

# Chemie der Hydrosphäre I

- **Der Wasserkreislauf**
- **Besondere Eigenschaften des Wassers**
- **Einheiten**
- **Verteilungsdiagramme als Funktion einer Variabler**
- *Der  $pE$ -Wert*
- *Verteilungsdiagramme als Funktion von zwei Variablen*
- *Das  $pH/pE$ -Diagramm*

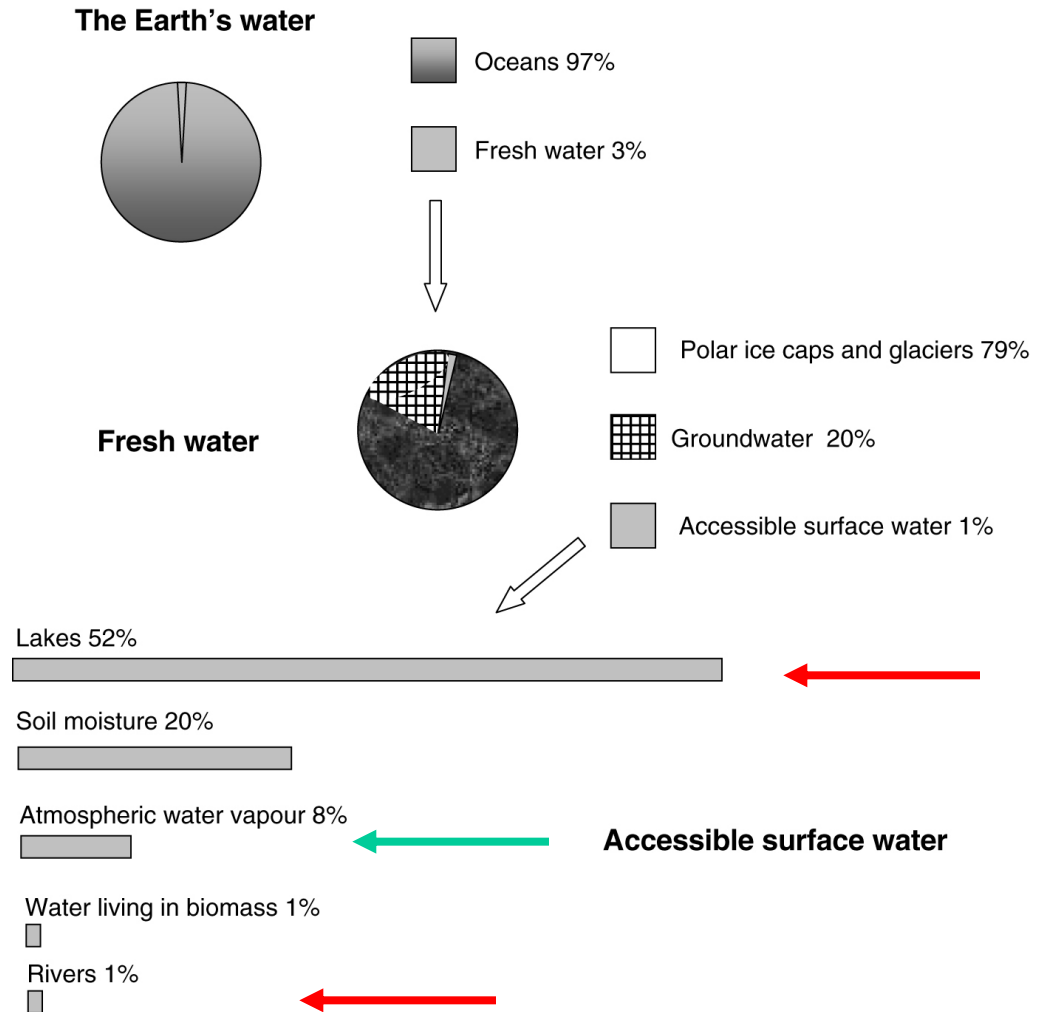


- **Bedeckung der Erdoberfläche zu 73%**
- **Wichtiger Bestandteil auch in der Atmosphäre und den Böden, insbesondere für chemische Prozesse**
- **Wasserverfügbarkeit eines der Hauptkriterien des Lebensstandards**

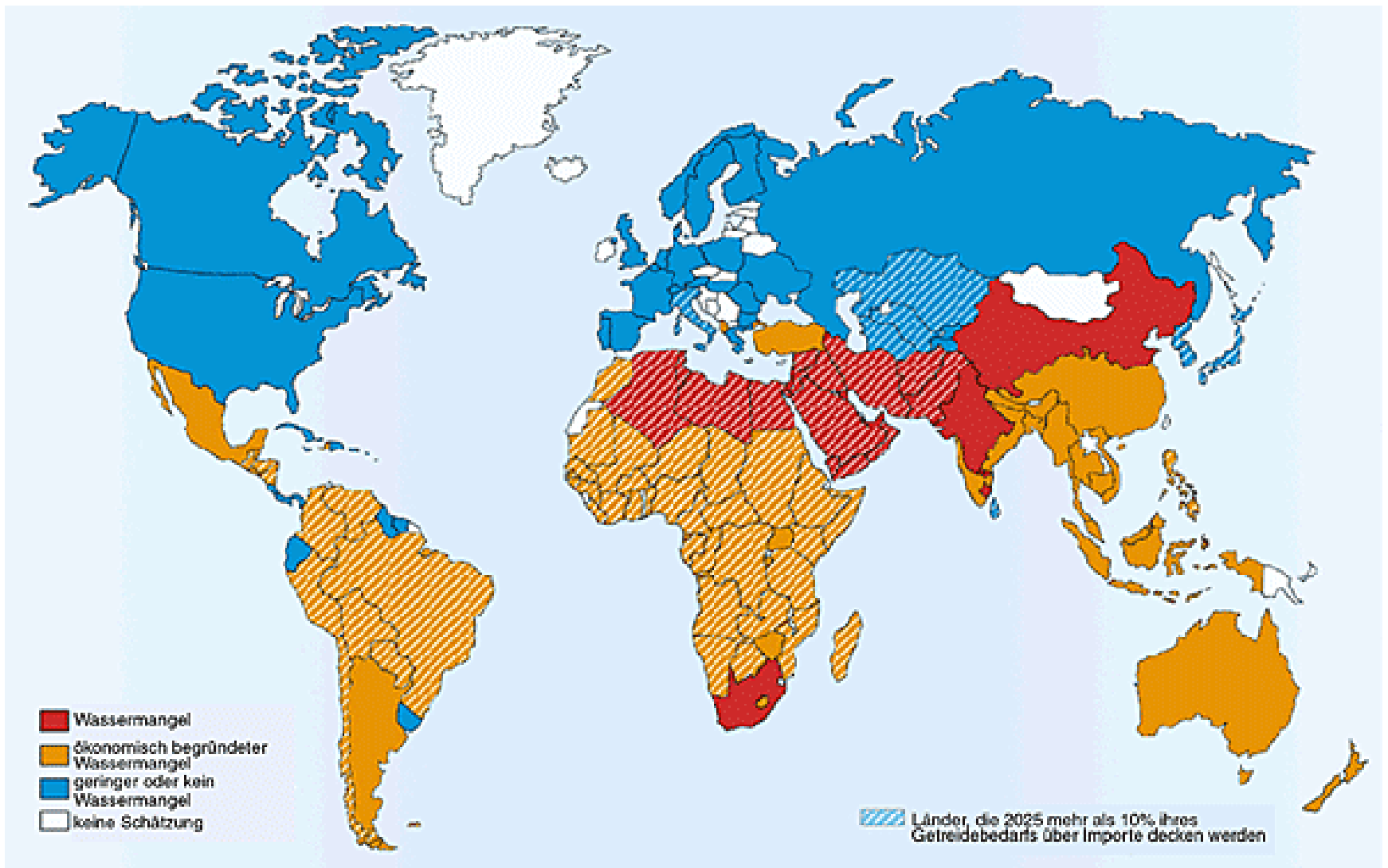


# Verteilung der Wasserreservoirs

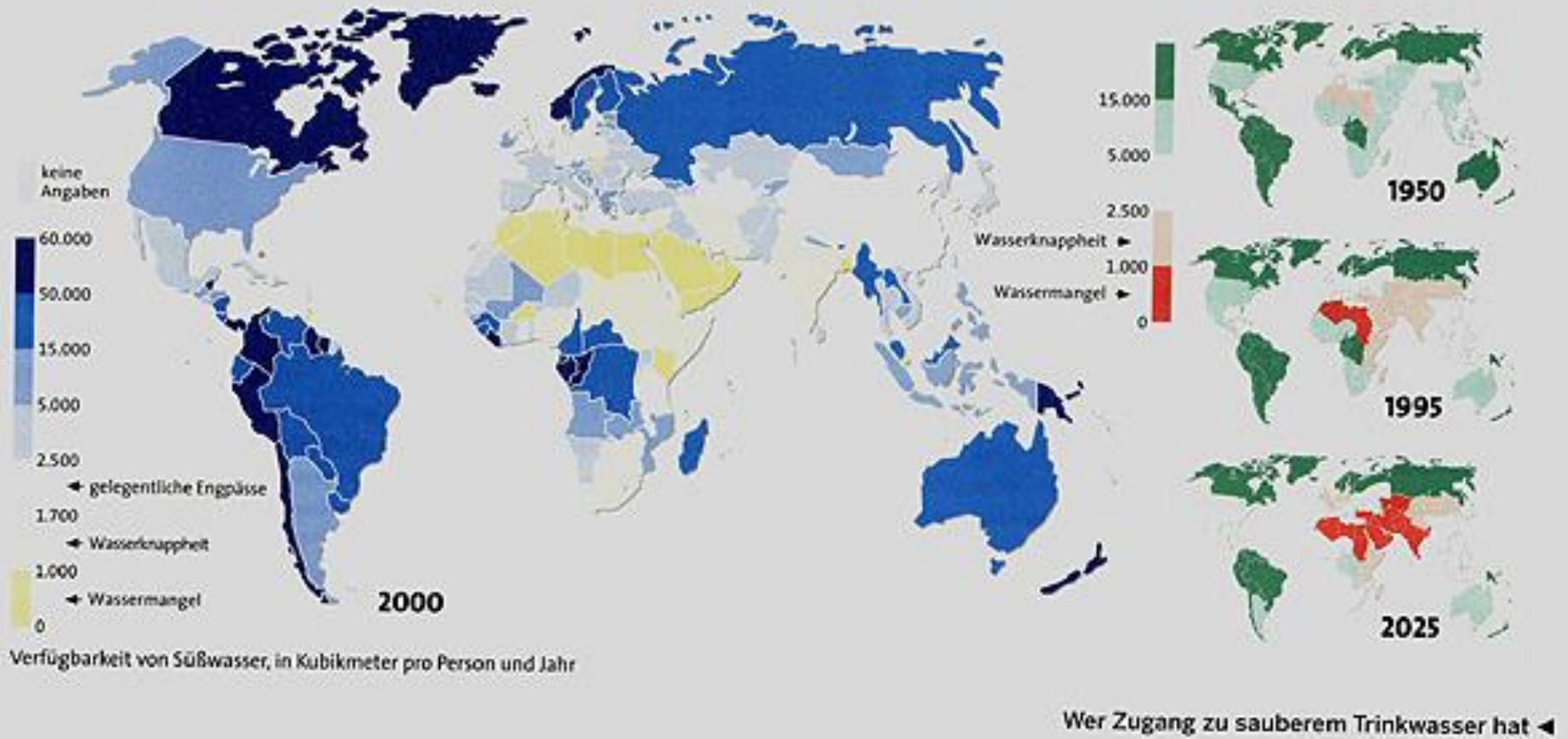
- 97% des globalen Wasserreservoirs in den Ozeanen
- 3% als Süßwasser vorhanden
  - Polare Eismassen (90% Antarktis)
  - Grundwasser
  - Nur etwa 0,5% (damit etwa 0.02 % des Gesamtwassers leicht erreichbares Frischwasser



# Wasserknappheit

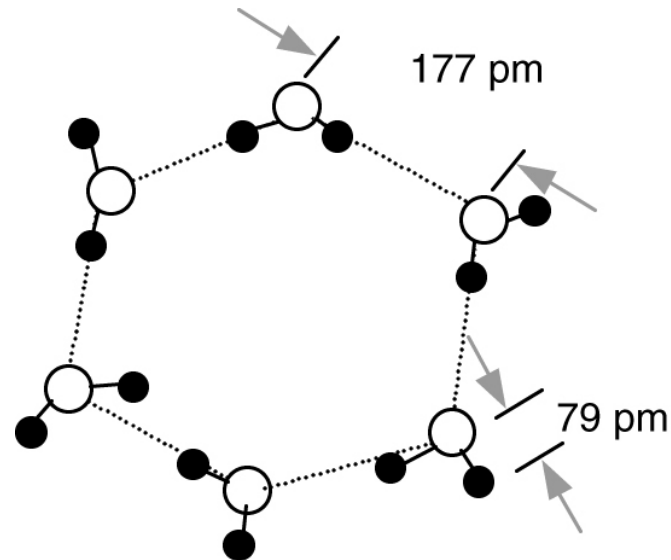


# Wasserknappheit



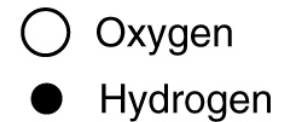
## EIS

- **Gewellte hexagonale Ringe, mit Vernetzung durch Wasserstoffbrücken**
- **Geringe Dichte von 0.917 kg/L, leichter als Wasser oder Seewasser**



$$\Delta H_{\text{OH}} = 463.5 \text{ kJ mol}^{-1}$$

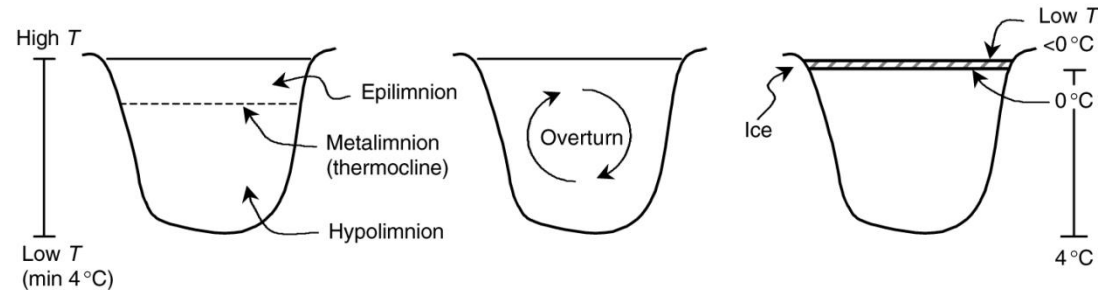
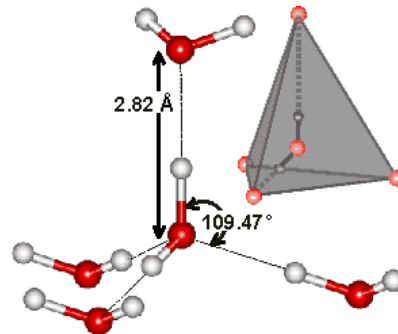
$$\Delta H_{\text{O}\dots\text{H}} = 10\text{--}40 \text{ kJ mol}^{-1}$$



## Wasser

- Beim Schmelzen nur Aufbruch von etwa 12% der Wasserstoffbrücken
- Etwa weitere 8% bis zum Siedepunkt
- => Dichteerhöhung
- Entgegenwirkender Effekt der thermischen Ausdehnung

$\Sigma$ : Temperatur maximaler Dichte



Warm climate (summer)

Solar radiation penetrates the epilimnion, stimulating algal photosynthesis and producing oxygen. Little solar radiation reaches the hypolimnion; there is no photosynthesis, but bacterial decomposition of organic matter causes depletion of oxygen.

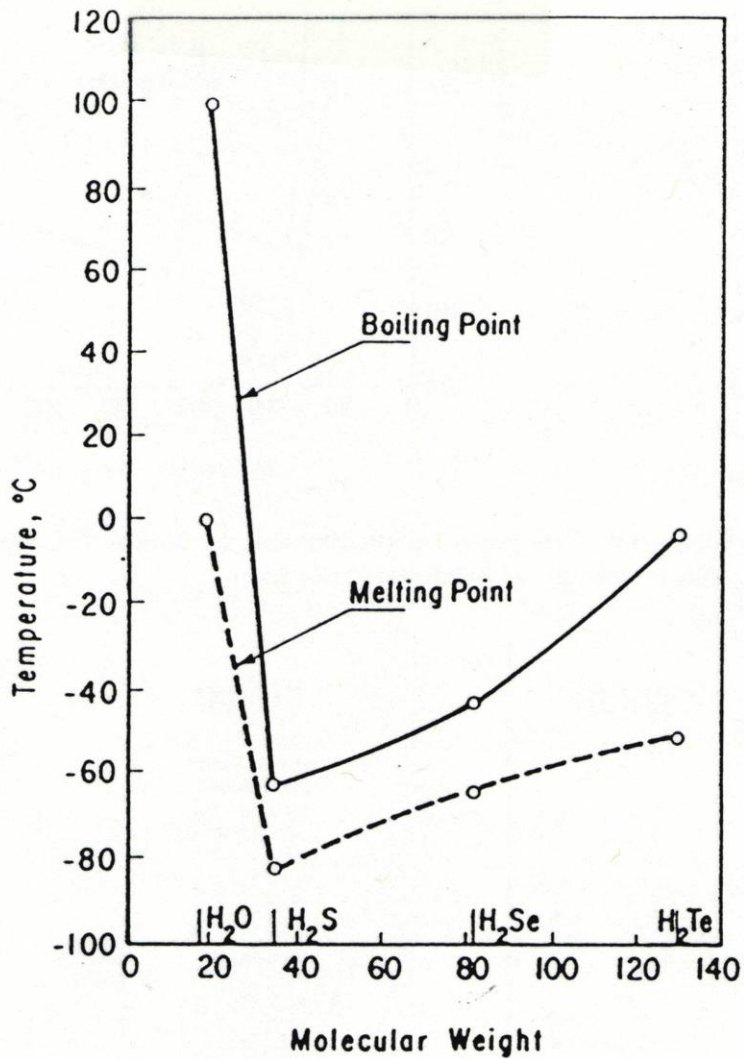
Cool weather (autumn)

Cooled surface water sinks to the bottom, forcing bottom water upwards, creating a homogeneous (T and nutrients) environment.

Cold weather (winter)

Ice forms on the surface; temperature relatively uniform below ice layer.





Drastisch erhöhte Siede- und Schmelztemperaturen im Vergleich zu den Wasserstoffverbindungen der schwereren Elemente der Hauptgruppe



# Besonderheiten des Wassers – Wärmekapazität und Phasenübergangsenthalpie

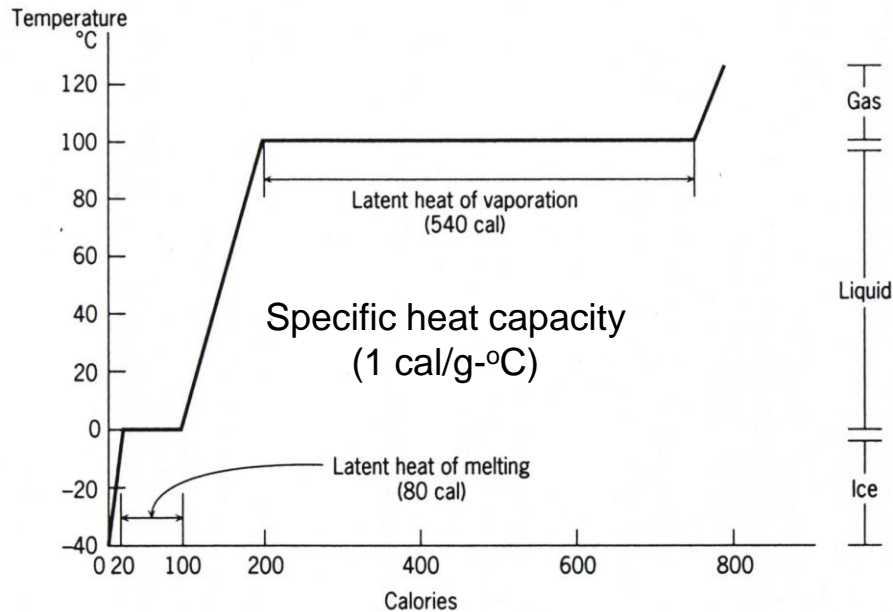


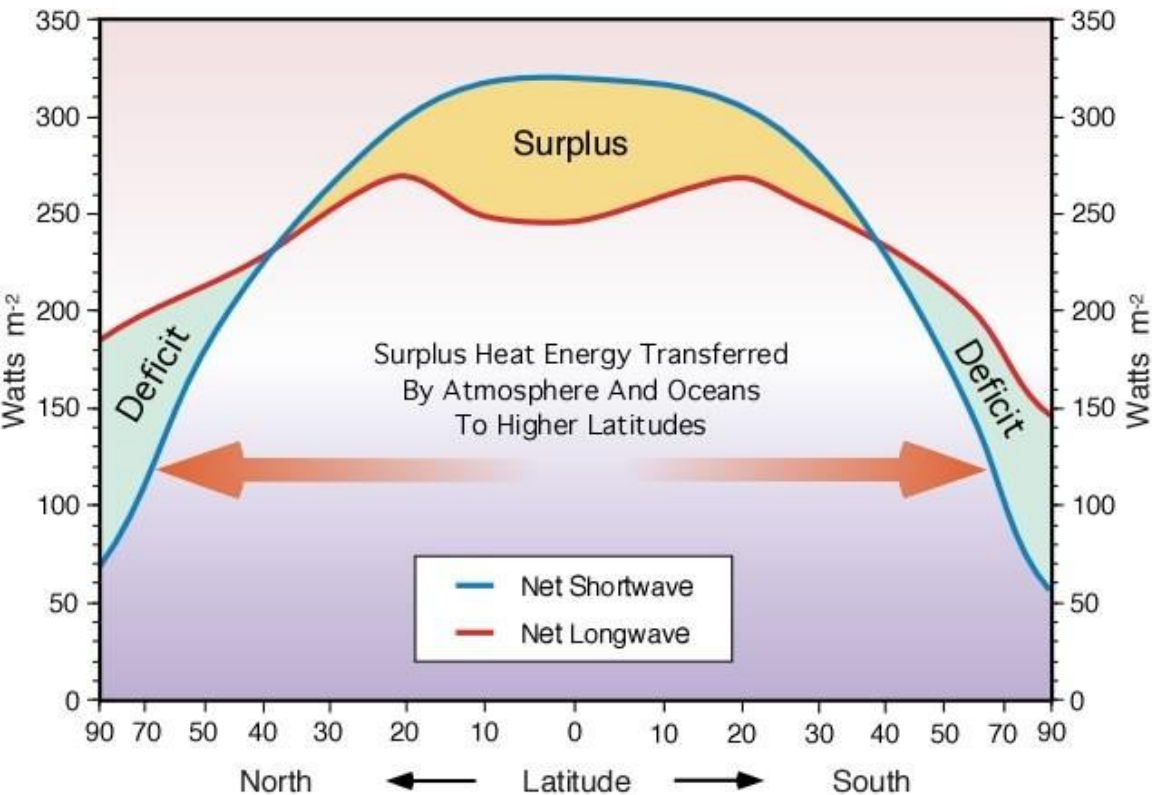
FIGURE 2.9. The phase transitions of water as caused by changing heat content. Slopes of the lines indicate heat capacity.

## Effective Climate Regulator

Spezifische Wärme und insbesondere Verdampfungsenthalpie des Wassers sind extrem hoch.

⇒ Extrem große Wärmemengen zur Erwärmung von Wasser und zur Evaporation benötigt.

⇒ Das große Meerwasservolumen mit seiner großen Oberfläche hat eine entscheidende Bedeutung für die Wärmeregulierung der Erde



## Regelt verringerten Temperaturgradienten

- zwischen Äquator und Polen
- zwischen Sommer und Winter
- zwischen Tag und Nacht

Effective Climate Regulator

| Property  | Comparison   | Importance   |
|---|--|--|
| Heat capacity ( $C_p$ ; $\text{cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ )<br>Thermal energy to raise 1 gm of a substance by 1 $^\circ\text{C}$ .          | Highest of all solids & liquids, except liquid $\text{NH}_3$             | Prevents extreme ranges in temperature; Energy transfer by water movements is large                                    |
| Heat of fusion ( $\Delta H = 79 \text{ cal g}^{-1}$ )<br>Energy needed to break the hydrogen bonds.   | Highest except for $\text{NH}_3$   | Absorption or release of latent heat results in large thermostatic effects. Important for energy transfer and climate. |
| Heat of vaporization ( $\Delta H = 540 \text{ cal g}^{-1}$ )<br>Energy needed to convert water to vapor   | Highest of all liquids   | Thermostatic effect; Energy transfer   |
| Boiling point (100 $^\circ\text{C}$ ; projected -68 $^\circ\text{C}$ )<br>Freezing point (0 $^\circ\text{C}$ ; projected -90 $^\circ\text{C}$ )           | Much higher than expected (compared to other hydrides)                   | Water exists in 3 phases within the critical temperature range that accommodates life                                  |
| Heat of freezing; only 1/7 that of evaporation  | Low; Water structure can move easily into ice.                           | Implying relatively small difference in the # of bonds between water and ice   |
| Surface tension; water likes itself relative to most other surfaces ( $7.2 \times 10^9 \text{ N m}^{-1}$ )<br>Measure of the strength of a liquid surface | Highest of all substances  | Waves, drops and aerosol sea salt formation. Cell physiology   |
| Dielectric constant; Charge insulation and dissolving power as a result of ion hydration (87 at 0 $^\circ\text{C}$ , 80 at 20 $^\circ\text{C}$ )          | Highest of all substances except $\text{H}_2\text{O}_2$ and $\text{HCN}$ | Solubility of salts & ion reactions  |
| Dissolving power  | Highest of all liquids both # of substances and quantities               | Implications for biological and physical phenomena   |
| Electrolytic dissociation   | Very small   | A neutral substance, yet contains both $\text{H}^+$ and $\text{OH}^-$ ions   |
| Transparency<br>Absorption of radiant energy is large in IR and UV; Relatively uniform in the visible.  | Relatively large   | Water is "colorless"; Important for photosynthetic and photochemical reactions   |
| Conduction of heat (a molecular process)  | Highest of all liquids   | Important for small-scale heat transfer, as in living cells.   |
| Molecular viscosity ( $= 10^{-3} \text{ N s m}^{-2}$ )<br>Measure of resistance to distortion (flow)  | Less than most other liquids at same temperature.                        | Water flows readily to equalize pressure differences.  |
| Compressibility   | Relatively low (more similar to a solid)                                 | Large increase in pressures with depth causes only slight increase in density  |
| Thermal expansion<br>(for pure water it is at 4 $^\circ\text{C}$ )  | Temperature of maximum density decreases with increasing salinity.       | Waters with salinity less than 25 have maximum density at temperatures above the freezing point                        |

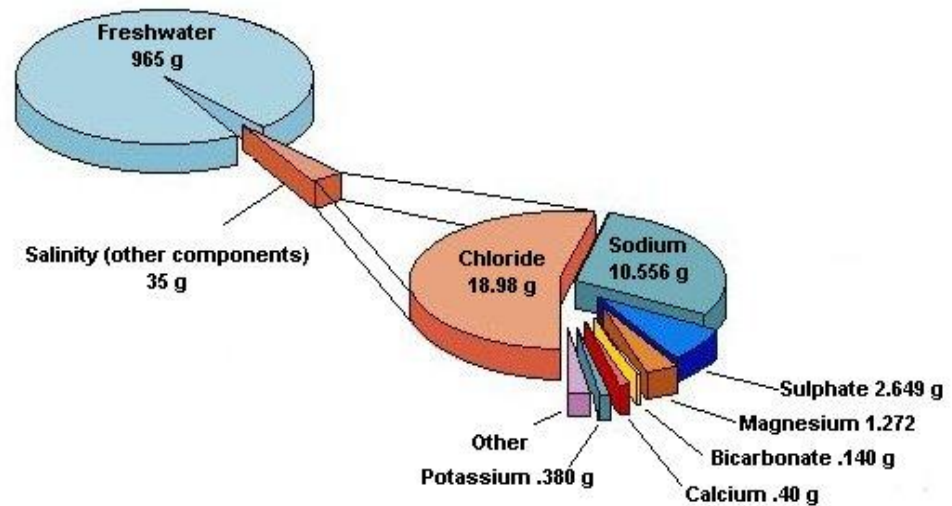


# Solvatationseigenschaften des Wassers

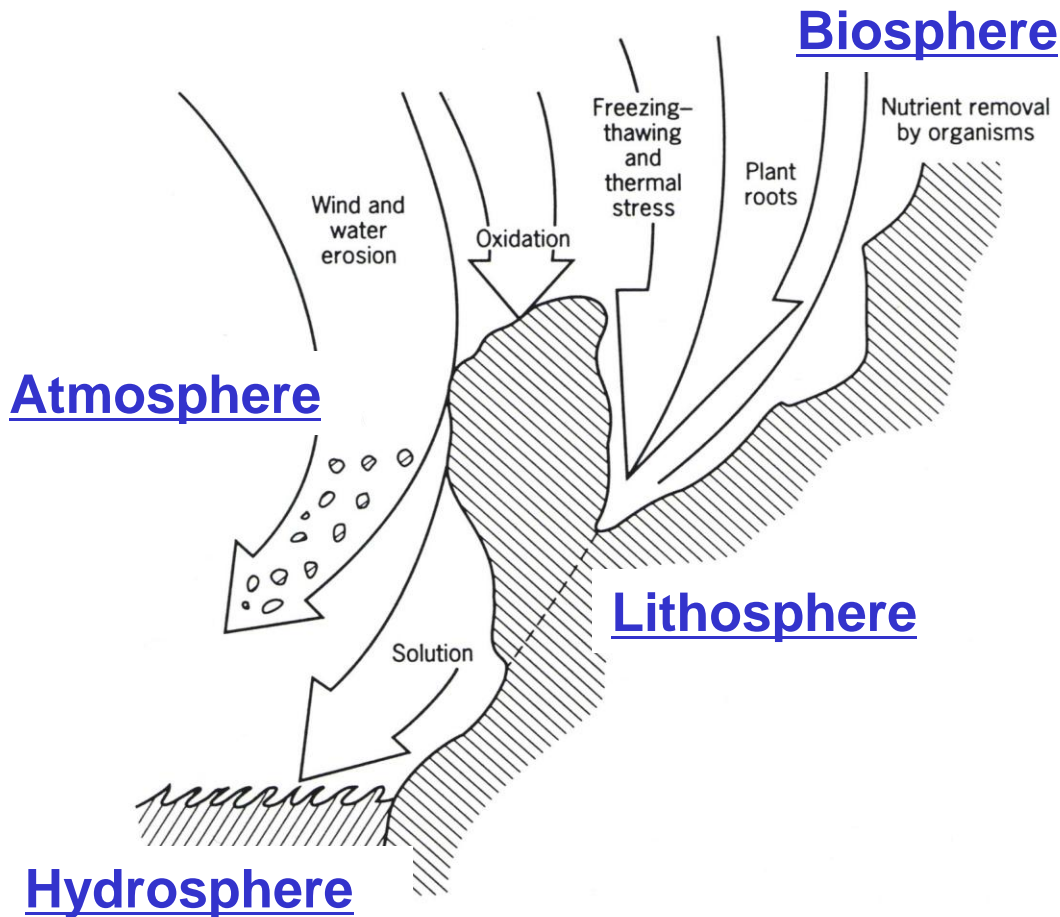
- Hohes Dipolmoment und Polarität führt zu guter Löslichkeit vieler ionischer Substanzen
- Hydratisierung in erster Näherung durch Ladungsdichte des Ions gegeben
- Folge der guten Lösungsmiteleigenschaften für ionische Verbindungen ist Anreicherung von Ionen im Meerwasser mit langen Verweilzeiten
- Bildung von Salzwasser

**Table 9.2** Charge and radius properties of the alkali metals in aqueous solution.

|                                     | Li <sup>+</sup> | Na <sup>+</sup> | K <sup>+</sup> | Rb <sup>+</sup> | Cs <sup>+</sup> |
|-------------------------------------|-----------------|-----------------|----------------|-----------------|-----------------|
| Ionic radius / pm                   | 60              | 95              | 133            | 148             | 169             |
| Charge density / C pm <sup>-1</sup> | 0.0167          | 0.0105          | 0.0075         | 0.0068          | 0.0059          |
| Hydrated radius / pm                | 340             | 276             | 232            | 228             | 228             |
| Hydration number                    | 23.3            | 16.6            | 10.5           | 10              | 9.9             |



## Where Does this Weathering Occur?



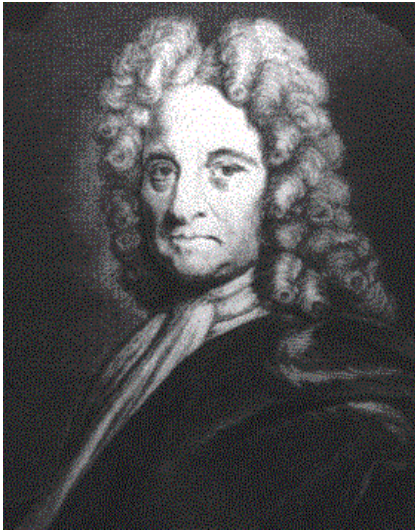
Water → physical leaching

Soils!

Facilitated by vegetation and other associated organisms (e.g., bacteria, fungi, etc)

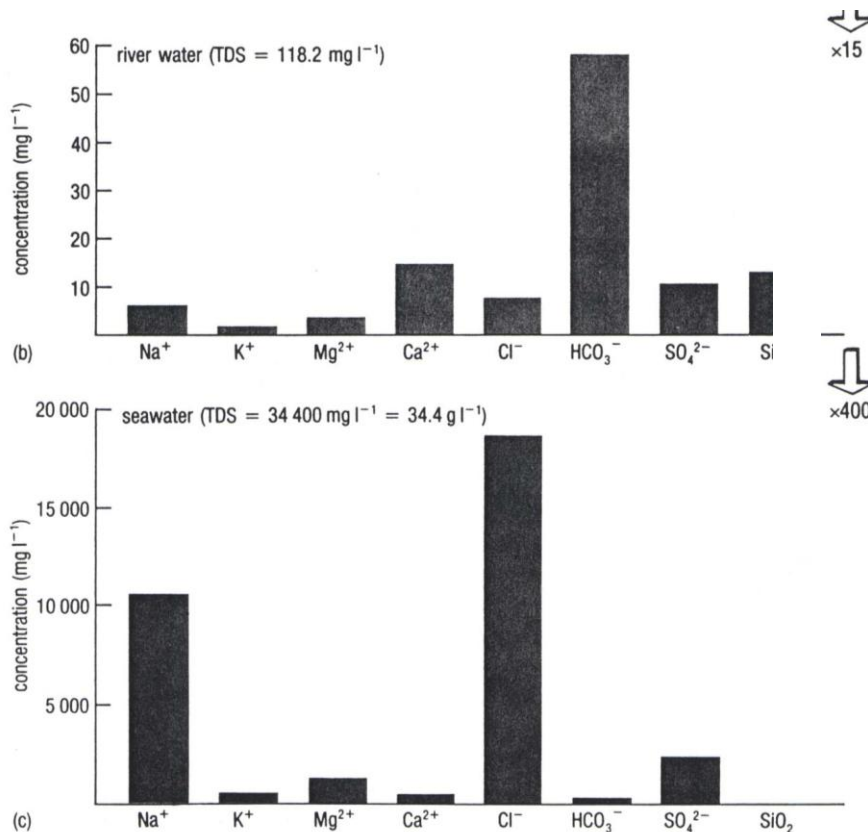
Anthropogenically sensitive!

[antwrp.gsfc.nasa.gov/apod/ap960706.html](http://antwrp.gsfc.nasa.gov/apod/ap960706.html)



Edmund Halley (1715) suggested “saltiness” represented the accumulation of salts washed into the ocean since their origin – thereby calculated the age of the ocean was ~11 My.

Halley's calculation is based on fact that seawater contains ~290x more salt than average riverwater and **residence time of water** in ocean with respect to river input is ~39Ky (age = 39000 yrs x 290 or ~11 My).



What's wrong with this calculation?

*Doesn't explain compositional difference between seawater and riverwater*



# Mass balance: Simple box models

## Concepts

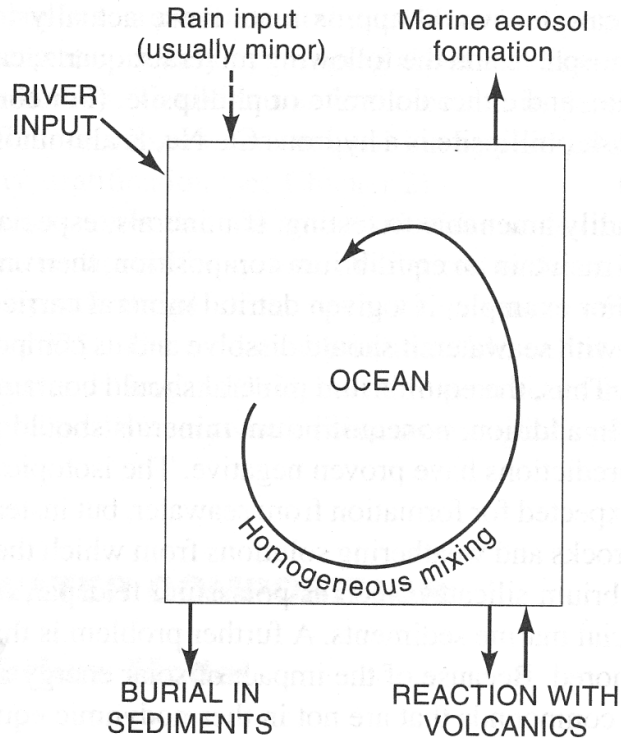


Fig 8.3 from Berner and Berner.  
Box model appropriate for  
conservative elements in seawater.

**Residence time:** turnover or replacement time

$$\tau = \text{size of reservoir} / \text{total input to (or outputs from) the reservoir.}$$

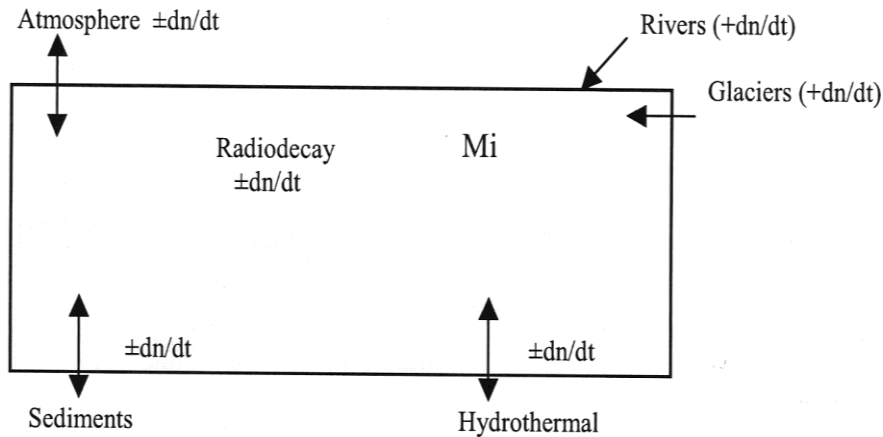
**Fluxes:** Amount of material transferred from one reservoir to another per unit time

**Cycle:** A system consisting of two or more connected reservoirs where a large fraction of the material is transferred through the system in a cyclic fashion. Budgets and cycles can be considered over wide range of spatial scales

**Steady state:** When the sources and sinks (as fluxes) are in balance.

# Mass balance: Simple box models

## Simple 1-Box ocean



$Q$  and  $S$  are input and output  
RATES (e.g. moles/yr)

$[M]$  total dissolved mass in the  
box (moles)

At **steady state**, the dissolved concentration  $M_i$  does not change with time, and the fluxes in are equal to the fluxes out:

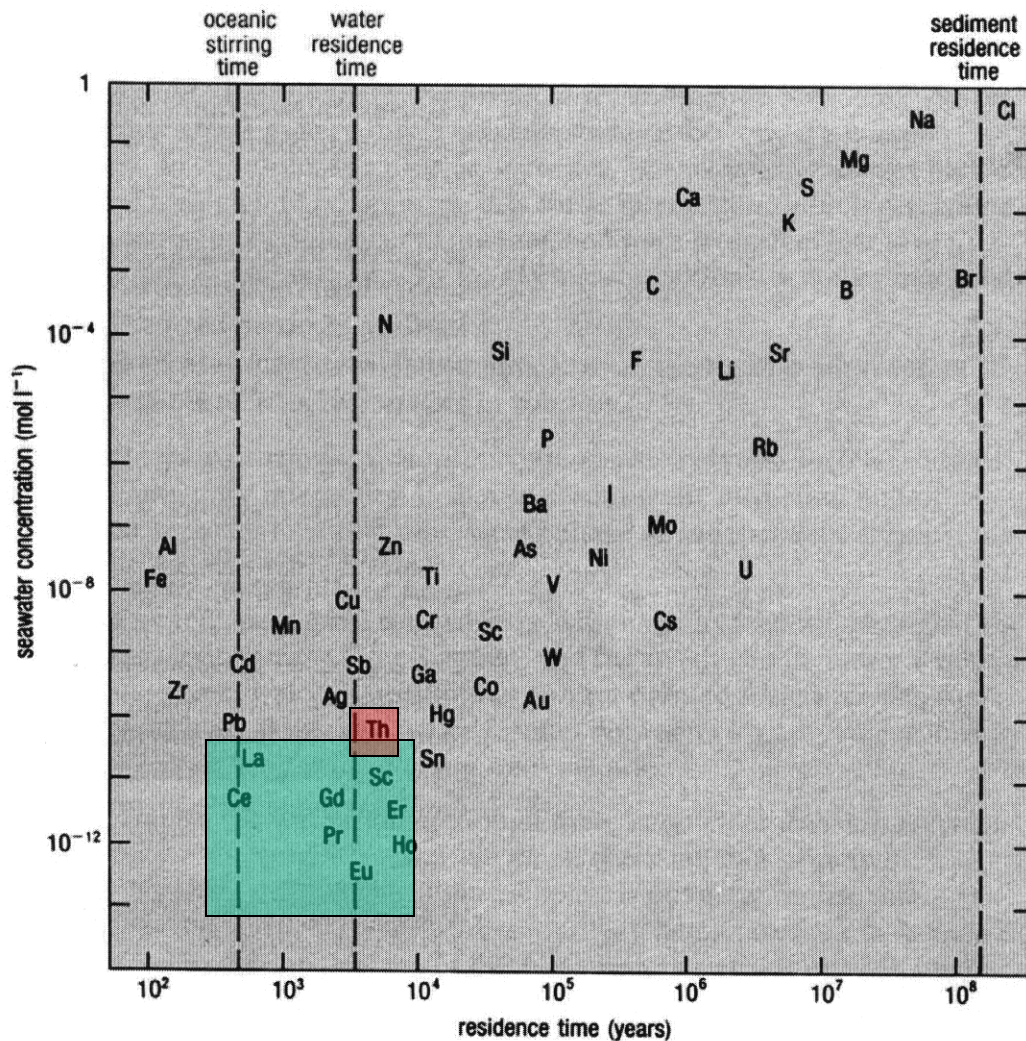
$$D[M_i]/dt = \sum dn_i/dt = 0$$

$$\sum (dn_i/dt)_{\text{sources}} = \sum (dn_i/dt)_{\text{sinks}} \text{ or}$$

$$Q = S$$

**Residence time:**

$$= [M]/Q = [M]/S$$



Graph showing the broad correlation between concentration ( $\text{mol l}^{-1}$ ) and residence time of several elements in seawater. Note that both scales are logarithmic.

From Whitfield and Turner, 1979

Cl: Highest abundance, and long residence time

Rare earth elements (La, Ce, Eu) and Th are very reactive (adsorption to particles).

If  $\tau$  for a given element is less than the residence time of water, that element will not be homogeneously distributed in the ocean.

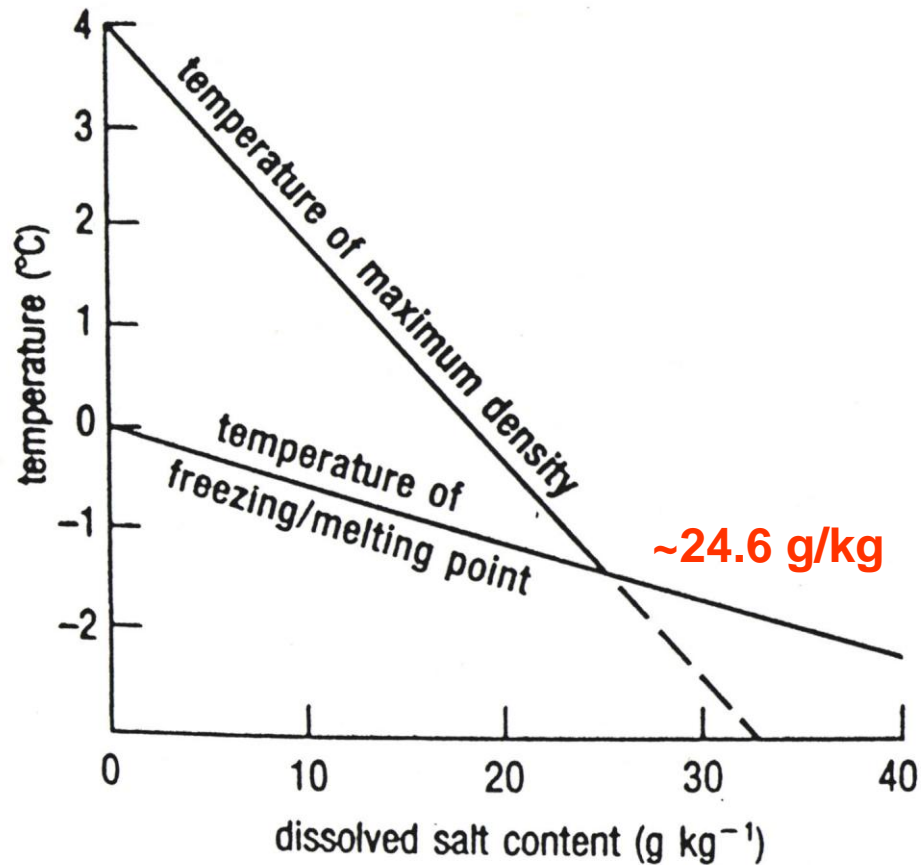


Die durch die guten Lösungsmitelegenschaften verursachte Anreicherung von Ionen verändert die Eigenschaften des Wassers:

### Meerwasser

**Comparison of Seawater and Pure Water Properties**

| Property   | Seawater (35%)        | Pure Water            |
|--|-----------------------|-----------------------|
| Density, $\text{g cm}^{-3}$ , 25 °C                              | 1.02412               | 1.0029                |
| Specific conductivity, $\text{ohm}^{-1} \text{cm}^{-1}$ , 25 °C, | 0.0532                | -                     |
| Viscosity, millipoise, 25 °C                                     | 9.02                  | 8.90                  |
| Vapor pressure, mm Hg, 20 °C                                     | 17.4                  | 17.34                 |
| Isothermal compressibility, $\text{vol/atm}$ , 0 °C              | $46.4 \times 10^{-6}$ | $50.3 \times 10^{-6}$ |
| Temperature of maximum density, °C                               | -3.25                 | 3.98                  |
| Freezing point °C  | -1.91                 | 0.00                  |
| Surface tension, $\text{dyne cm}^{-1}$ , 25 °C                   | 72.74                 | 71.97                 |
| Velocity of sound, $\text{m s}^{-1}$ , 0 °C                      | 1450                  | 1407                  |
| Specific heat, $\text{J g}^{-1} \text{°C}^{-1}$ , 17.5 °C        | 3.898                 | 4.182                 |



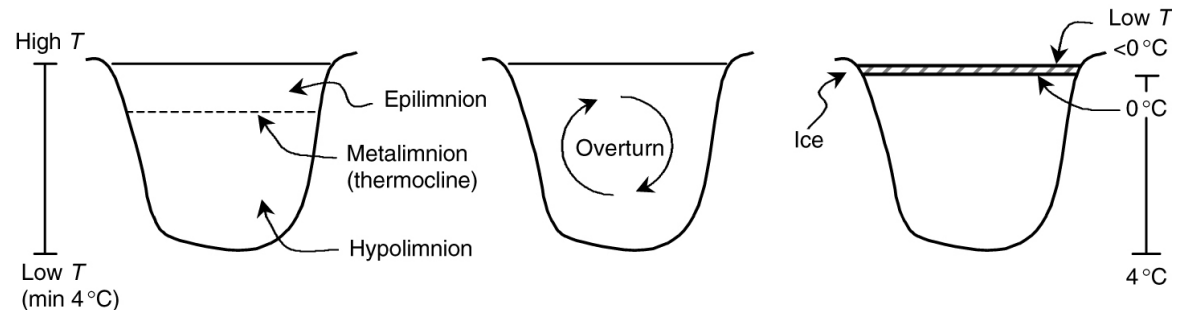
**Achtung:**

Die Anwesenheit von Ionen ändert das Verhältnis der Lage von **Temperatur** maximaler Dichte und **Gefrierpunkt** !!

**Umweltrelevante und klimatische Folge?**

## Seen

- Kühlung unter 4° C an Oberfläche führt zu stabiler Schichtung
- Neben Eisbildung wichtig zur Verhinderung des „Durchfrierens“



Warm climate (summer)

Solar radiation penetrates the epilimnion, stimulating algal photosynthesis and producing oxygen. Little solar radiation reaches the hypolimnion; there is no photosynthesis, but bacterial decomposition of organic matter causes depletion of oxygen.

Cool weather (autumn)

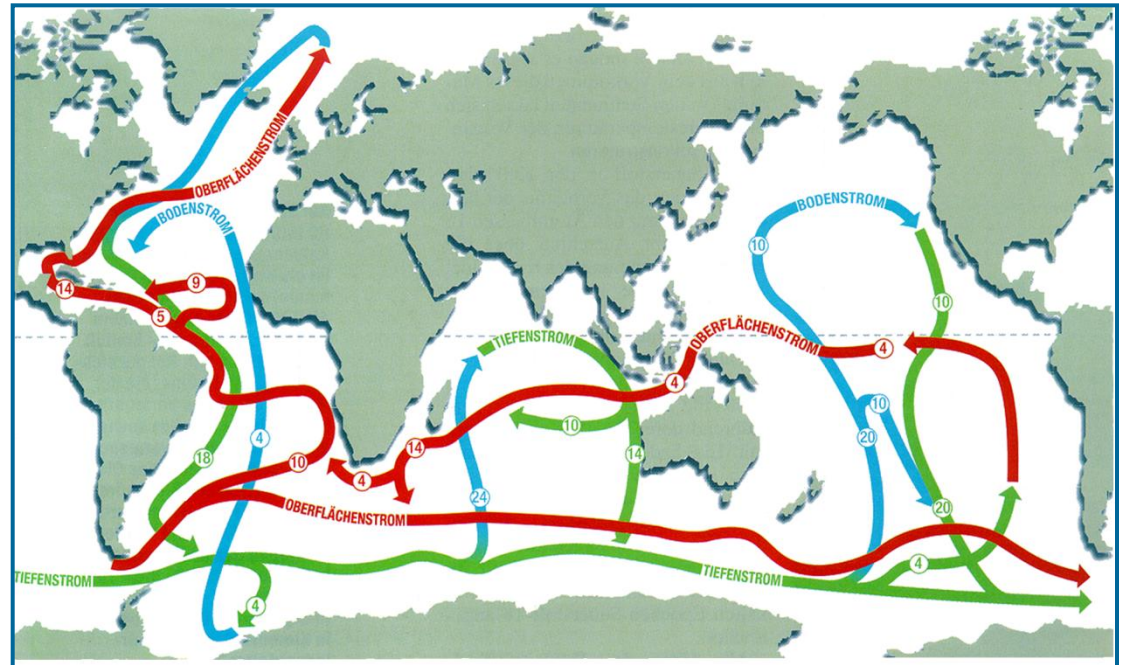
Cooled surface water sinks to the bottom, forcing bottom water upwards, creating a homogeneous ( $T$  and nutrients) environment.

Cold weather (winter)

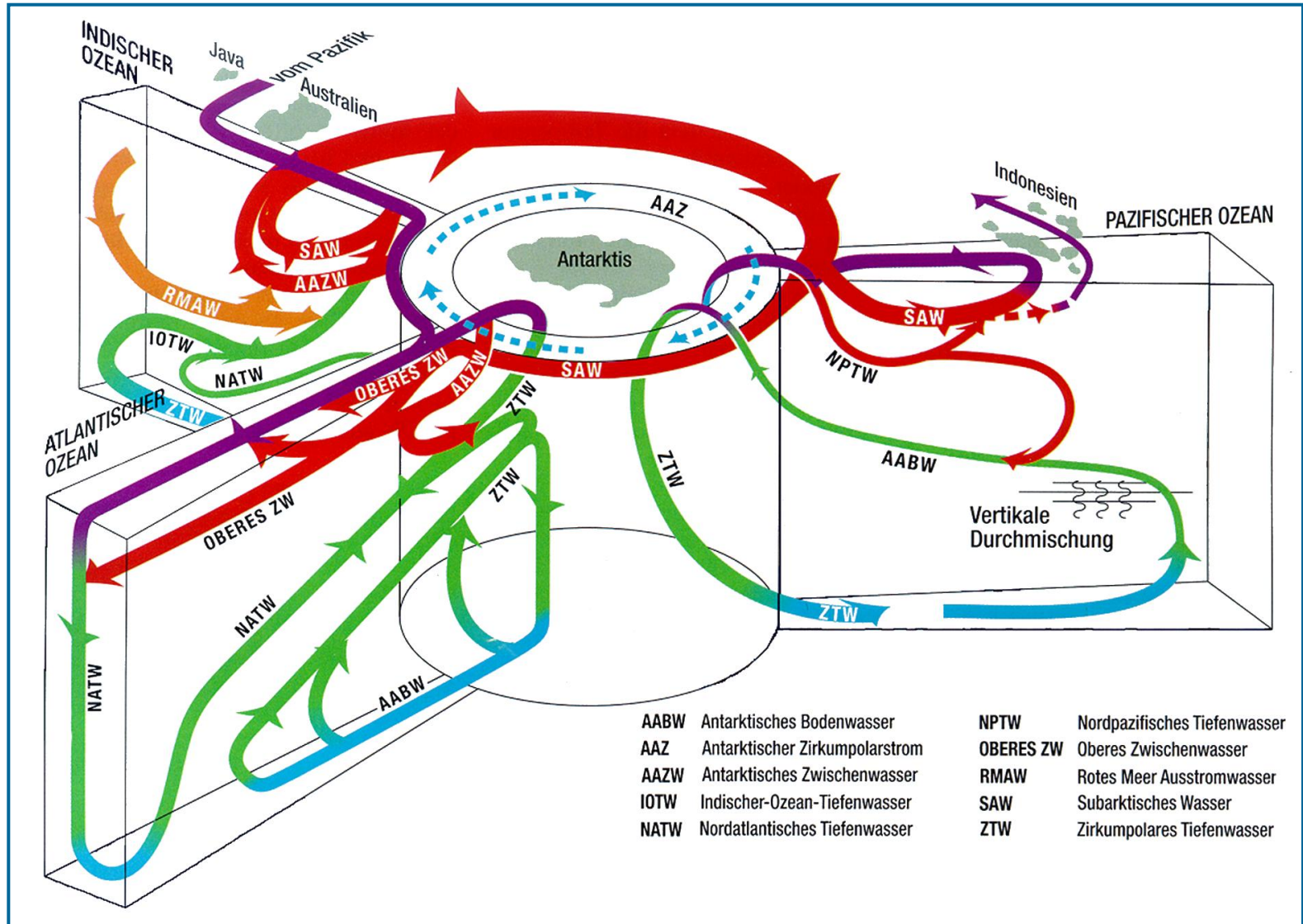
Ice forms on the surface; temperature relatively uniform below ice layer.

## Ozean

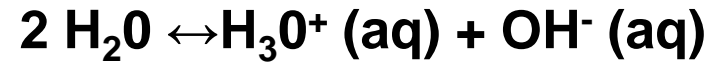
- Kaltes Wasser (bis  $-1.9^{\circ}\text{C}$ ) sinkt aufgrund der höheren Dichte
- Treibt neben Eisbildung (Salzanreicherung) die Tiefenkonvektion und damit den Wärmetransport







- Autoprotolyse – pH



$$K_w = 1.01 \times 10^{-14} (25^\circ \text{C})$$

- Beachte T-Abhängigkeit

$$K_w = 1.148 \times 10^{-15} (0^\circ \text{C})$$

$$\Rightarrow \text{pH} = -\log \text{H}_3\text{O}^+ = 7.47$$

- Vorsicht mit Konzentrationsangaben

- mol/L
- mg/kg
- mol/kg
- oft sinnvoll Bezug auf Element unter Betrachtung

(18mg/L  $\text{NH}_4^+$  ~ 62 mg/L  $\text{NO}_3^-$ )

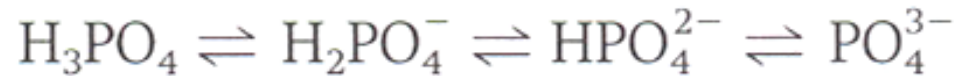
$\Rightarrow$  **14 mg/L N**

Verhalten eines Elements oder einer Verbindung von Spezies abhängig, die in der Regel von der Umgebung abhängig ist

Erste Näherung:  
Aktivität =  
Konzentration

Oft sinnvoll,  
Abhängigkeit von einer Schlüsselgröße, z.B. Protonierung als Funktion des pH

### Beispiel Phosphorsäure



**Table 10.1** Acid dissociation constants for phosphoric acid.

|                     | $K_a$                 | $\text{p}K_a$ |
|---------------------|-----------------------|---------------|
| First dissociation  | $7.1 \times 10^{-3}$  | 2.15          |
| Second dissociation | $6.3 \times 10^{-8}$  | 7.20          |
| Third dissociation  | $4.2 \times 10^{-13}$ | 12.38         |

## Berechnung der Verteilung in Abhängigkeit vom pH

- Darstellung aller Spezies als Anteil am Gesamtphosphat
- Berechnung der Konzentrationen aller Spezies als Ausdruck der undissoziierten Säure und der Hydroniumkonzentration mit Hilfe der Gleichgewichtskonstanten
- Darstellung der Gesamtphosphatkonzentration als Ausdruck der undissoziierten Säure und der Hydroniumkonzentration mit Hilfe der Gleichgewichtskonstanten

The fraction,  $\alpha_{\text{H}_3\text{PO}_4}$ , of undissociated  $\text{H}_3\text{PO}_4$  in a solution containing phosphate species is

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} = \frac{[\text{H}_3\text{PO}_4]}{C_p} \quad (10.3)$$

where  $C_p$  = the total concentration of all four orthophosphate species.

For the other phosphate species, similar fractions are given by

$$\alpha_{\text{H}_2\text{PO}_4^-} = \frac{[\text{H}_2\text{PO}_4^-]}{C_p} \quad (10.4)$$

$$\alpha_{\text{HPO}_4^{2-}} = \frac{[\text{HPO}_4^{2-}]}{C_p} \quad (10.5)$$

$$\alpha_{\text{PO}_4^{3-}} = \frac{[\text{PO}_4^{3-}]}{C_p} \quad (10.6)$$

The three dissociation constant expressions can be rearranged to give the concentration of each individual species in terms of  $[\text{H}_3\text{PO}_4]$  and  $[\text{H}_3\text{O}^+]$ .

$$[\text{H}_2\text{PO}_4^-] = \frac{K_{a1} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]} \quad (10.7)$$

$$[\text{HPO}_4^{2-}] = \frac{K_{a1} \times K_{a2} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^2} \quad (10.8)$$

$$[\text{PO}_4^{3-}] = \frac{K_{a1} \times K_{a2} \times K_{a3} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^3} \quad (10.9)$$

$$\begin{aligned} C_p &= [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \\ &= [\text{H}_3\text{PO}_4] \left( 1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3} \right) \end{aligned} \quad (10.10)$$

From eqn 10.3

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] \left( 1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3} \right)} \quad (10.11)$$

## Berechnung der Verteilung in Abhängigkeit vom pH

- Darstellung aller Spezies als Anteil am Gesamtphosphat
- Berechnung der Konzentrationen aller Spezies als Ausdruck der undissoziierten Säure und der Hydroniumkonzentration mit Hilfe der Gleichgewichtskonstanten
- Darstellung der Gesamtphosphatkonzentration als Ausdruck der undissoziierten Säure und der Hydroniumkonzentration mit Hilfe der Gleichgewichtskonstanten

The fraction,  $\alpha_{\text{H}_3\text{PO}_4}$ , of undissociated  $\text{H}_3\text{PO}_4$  in a solution containing phosphate species is

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} = \frac{[\text{H}_3\text{PO}_4]}{C_p} \quad (10.3)$$

where  $C_p$  = the total concentration of all four orthophosphate species.

For the other phosphate species, similar fractions are given by

$$\alpha_{\text{H}_2\text{PO}_4^-} = \frac{[\text{H}_2\text{PO}_4^-]}{C_p} \quad (10.4)$$

$$\alpha_{\text{HPO}_4^{2-}} = \frac{[\text{HPO}_4^{2-}]}{C_p} \quad (10.5)$$

$$\alpha_{\text{PO}_4^{3-}} = \frac{[\text{PO}_4^{3-}]}{C_p} \quad (10.6)$$

The three dissociation constant expressions can be rearranged to give the concentration of each individual species in terms of  $[\text{H}_3\text{PO}_4]$  and  $[\text{H}_3\text{O}^+]$ .

$$[\text{H}_2\text{PO}_4^-] = \frac{K_{a1} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]} \quad (10.7)$$

$$[\text{HPO}_4^{2-}] = \frac{K_{a1} \times K_{a2} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^2} \quad (10.8)$$

$$[\text{PO}_4^{3-}] = \frac{K_{a1} \times K_{a2} \times K_{a3} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^3} \quad (10.9)$$

$$\begin{aligned} C_p &= [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \\ &= [\text{H}_3\text{PO}_4] \left( 1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3} \right) \end{aligned} \quad (10.10)$$

From eqn 10.3

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] \left( 1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3} \right)} \quad (10.11)$$

## Berechnung der Verteilung in Abhängigkeit vom pH II

• Einsetzen in Ausdruck der Anteile am Gesamtphosphat eliminiert Konzentration der freien Säure:

•=> Abhängigkeit rein von pH

From eqn 10.3

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] \left( 1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3} \right)} \quad (10.11)$$

We then multiply the top and bottom of the right-hand side of the equation by  $[\text{H}_3\text{O}^+]^3$

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{O}^+]^3}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 \times K_{a1} + [\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.12)$$

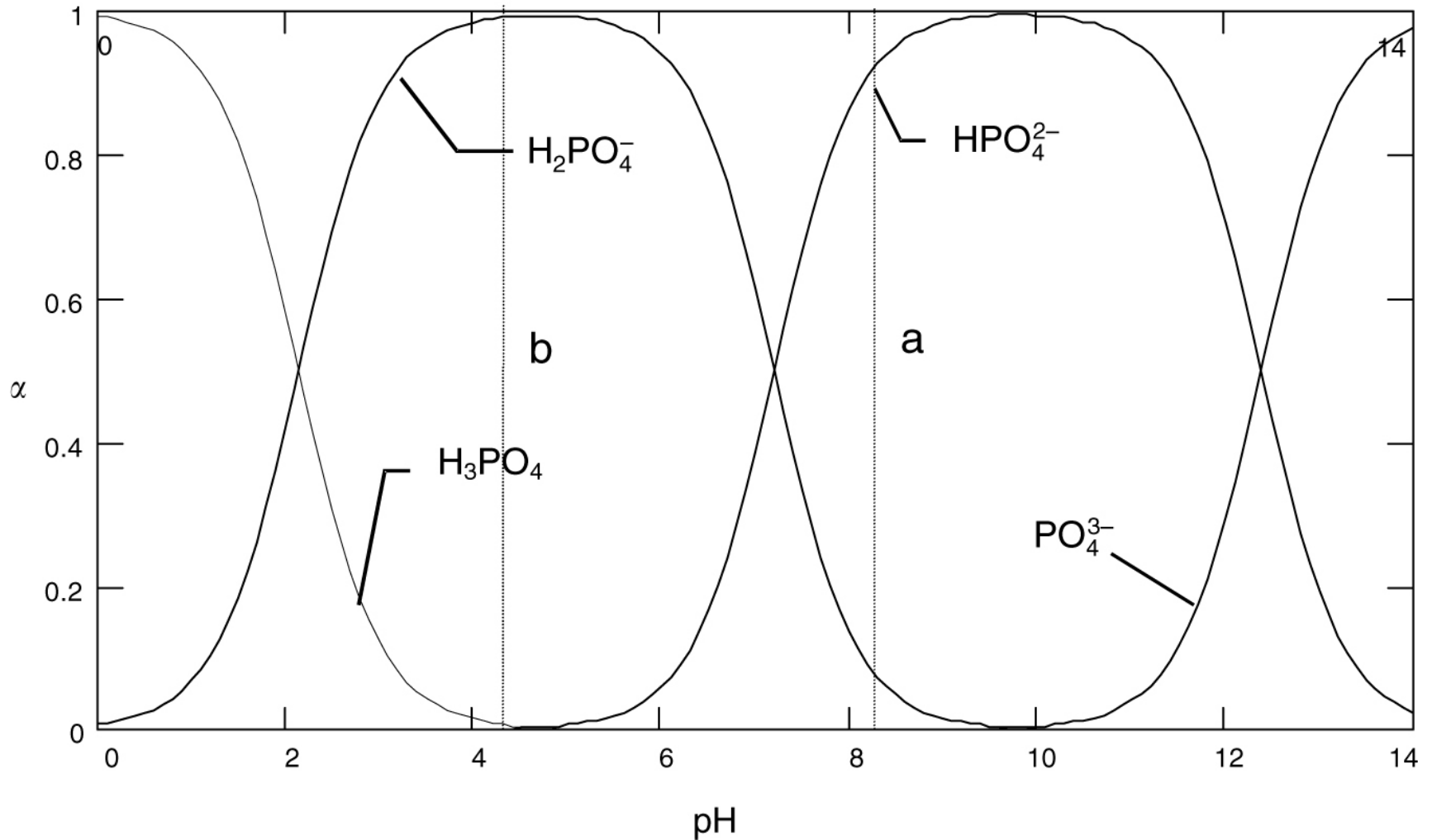
Using similar calculations, we find that

$$\alpha_{\text{H}_2\text{PO}_4^-} = \frac{[\text{H}_3\text{O}^+]^2 \times K_{a1}}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 \times K_{a1} + [\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.13)$$

$$\alpha_{\text{HPO}_4^{2-}} = \frac{[\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 \times K_{a1} + [\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.14)$$

$$\alpha_{\text{PO}_4^{3-}} = \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 \times K_{a1} + [\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.15)$$

## Phosphatspezies als Funktion des pH



Verteilung der einzelnen Phosphatspezies als Anteile an Gesamtphosphat für eine wässrige Lösung als Funktion des pH



## Einige Voraussetzungen waren:

- geringe Ionenstärke (ci = ai)

- keine Wechselwirkung mit anderen Spezies

- Auswirkungen gut sichtbar beim Unterschied Wasser - Seewasser

## Wasser

**Table 10.1** Acid dissociation constants for phosphoric acid.

|                     | $K_a$                 | $pK_a$ |
|---------------------|-----------------------|--------|
| First dissociation  | $7.1 \times 10^{-3}$  | 2.15   |
| Second dissociation | $6.3 \times 10^{-8}$  | 7.20   |
| Third dissociation  | $4.2 \times 10^{-13}$ | 12.38  |

## Meerwasser

$$K_{a1} = 2.4 \times 10^{-2} \quad pK_{a1} = 1.62$$

$$K_{a2} = 8.8 \times 10^{-7} \quad pK_{a2} = 6.06$$

$$K_{a3} = 1.4 \times 10^{-9} \quad pK_{a3} = 8.85$$

# Calculation of single ion activity coefficients

$$a_i = \gamma_i \cdot m_i$$

$$\text{Ionic Strength: } I = 1/2 \sum m_i \cdot z_i^2$$

TABLE 5.2  
Various Expressions for the Calculation of Single Ion Activity Coefficients

| Approximation         | Equation <sup>a</sup>  | Approximate Applicability [ionic strength (M)]         |
|-----------------------|--|--|
| Debye-Hückel          | $\log \gamma = -Az^2\sqrt{I}$  | $<10^{-2}$   |
| Extended Debye-Hückel | $= -Az^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}}$  | $<10^{-1}$   |
| Güntelberg            |  | $<10^{-1}$ useful in solutions of several electrolytes |
| Davies                | $= -Az^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$  | $<0.5$   |
| Brönsted-Guggenheim   | $\ell n \gamma_s = \ell n \gamma_{DHs} + \sum_j A_{sj}(C_j) + \sum_k B_{sk}(C_k)(C_k) + \dots$ | $\leq 4$   |

Source: From *Aquatic Chemistry*, W. Stumm and J. J. Morgan, copyright © 1981 by John Wiley & Sons, Inc., New York, p. 135. Reprinted by permission.  
<sup>a</sup>Values for the constants can be found in Stumm and Morgan (1981).

A = constant, characteristic of the ion

Z = charge of the ion

$\gamma_i$

Bronsted – Lowry

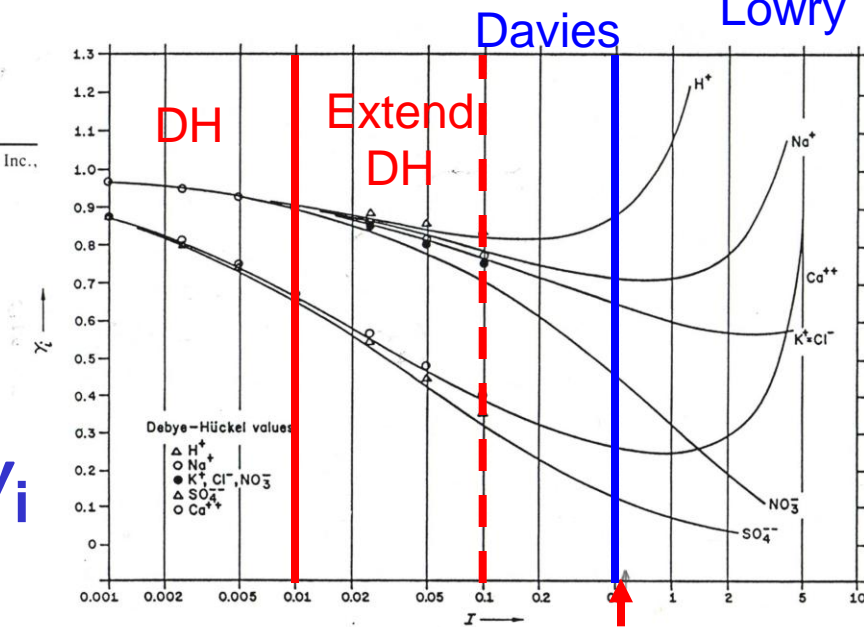
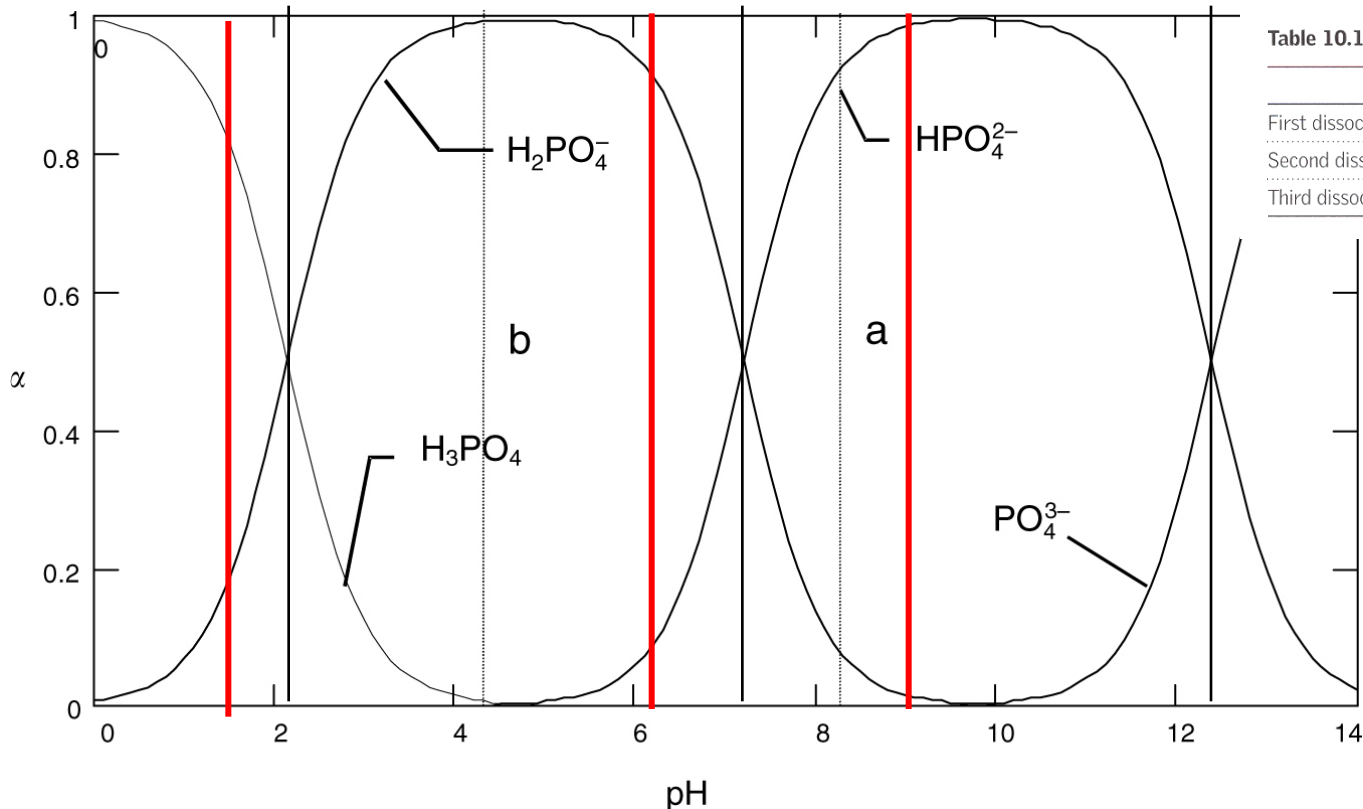


FIG. 2.15. Single ion activity coefficients vs. ionic strength for some common ions. Solid lines represent the values calculated by the mean salt method. Debye-Hückel values were calculated using equation (2.76), with  $10^6 a_i = 9$  for H<sup>+</sup>; 4 for Na<sup>+</sup>; 3 for K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>; 6 for Ca<sup>2+</sup>; and 4 for SO<sub>4</sub><sup>2-</sup>. The Debye-Hückel  $\gamma_i$  values for the monovalent ions converge, within experimental error, for  $I < 0.01$ .

# Verschiebung der pK-Werte aufgrund höherer Ionenstärke



**Table 10.1** Acid dissociation constants for phosphoric acid.

|                     | $K_a$                 | $pK_a$ |
|---------------------|-----------------------|--------|
| First dissociation  | $7.1 \times 10^{-3}$  | 2.15   |
| Second dissociation | $6.3 \times 10^{-8}$  | 7.20   |
| Third dissociation  | $4.2 \times 10^{-13}$ | 12.38  |

Verteilung der einzelnen Phosphatspezies als Anteile an Gesamtphosphat für eine wässrige Lösung als Funktion des pH

$$K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}$$

## Meerwasser

$$K_{a1} = 2.4 \times 10^{-2} \quad pK_{a1} = 1.62$$

$$K_{a2} = 8.8 \times 10^{-7} \quad pK_{a2} = 6.06$$

$$K_{a3} = 1.4 \times 10^{-9} \quad pK_{a3} = 8.85$$

# Speciation

$\text{H}_3\text{PO}_4$  – a triprotic acid!

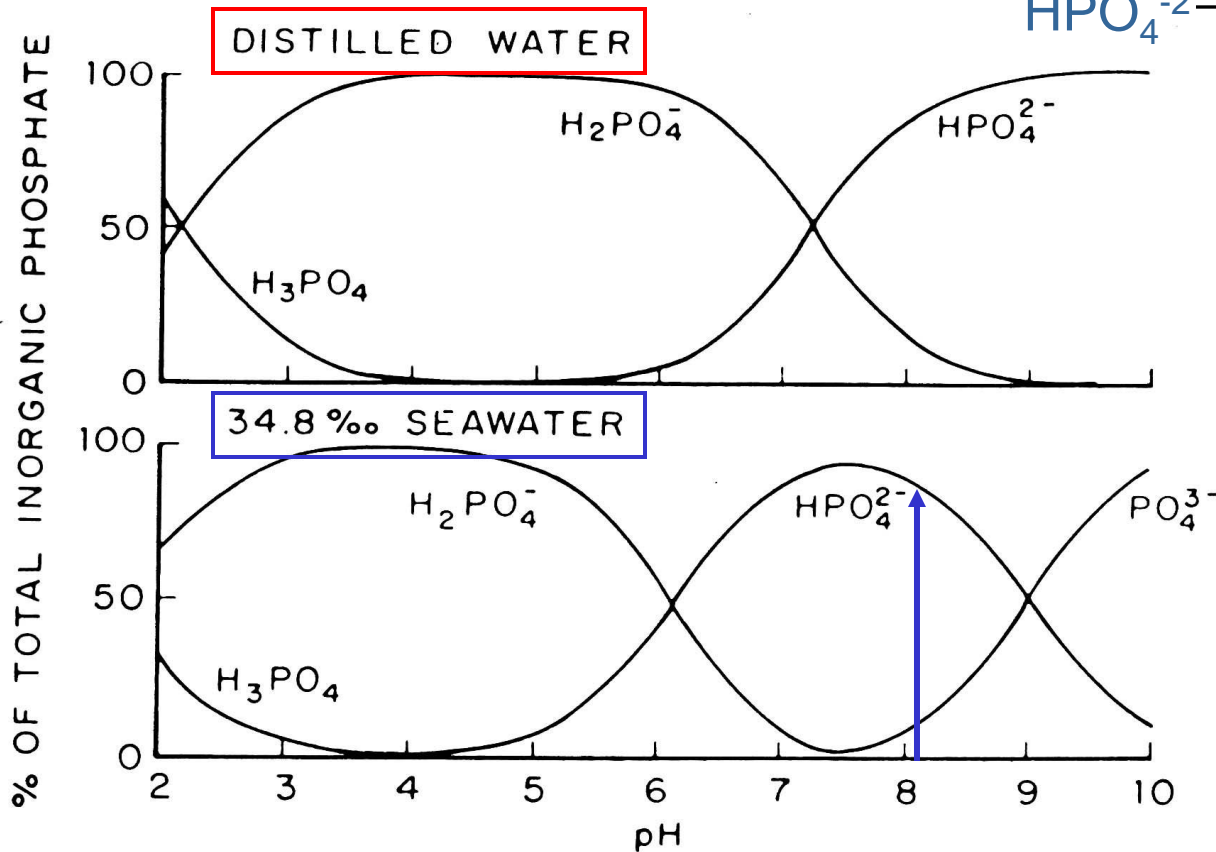
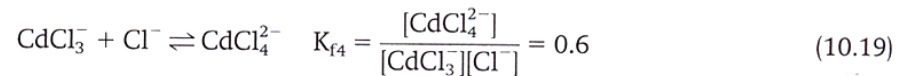
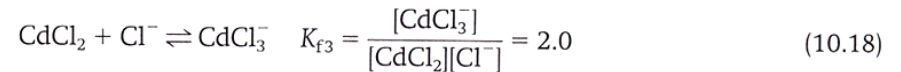
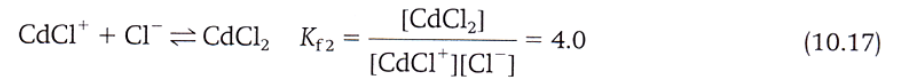
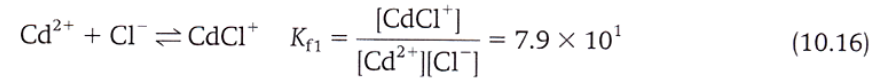


Fig. 14-1 Distribution of phosphoric acid species as a function of pH in distilled water and seawater (Atlas, 1975). 32

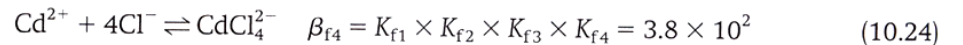
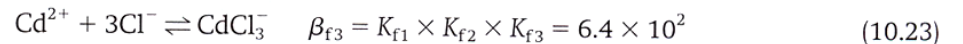
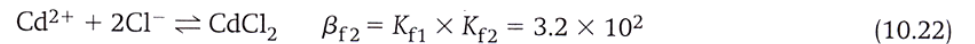
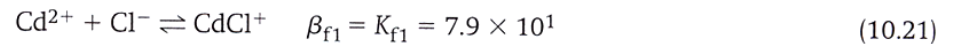
## Beispiel Cd-Chlorokomplexe

Durch geeignete Wahl der Darstellung lassen sich die relativen Anteile aller Spezies als Funktion der Chlorid-Konzentration darstellen



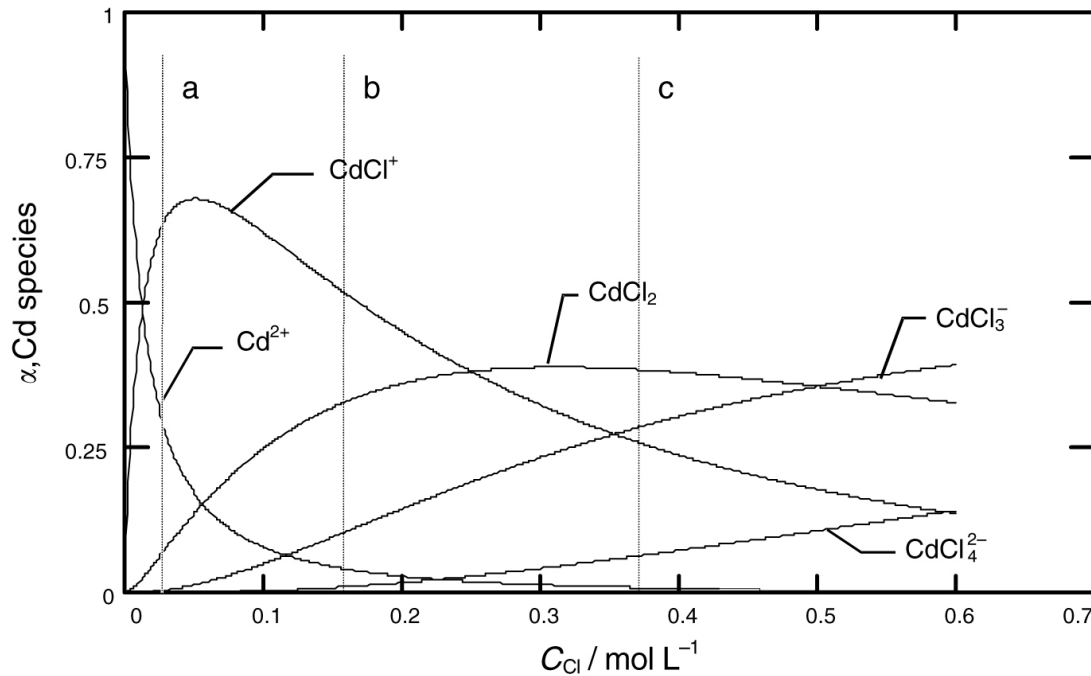
The reactions may also be described using 'overall' steps and the overall stability constants are symbolized as  $\beta_f$ . It is readily seen that

$$\beta_{fn} = K_{f1} \times K_{f2} \times \dots \times K_{fn} \quad (10.20)$$



The total concentration of cadmium in an aqueous solution containing chloride is then

$$C_{\text{Cd}} = [\text{Cd}^{2+}] + [\text{CdCl}^+] + [\text{CdCl}_2] + [\text{CdCl}_3^-] + [\text{CdCl}_4^{2-}] \quad (10.25)$$



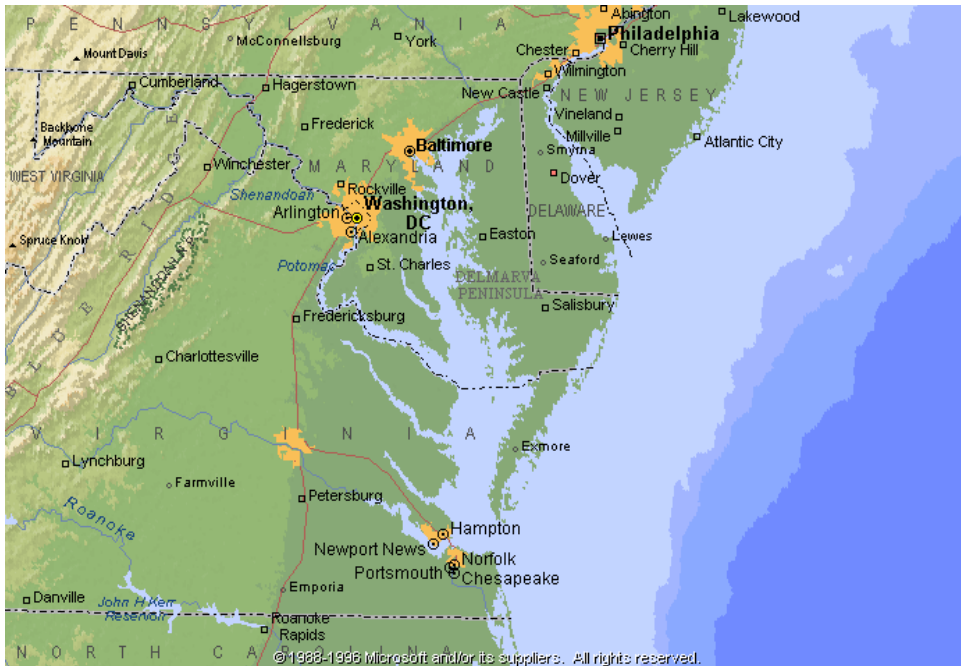
Verteilung der Cd-Chlorokomplexe in Abhängigkeit vom Chloridgehalt; 0.56 mol/L Chlorid ~ 35 ‰ Salzgehalt

## Toxikologische Bedeutung:

- $\text{Cd}^{2+}$  für viele Organismen (eingenommen Menschen) toxisch wegen Bindungsähnlichkeit zum Calcium
- Chlorokomplexe hingegen deutlich weniger physiologisch wirksam

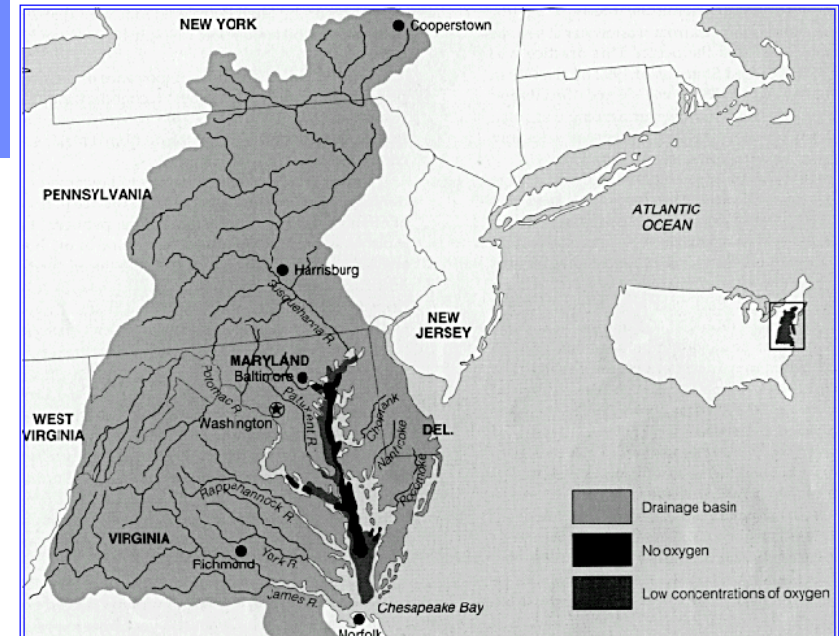


# Chesapeake Bay



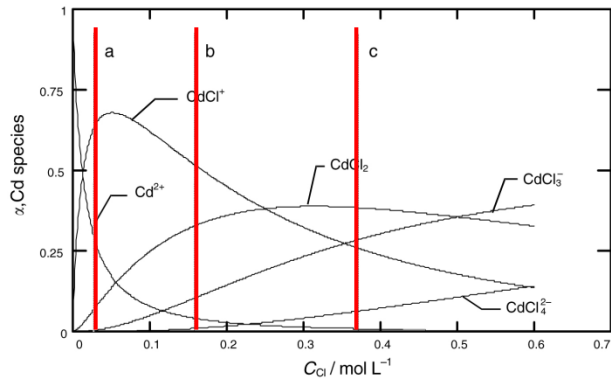
Karte der Chesapeake Bay

- Mehrere Flüsse, die in den Estuarkomplex münden
- Fläche von ~160.000 km<sup>2</sup> (1/3 der Fläche der Ostsee)
- Sehr grosses Drainage Basin
- “Hausgarten” von drei grossen Universitäten



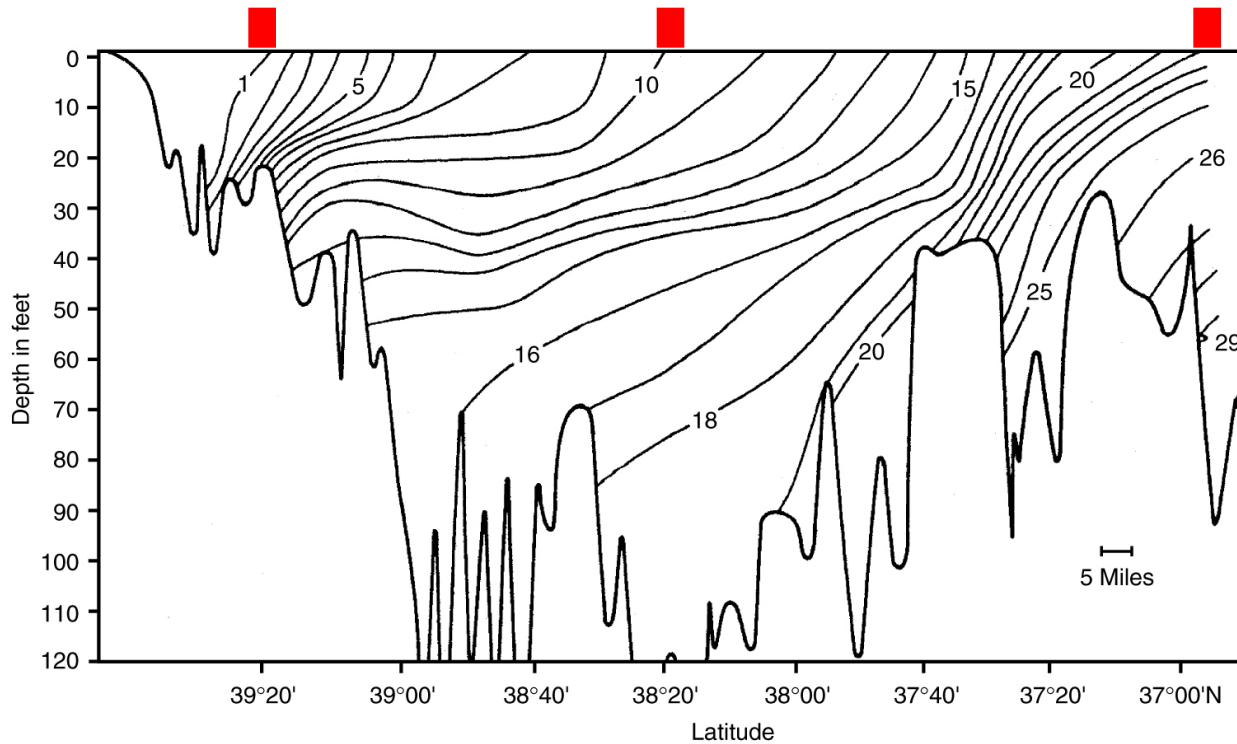


# Ein-Variablengehalt - Chloridgehalt



Beispiel:

- Chesapeake Bay, Susquehanna River
- Größtes Atlantikestuar der US
- Extrem gut untersucht, ...



- Der Wasserkreislauf
- Besondere Eigenschaften des Wassers
- Einheiten
- Verteilungsdiagramme als Funktion einer Variablen
- **Der pE-Wert**
- **Verteilungsdiagramme als Funktion von zwei Variablen**
- **Das pH/pE-Diagramm**



## Das pE/pH-Diagramm => pE

- **Elektronenaktivität als pE**  
 $pE = -\log a_e$
- **Maß für den Redoxzustand einer Lösung:**
  - Stark negativ => reduzierend
  - Stark positiv => oxidierend
- **Zurückzuführen auf Elektrochemisches Potential (Nernst'sche Gleichung)**

## Beispiel Eisen II-III



$$K_{eq} = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}} \times a_{e^-}}$$

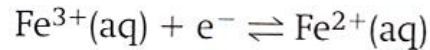
$$\frac{1}{a_{e^-}} = \frac{K_{eq} \times a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

$$pE = -\log a_e = \log K_{eq} + \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

$$\Delta G^\circ = -2.303 RT \log K_{eq}$$

$$= -nFE^\circ$$

## Beispiel Eisen II-III



$$K_{\text{eq}} = \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}} \times a_{\text{e}^{-}}}$$

$$\frac{1}{a_{\text{e}^{-}}} = \frac{K_{\text{eq}} \times a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}}$$

$$\text{pE} = -\log a_{\text{e}^{-}} = \log K_{\text{eq}} + \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}}$$

$$\Delta G^{\circ} = -2.303 RT \log K_{\text{eq}}$$

$$= -nFE^{\circ}$$

Mit  $T = 25^{\circ} \text{C}$ ,  $R = 8.314 \text{ J/Kmol}$  und  $F = 96485 \text{ C/mol}$

$$\log K_{\text{eq}} = \frac{nFE^{\circ}}{2.303 RT} = \frac{nE^{\circ}}{0.0591}$$

$$\log K_{\text{eq}} = \frac{E^{\circ}}{0.0591}$$

$$\text{pE} = \frac{E^{\circ}}{0.0591} + \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}}$$

$$a_{\text{Fe}^{3+}} = a_{\text{Fe}^{2+}} = 1,$$

$$\log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} = 0$$

$$\text{pE} = \text{pE}^{\circ} = \frac{E^{\circ}}{0.0591}$$

$$\text{pE} = \text{pE}^{\circ} + \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}}$$

## $pE^{\circ}$ -Werte

- Berechnung von  $pE^{\circ}$ -Werten

- 1.) bei bekannten  $E^{\circ}$ -Werten

$$\log K_{\text{eq}} = \frac{nFE^{\circ}}{2.303 RT} = \frac{nE^{\circ}}{0.0591}$$

$$pE = pE^{\circ} = \frac{E^{\circ}}{0.0591}$$

- 2.) bei bekannter Gleichgewichtskonstante

$$\log K_{\text{eq}} = \frac{nE^{\circ}}{0.0591} = npE^{\circ}$$

$$\therefore pE^{\circ} = \frac{\log K_{\text{eq}}}{n}$$

- 3.) bei bekannter freier Standardenthalpie

$$\Delta G^{\circ} = -2.303 RTn pE^{\circ}$$

$$pE^{\circ} = \frac{-\Delta G^{\circ}}{2.303RTn}$$



# Das pE/pH-Diagramm in Wasser - Stabilitätsgrenzen

## Stabilitätsgrenzen in Wasser

Reduktive Grenze



$$\text{pE} = \text{pE}^0 - \frac{1}{2} \log \left( \left( \frac{P_{\text{H}_2}}{P^0} \right) \times (a_{\text{OH}^-})^2 \right)$$

Stabilitätsgrenze bezüglich  
Gasfreisetzung bei  $P_{\text{H}_2} = P^0 = 1 \text{atm}$

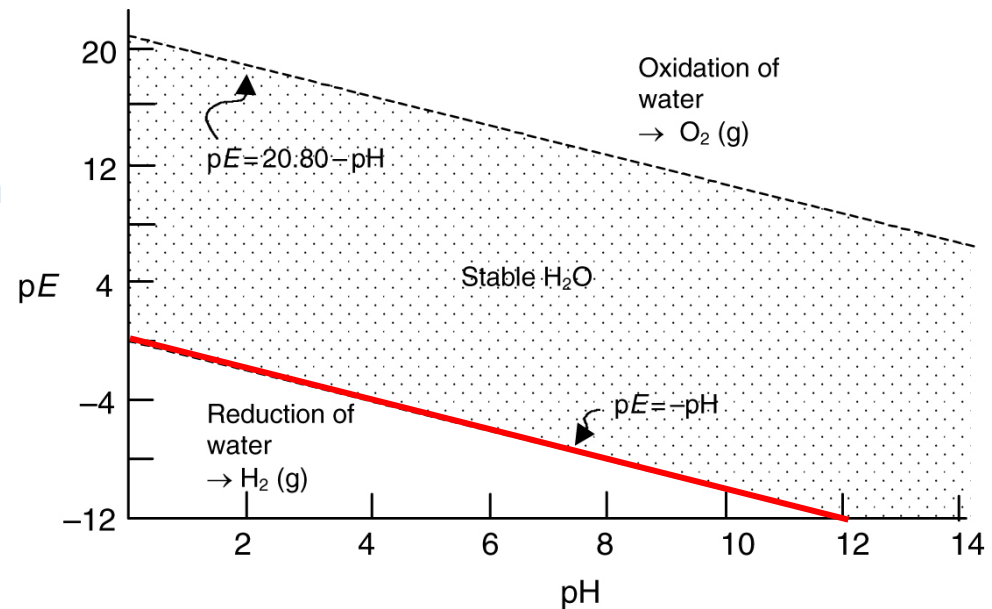
$$\begin{aligned} \text{pE} &= \text{pE}^0 \cdot \log (a_{\text{OH}^-}) \\ &= -14 + \text{pOH} \end{aligned}$$

$$\Rightarrow (\text{pH} + \text{pOH} = 14)$$

$$\text{pE} = -\text{pH}$$

$$E^0 = -0.828 \text{ V}$$

$$\Rightarrow \text{pE}^0 = E^0 / 0.0591 = -14$$



# Das pE/pH-Diagramm in Wasser - Stabilitätsgrenzen

## Stabilitätsgrenzen in Wasser

Oxidative Grenze



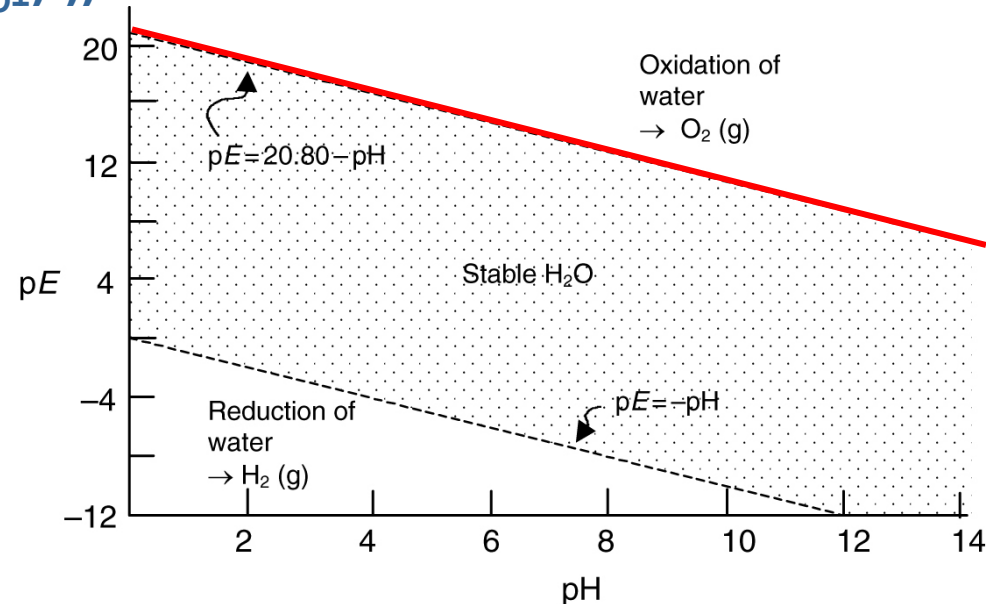
$$\text{pE} = \text{pE}^0 - 1/4 \log (1/((\text{P}_{\text{O}_2}/\text{P}^0) \times (\text{a}_{\text{H}_3\text{O}^+})^4))$$

Stabilitätsgrenze bezüglich  
Gasfreisetzung bei  $\text{P}_{\text{O}_2} = \text{P}^0 = 1\text{atm}$

$$\begin{aligned} \text{pE} &= \text{pE}^0 - \log (1/ (\text{a}_{\text{H}_3\text{O}^+})) \\ &= 20.80 - \text{pH} \end{aligned}$$

$$\text{E}^0 = 1.229 \text{ V}$$

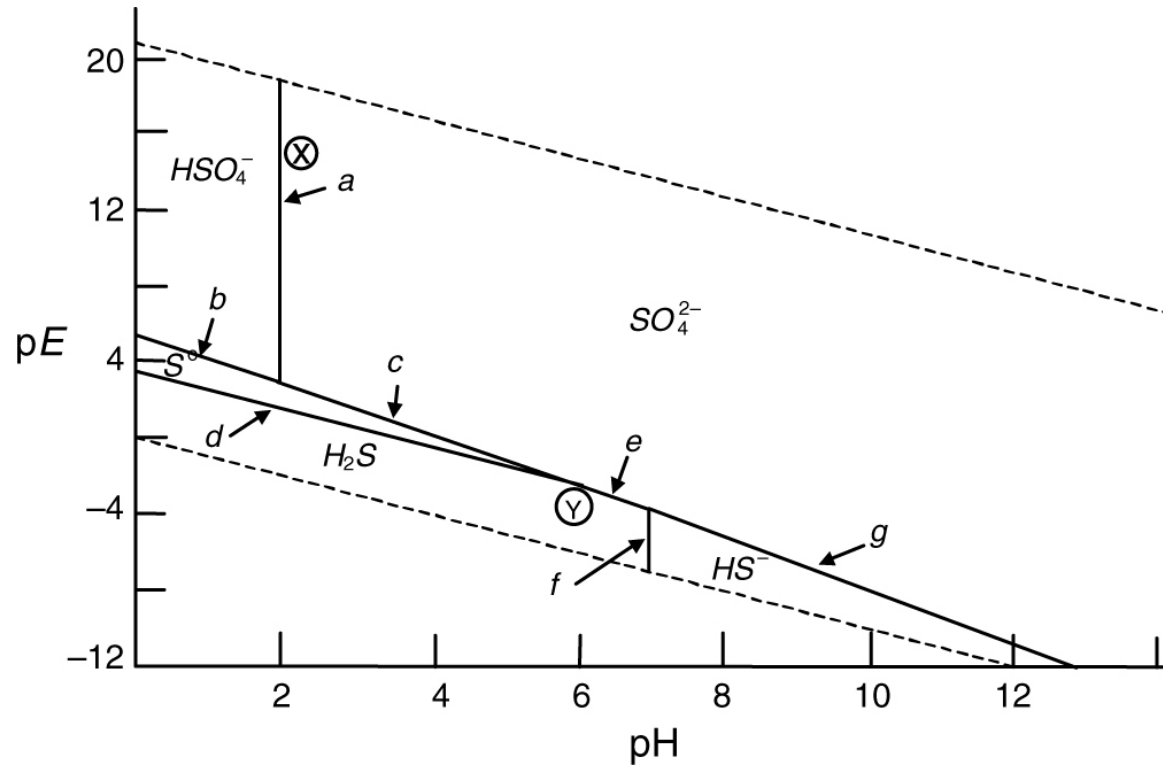
$$\Rightarrow \text{pE}^0 = \text{E}^0 / 0.0591 = 20.8$$



## Das Schwefelsystem im pE/pH-Diagramm

- Oxidationsstufen von -6 bis +2, mehrere Säure-Base Reaktionen

- Für gelöste Spezies:
- Phasengrenze bei  $10^{-2}$  mol/L

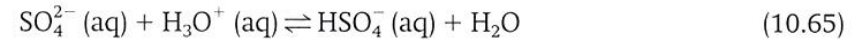


# Das Schwefelsystem im pE/pH-Diagramm – $\text{SO}_4^{2-}$ - $\text{HSO}_4^-$ Grenze

- Deprotonierung
- Keine Redox-Reaktion

The  $\text{SO}_4^{2-}$  /  $\text{HSO}_4^-$  boundary

The equation describing this boundary is an acid-base reaction and requires hydronium ion, but there is no oxidation or reduction involved.



To make things easier, we use  $\text{H}^+$  as an abbreviation for  $\text{H}_3\text{O}^+$ , the hydronium ion, but, of course, the result would be the same if the latter species were used in the equations and calculations.  $\Delta G$  values are found in Appendix B.2.

$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{HSO}_4^-) - \Delta G_f^\circ(\text{SO}_4^{2-}) - \Delta G_f^\circ(\text{H}^+) \\ &= -755.99 - (-744.60) - 0 \\ &= -11.39 \text{ kJ} = -11\,390 \text{ J} \end{aligned}$$

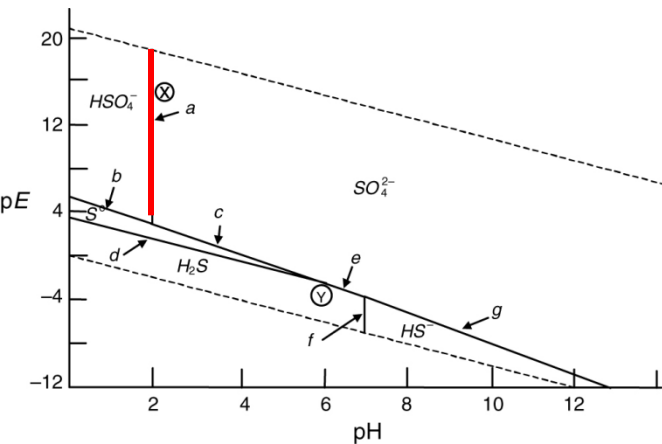
$$\begin{aligned} \log K &= \frac{-\Delta G^\circ}{2.303 RT} \\ &= \frac{+11\,390}{2.303 \times 8.314 \times 298.2} \\ &= 1.995 \end{aligned}$$

$$K = \frac{[\text{HSO}_4^-]}{[\text{SO}_4^{2-}] a_{\text{H}^+}}$$

At the boundary,  $[\text{HSO}_4^-] = [\text{SO}_4^{2-}] = 10^{-2} \text{ M}$ , and

$$K = \frac{1}{a_{\text{H}^+}}$$

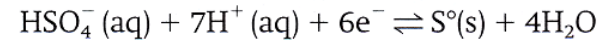
$$\log K = \text{pH} = 1.995$$



# Das Schwefelsystem im pE/pH-Diagramm – $\text{HSO}_4^-$ - $\text{S}^0$ Grenze

- pH-sensitive Redox-Reaktion**

The  $\text{HSO}_4^- / \text{S}^0$  boundary



$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{S}) + 4\Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{HSO}_4^-) - 7\Delta G_f^\circ(\text{H}^+) - 6\Delta G_f^\circ(\text{e}^-) \\ &= 0 + 4(-237.18) - (-755.99) - 0 - 0 \\ &= -192.73 \text{ kJ} = -192\,730 \text{ J} \end{aligned}$$

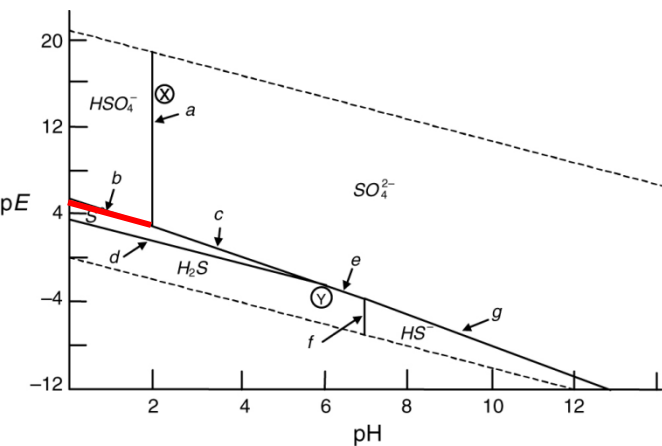
$$\text{pE}^\circ = \frac{-\Delta G^\circ}{2.303nRT} = \frac{+192\,730}{2.303 \times 6 \times 8.314 \times 298.2} = 5.626$$

$$\text{pE} = \text{pE}^\circ - \frac{1}{6} \log \frac{1}{[\text{HSO}_4^-](a_{\text{H}^+})^7}$$

At the boundary,  $[\text{HSO}_4^-] = 10^{-2} \text{ mol L}^{-1}$  so

$$\begin{aligned} \text{pE} &= 5.626 - \frac{7}{6} \log \frac{1}{a_{\text{H}^+}} - \frac{1}{6} \log \frac{1}{10^{-2}} \\ &= 5.626 - \frac{7}{6} \text{pH} - 0.333 \\ &= 5.293 - 1.167 \text{pH} \end{aligned}$$

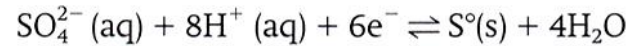
This is line 'b' on Fig. 10.5. Above it is the domain of  $\text{HSO}_4^-$ ; below it is  $\text{S}^0$ .





# Das Schwefelsystem im pE/pH-Diagramm – $\text{SO}_4^{2-}$ - $\text{S}^0$ Grenze

The  $\text{SO}_4^{2-}$  /  $\text{S}^0$  boundary



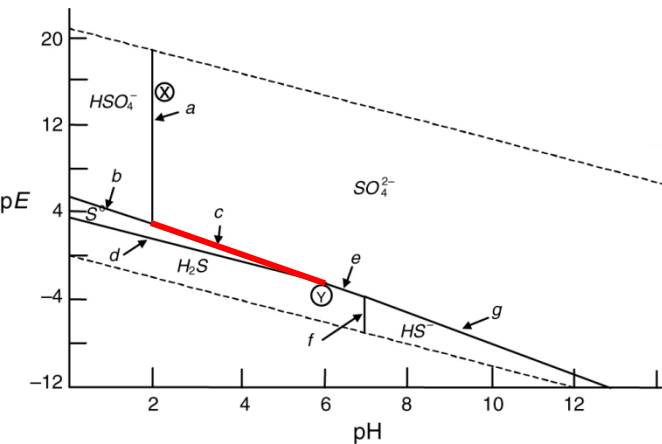
$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{S}) + 4\Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{SO}_4^{2-}) - 8\Delta G_f^\circ(\text{H}^+) - 6\Delta G_f^\circ(\text{e}^-) \\ &= 0 + 4(-237.18) - (-744.60) - 0 - 0 \\ &= -204.12 \text{ kJ} = -204\,120 \text{ J} \end{aligned}$$

$$\text{pE}^\circ = \frac{-\Delta G^\circ}{2.303nRT} = \frac{+204\,120}{2.303 \times 6 \times 8.314 \times 298.2} = 5.958$$

$$\text{pE} = \text{pE}^\circ - \frac{1}{6} \log \frac{1}{[\text{SO}_4^{2-}](a_{\text{H}^+})^8}$$

At the boundary,  $[\text{SO}_4^{2-}] = 10^{-2} \text{ mol L}^{-1}$  so

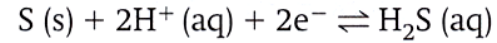
$$\begin{aligned} \text{pE} &= 5.958 - \frac{8}{6} \log \frac{1}{a_{\text{H}^+}} - \frac{1}{6} \log \frac{1}{10^{-2}} \\ &= 5.958 - \frac{8}{6} \text{pH} - 0.333 \\ &= 5.625 - 1.333 \text{ pH} \end{aligned}$$



This is line 'c' on Fig. 10.5. Above it is the domain of  $\text{SO}_4^{2-}$ ; below it  $\text{S}^0$ .

# Das Schwefelsystem im pE/pH-Diagramm – S<sub>0</sub>- H<sub>2</sub>S Grenze

## The S<sup>0</sup> / H<sub>2</sub>S boundary



$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{H}_2\text{S}) - \Delta G_f^\circ(\text{S}) - 2\Delta G_f^\circ(\text{H}^+) - 2\Delta G_f^\circ(\text{e}^-) \\ &= -27.86 - 0 - 0 - 0 \\ &= -27.86 \text{ kJ} = -27\,860 \text{ J} \end{aligned}$$

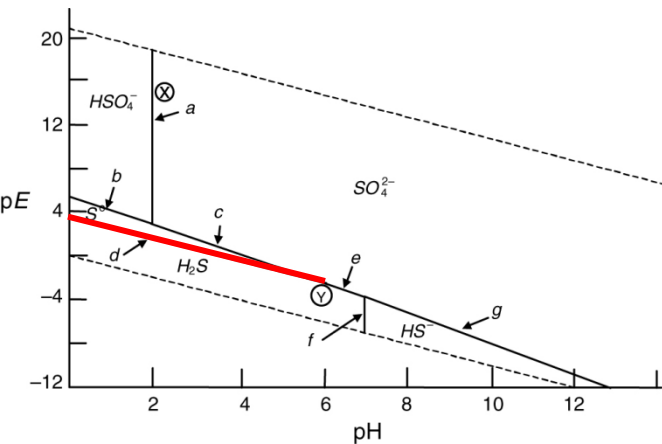
$$\text{pE}^\circ = \frac{-\Delta G^\circ}{2.303nRT} = \frac{+27\,860}{2.303 \times 2 \times 8.314 \times 298.2} = 2.440$$

$$\text{pE} = \text{pE}^\circ - \frac{1}{2} \log \frac{[\text{H}_2\text{S}]}{(\text{a}_{\text{H}^+})^2}$$

At the boundary,  $[\text{H}_2\text{S}] = 10^{-2} \text{ mol L}^{-1}$  so

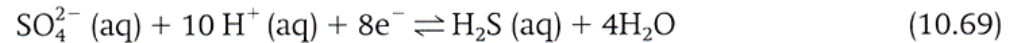
$$\begin{aligned} \text{pE} &= 2.440 + 1 - \text{pH} \\ &= 3.440 - \text{pH} \end{aligned}$$

This is line 'd' on Fig. 10.5. Above it is the domain of S<sup>0</sup>; below it H<sub>2</sub>S.



# Das Schwefelsystem im pE/pH-Diagramm – $\text{SO}_4^{2-}$ - $\text{H}_2\text{S}$ Grenze

The  $\text{SO}_4^{2-}$  /  $\text{H}_2\text{S}$  boundary



$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{H}_2\text{S}) + 4\Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{SO}_4^{2-}) - 10\Delta G_f^\circ(\text{H}^+) - 8\Delta G_f^\circ(\text{e}^-) \\ &= -27.86 + 4(-237.18) - (-744.60) - 0 - 0 \\ &= -231.98 \text{ kJ} = -231\,980 \text{ J} \end{aligned}$$

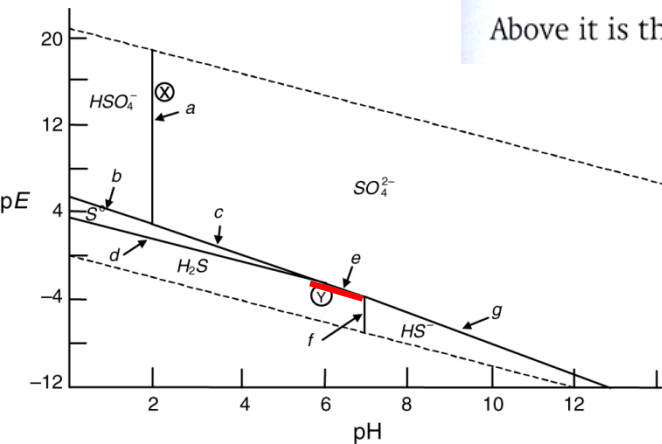
$$\text{pE}^\circ = \frac{-\Delta G^\circ}{2.303nRT} = \frac{+231\,980}{2.303 \times 8 \times 8.314 \times 298.2} = 5.079$$

$$\text{pE} = \text{pE}^\circ - \frac{1}{8} \log \frac{[\text{H}_2\text{S}]}{[\text{SO}_4^{2-}](a_{\text{H}^+})^{10}}$$

At the boundary,  $[\text{H}_2\text{S}] = [\text{SO}_4^{2-}] = 10^{-2} \text{ mol L}^{-1}$ , so

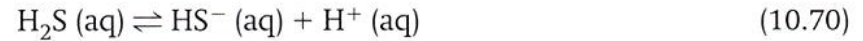
$$\begin{aligned} \text{pE} &= 5.079 - \frac{10}{8} \log \frac{1}{a_{\text{H}^+}} \\ &= 5.079 - 1.25 \text{ pH} \end{aligned}$$

This is line 'e' on Fig. 10.5 (a very small segment, difficult to distinguish from line 'd'). Above it is the domain of  $\text{SO}_4^{2-}$ ; below it  $\text{H}_2\text{S}$ .



# Das Schwefelsystem im pE/pH-Diagramm – H<sub>2</sub>S – HS<sup>-</sup> Grenze

The H<sub>2</sub>S / HS<sup>-</sup> boundary



As for the HSO<sub>4</sub><sup>-</sup> / SO<sub>4</sub><sup>2-</sup> boundary, this is not a redox reaction and therefore the line will be vertical with the protonated species on the left.

$$\begin{aligned} \Delta G^\circ &= -\Delta G_f^\circ(\text{HS}^-) + \Delta G_f^\circ(\text{H}^+) - \Delta G_f^\circ(\text{H}_2\text{S}) \\ &= 12.08 + 0 - (-27.86) \\ &= 39.94 \text{ kJ} = 39\,940 \text{ J} \end{aligned}$$

$$\begin{aligned} \log K &= \frac{-\Delta G^\circ}{2.303RT} = \frac{-39\,940}{2.303 \times 8.314 \times 298.2} \\ &= -6.995 \end{aligned}$$

$$K = \frac{[\text{HS}^-]a_{\text{H}^+}}{[\text{H}_2\text{S}]}$$

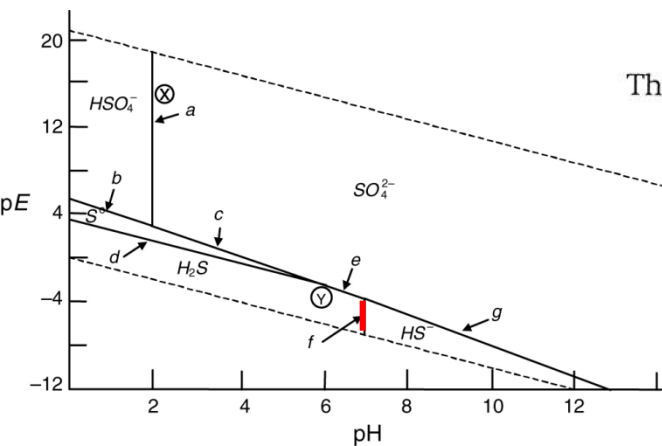
At the boundary, [HS<sup>-</sup>] = [H<sub>2</sub>S] = 10<sup>-2</sup> mol L<sup>-1</sup>, so

$$K = a_{\text{H}^+}$$

$$\log K = \log [\text{H}^+] = -\text{pH} = -6.995$$

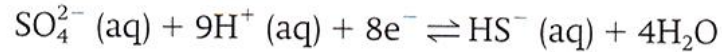
$$\text{pH} = 6.995$$

This is line 'f' on Fig. 10.5. To the left is the domain of H<sub>2</sub>S and to the right that of HS<sup>-</sup>.



# Das Schwefelsystem im pE/pH-Diagramm – $\text{SO}_4^{2-}$ - $\text{HS}^-$ - Grenze

The  $\text{SO}_4^{2-}$  /  $\text{HS}^-$  boundary



$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{HS}^-) + 4\Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{SO}_4^{2-}) - 9\Delta G_f^\circ(\text{H}^+) - 8\Delta G_f^\circ(\text{e}^-) \\ &= 12.08 + 4(-237.18) - (-744.60) - 0 - 0 \\ &= -192.04 \text{ kJ} = -192\,040 \text{ J} \end{aligned}$$

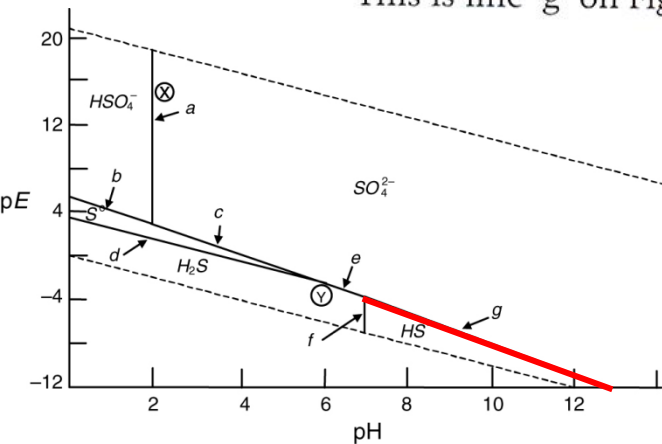
$$\text{pE}^\circ = \frac{-\Delta G^\circ}{2.303nRT} = \frac{+192\,040}{2.303 \times 8 \times 8.314 \times 298.2} = 4.204$$

$$\text{pE} = \text{pE}^\circ - \frac{1}{8} \log \frac{[\text{HS}^-]}{[\text{SO}_4^{2-}](a_{\text{H}^+})^9}$$

At the boundary,  $[\text{HS}^-] = [\text{SO}_4^{2-}] = 10^{-2} \text{ mol L}^{-1}$ , so

$$\begin{aligned} \text{pE} &= 4.202 - \frac{9}{8} \log \frac{1}{a_{\text{H}^+}} \\ &= 4.204 - 1.25 \text{ pH} \end{aligned}$$

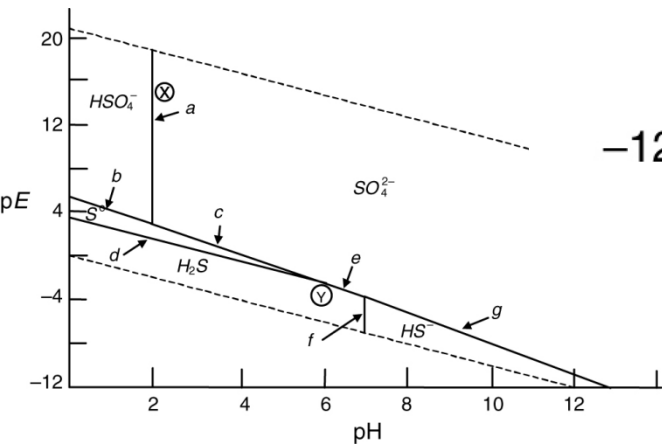
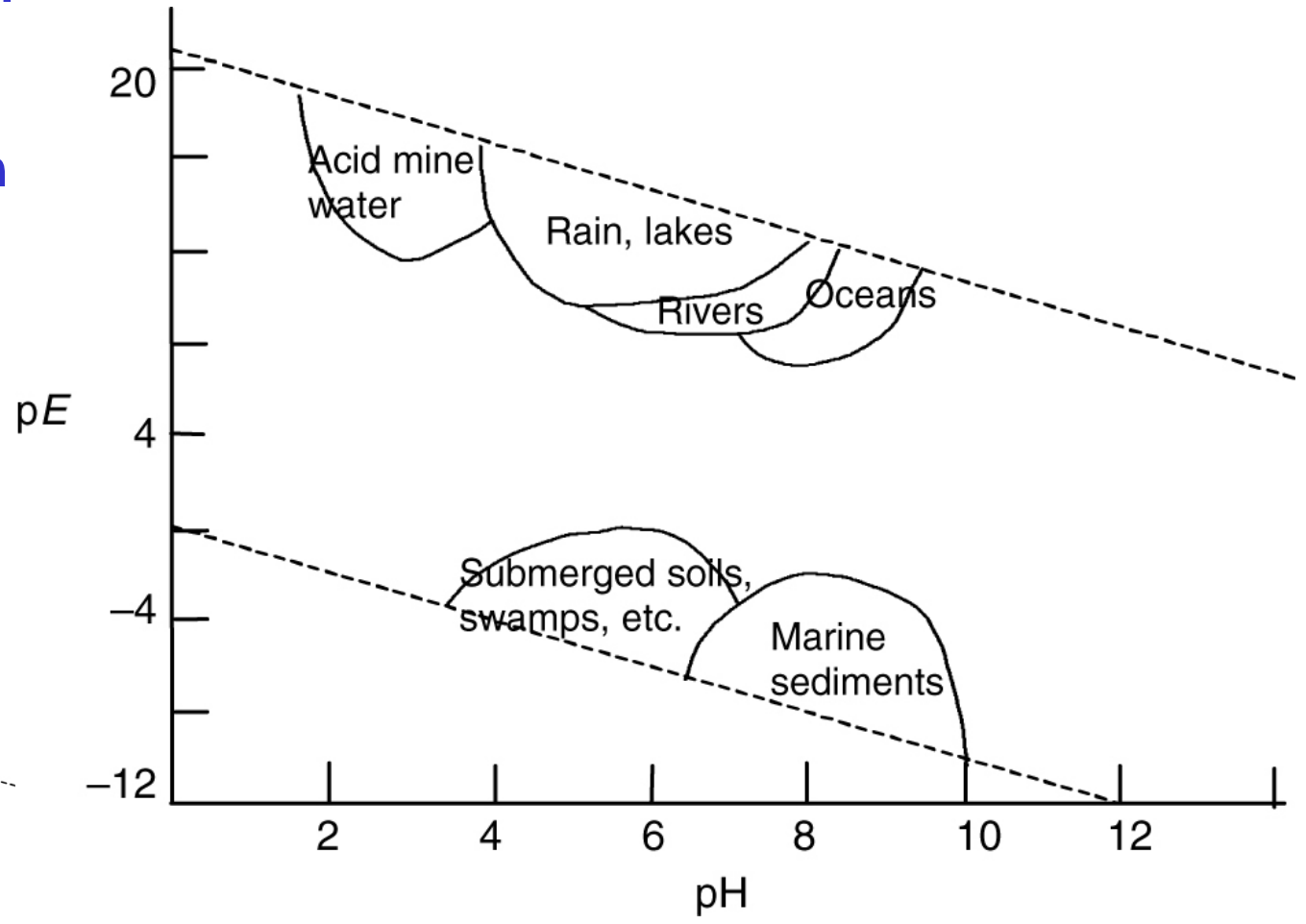
This is line 'g' on Fig. 10.5. Above it is the domain of  $\text{SO}_4^{2-}$ ; below it  $\text{HS}^-$ .





# Das Schwefelsystem im pE/pH-Diagramm – $\text{SO}_4^{2-}$ - $\text{HSO}_4^-$ Grenze

- Oxidationsstufen von +6 bis -2, mehrere Säure-Base Reaktionen



Anwendungen

