text{H}_2\text{O}$	+1.44
$\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+}$	+1.44
$\text{BrO}_3^- + 5\text{H}^+ + 4e^- \rightleftharpoons \text{HBrO}(aq) + 2\text{H}_2\text{O}$	+1.45
$\beta\text{-PbO}_2(s) + 4\text{H}^+ + 2e^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	+1.460
$\alpha\text{-PbO}_2(s) + 4\text{H}^+ + 2e^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	+1.468
$2\text{BrO}_3^- + 12\text{H}^+ + 10e^- \rightleftharpoons \text{Br}_2(l) + 6\text{H}_2\text{O}$	+1.48
$2\text{ClO}_3^- + 12\text{H}^+ + 10e^- \rightleftharpoons \text{Cl}_2(g) + 6\text{H}_2\text{O}$	+1.49
$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51

Soluções de permanganato de potássio decompõem-se lentamente. A decomposição é acelerada por MnO_2 . Auto-catalítica.



Eletroneutralidade

- Na água pura, segundo o princípio de eletroneutralidade, as concentrações de íons hidróxido e hidrônio são iguais.
- O princípio de eletroneutralidade é estendido implicitamente a quaisquer sistemas, mas tem sido questionado.

Princípio da Electroneutralidade?

- Toda substância pura é eletroneutra
 - IUPAC *Gold Book*,
<http://goldbook.iupac.org/E01992.html>.
- Objeção:
 - One of the basic **assumptions** of chemical thermodynamics is that bulk matter is **electrically neutral**; **abandoning that assumption allows us** to contemplate, for example, the free energy of transferring a single ion from one phase to another.
 - L.S.McCarty and G.M.Whitesides, *Electrostatic Charging due to Separation of Ions at Interfaces: Contact Electrification of Ionic Electrets*, **Angew. Chemie Int. Ed.** **2008**, 47, 2188-2207

Contaminação

- Na prática, água é facilmente contaminada:
 - no laboratório:
 - pelo CO_2 atmosférico, que reduz o pH até 5,5
 - por produtos de hidrólise de vidro (NaOH , Ca(OH)_2 , que aumentam o pH
 - por sal e gordura das mãos do experimentador
 - por siliconas e plastificantes dos materiais poliméricos
 - por hidrocarbonetos da atmosfera urbana

Condutividade da água

E16

Electrochemical and Solid-State Letters, 8 (1) E16-E19 (2005)
1099-0062/2004/8(1)/E16/4/\$7.00 © The Electrochemical Society, Inc.



The Fundamental Conductivity and Resistivity of Water

Truman S. Light,^a Stuart Licht,^{b,*} Anthony C. Bevilacqua,^c
and Kenneth R. Morash^c

^a*Auburndale, Massachusetts 02466, USA*

^b*Department of Chemistry, University of Massachusetts, Boston, Massachusetts 02125-3399, USA*

^c*Mettler-Toledo Thornton, Incorporated, Bedford, Massachusetts 01730, USA*

The most accurate values to date were determined for conductivity of water from 0-100°C, permitting new determination of high-temperature hydroxide ion equivalent conductance. These values were incorporated into a fundamental water coefficient table including hydroxide and hydrogen ion mobilities, water ionization constant, density, conductivity, and resistivity. The conductivity/resistivity values were measured with a multiple-pass, closed, recirculating flow conductivity system, with improved multiple resistance temperature device measurement, and improved analysis of temperature and impurity effects. An accurate conductivity knowledge is necessary to understand water-limiting processes and to facilitate the analysis of trace ionic impurities in water.

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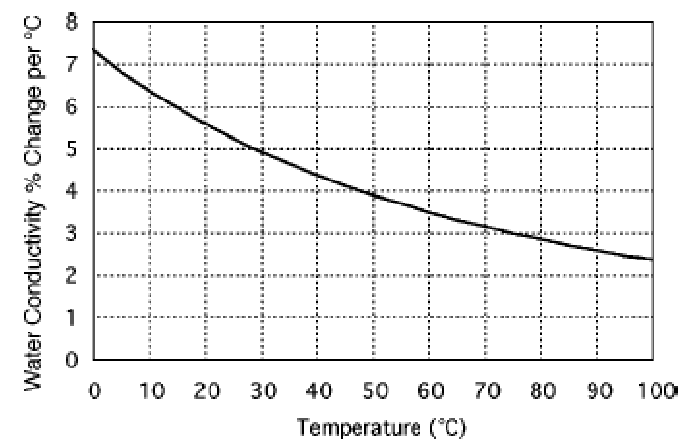
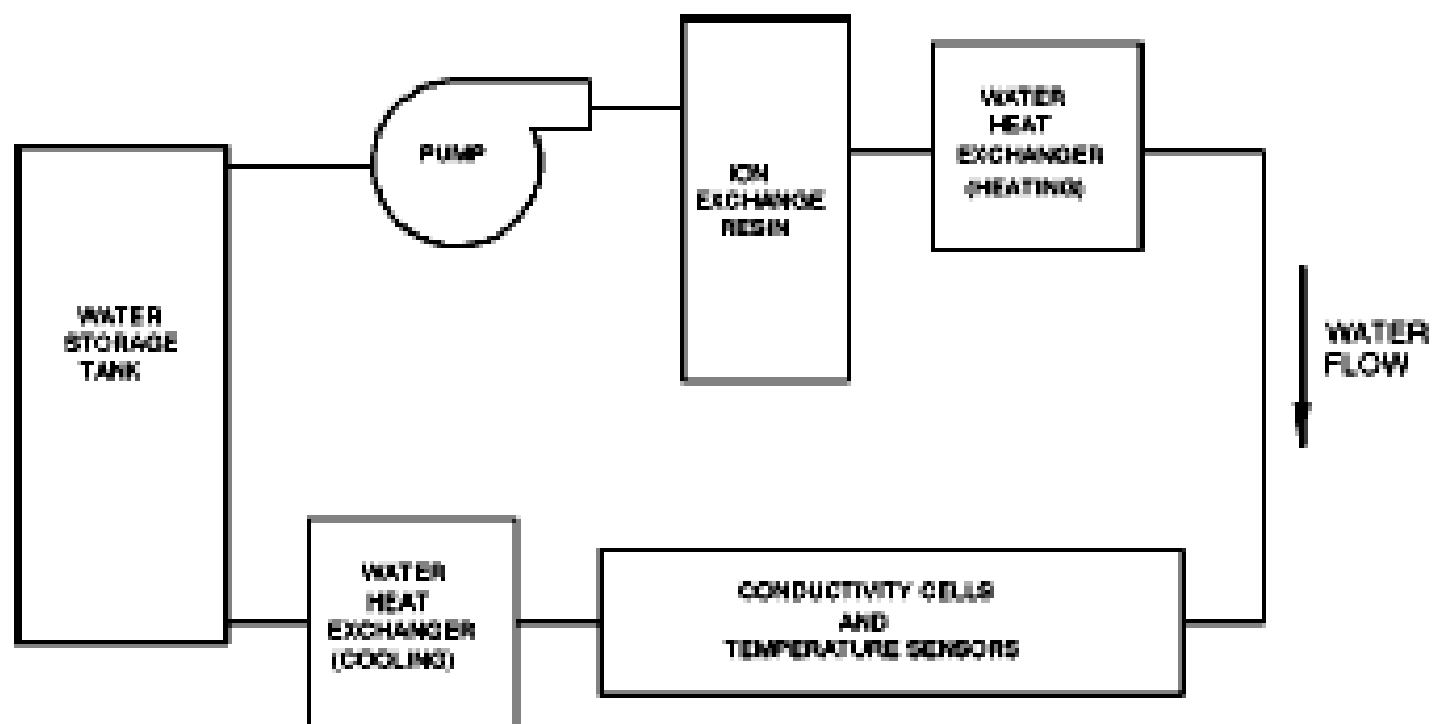


Figure 1. Schematic of the UPW multipass conductance determination.

Chuva ácida

- Toda chuva tem alguma acidez, devido ao CO_2 atmosférico.
- Em atmosferas contaminadas com SO_2 e NO_x , a acidez pode aumentar, devido à formação de ácidos fortes: sulfúrico e nítrico.
- <http://java.epa.gov/castnet/maps.do?mapType=MAPCONC>

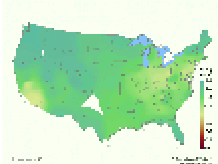
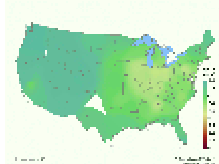
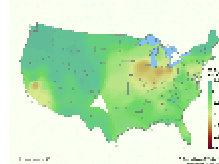
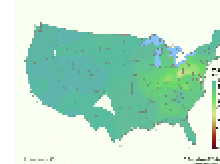
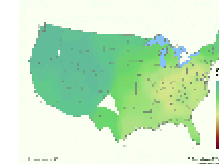
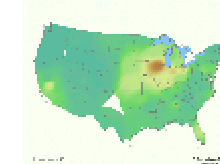
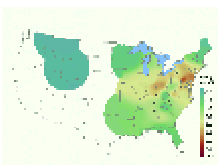
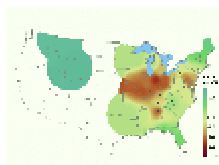
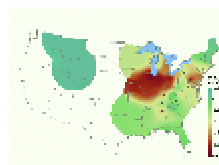
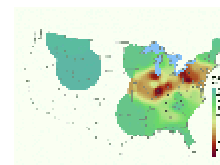
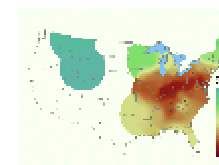
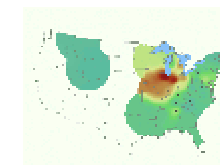
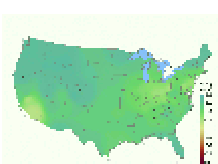
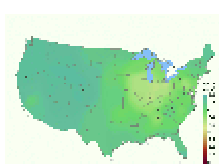
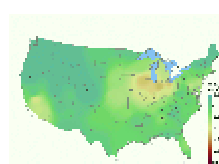
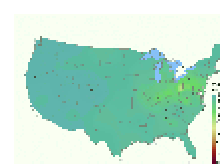
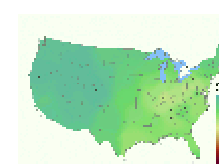
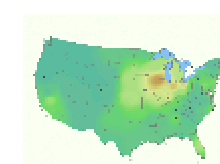
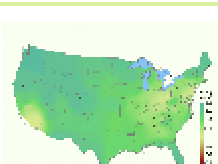
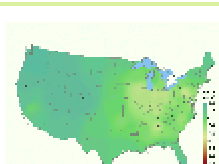
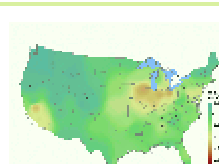
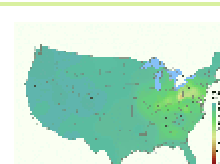
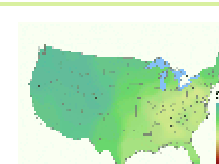
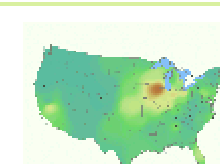
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Ambient Concentrations

Year	Gaseous Nitric Acid	Particulate Ammonium	Total Nitrate (Nitric Acid + Nitrate)	Gaseous Sulfur Dioxide	Particulate Sulfate	Particulate Nitrate
2007-2009						
1989-1991						
2009						
2008						

Exercícios

1. Identifique uma reação química que poderia ser utilizada para produzir água super-pura. Descreva todo o processo.
2. Por que a determinação da condutividade da água é sempre feita em sistema em fluxo? Como você faria para determinar a condutividade do etanol?
3. Escreva pelo menos dez tipos de reações de hidrólise, informando sobre as condições e o uso (ou não) de catalisador. Justifique suas escolhas considerando a importância de cada reação.