

## Regionale Ozeanographie

### 02 – Physikalische Eigenschaften des Meerwassers

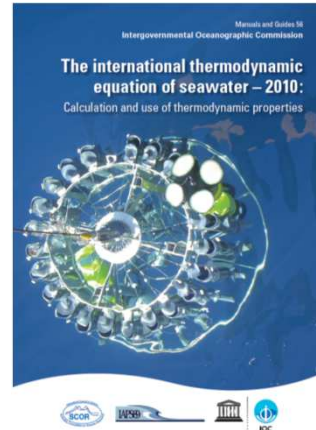
#### Literatur:

#### **The international thermodynamic equation of seawater – 2010:** Calculation and use of thermodynamic properties

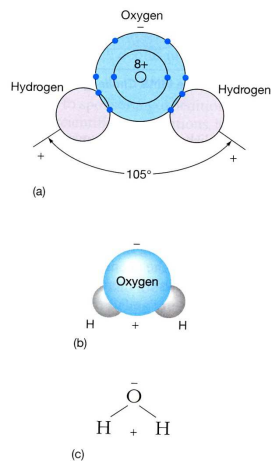
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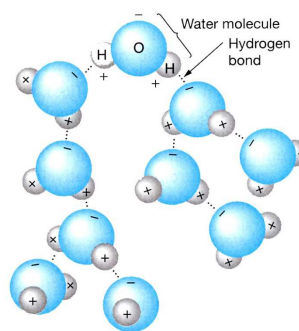
[http://www.teos-10.org/pubs/TEOS-10\\_Manual.pdf](http://www.teos-10.org/pubs/TEOS-10_Manual.pdf)



## Dipolstruktur und Cluster Bildung



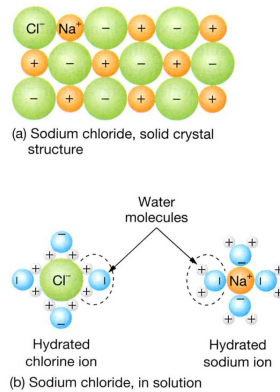
**Figure 5-2 The water molecule.** (a) Geometry of a water molecule. The oxygen end of the molecule is negatively charged, and the hydrogen regions exhibit a positive charge. Covalent bonds occur between the oxygen and the two hydrogen atoms (b) A three-dimensional representation of the water molecule. (c) The water molecule represented by letters (H = hydrogen, O = oxygen).



**Figure 5-3 Hydrogen bonds.** Dashed lines indicate locations of hydrogen bonds, which occur between water molecules.

Thurman & Trujillo, 2003

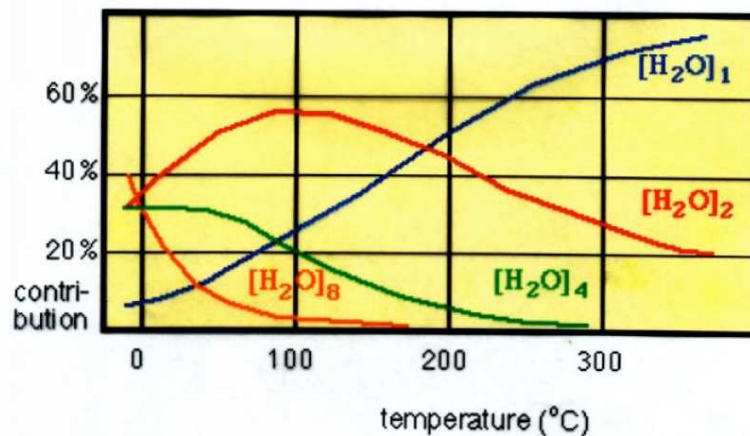
## Wasser als Lösungsmittel



**Figure 5-4 Water as a solvent.** (a) Table salt, composed of sodium chloride ( $\text{Na}^+$  = sodium ion,  $\text{Cl}^-$  = chlorine ion). (b) As sodium chloride is dissolved, the positively charged ends of water molecules are attracted to the negatively charged  $\text{Cl}^-$  ion, while the negatively charged ends are attracted to the positively charged  $\text{Na}^+$  ion.

Thurman & Trujillo, 2003

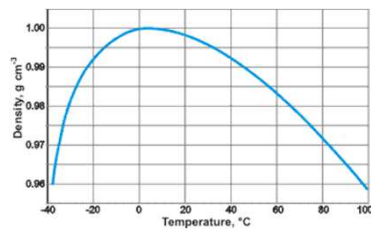
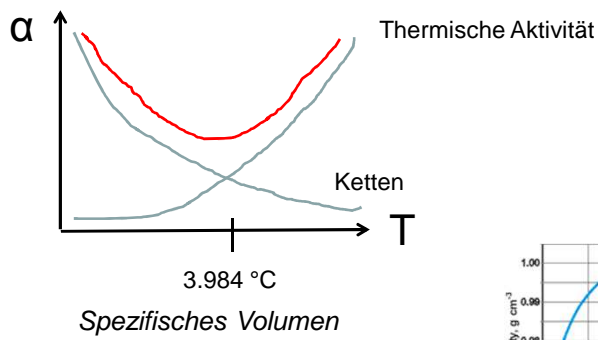
## Molekülketten



Fraction of molecule aggregates/chains (8, 4, 2, 1 molecules) as function on temperature. At low temperature, longer chains are more abundant which occupy larger volume. Combined with the "normal" thermal expansion effect with increasing temperatures, a density maximum results at a temperature of 4degC

Thurman & Trujillo, 2003

## Dichtemaximum



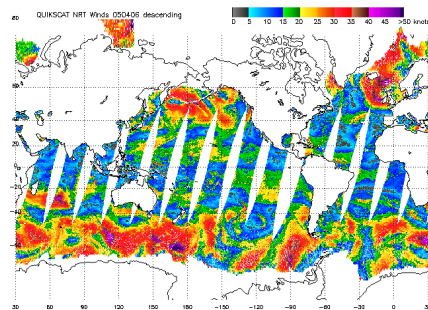
Dichte

## Kapillarwellen



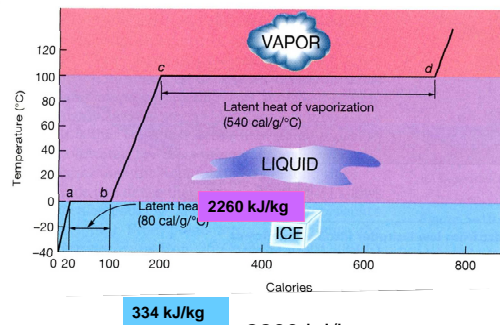
Hohe Oberflächenspannung

Anwendungen: Windmessungen vom Satelliten aus, z.B. Quikscat



<http://manati.orbit.nesdis.noaa.gov/quikscat/>

## Latente Wärme



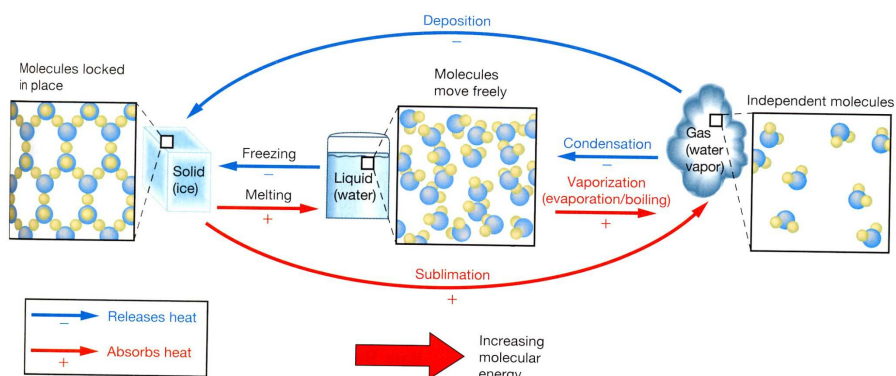
**Figure 5-7 Latent heats and changes of state of water.** The latent heat of melting (80 calories) is much less than the latent heat of vaporization (540 calories). See text for description of points *a*, *b*, *c*, and *d*.

334 kJ/kg      2260 kJ/kg

Si-Einheiten:    Wärmeenergie      Joule      J    Nm    m<sup>2</sup> kg s<sup>-2</sup>

Thurman & Trujillo, 2003

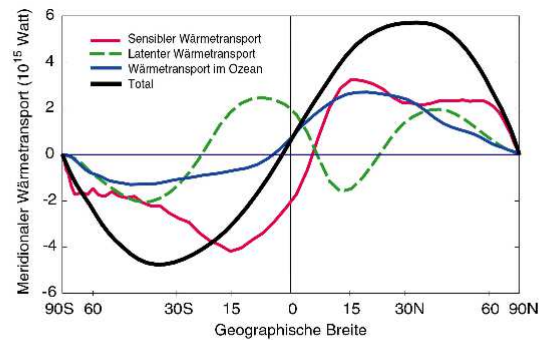
## Drei Aggregatzustände



**Figure 5-5 Water in the three states of matter.** Blue arrows (-) indicate heat released by water (which warms the environment) as it changes state; red arrows (+) indicate heat absorbed by water (which cools the environment).

Thurman & Trujillo, 2003

## Meridionaler Wärmetransport



Ozean sensibel  
Atmosphäre sensibel

Atmosphäre latent

- Verdunstung in Tropen
- Kondensation in hohen Breiten

Figur 1: Meridionaler Wärmetransport im Klimasystem. Ozean und Atmosphäre tragen in der Nordhemisphäre etwa gleich viel zum Transport bei. (Figur nach Bryden & Imawaki, 2001).

## Phasendiagramm für Wasser

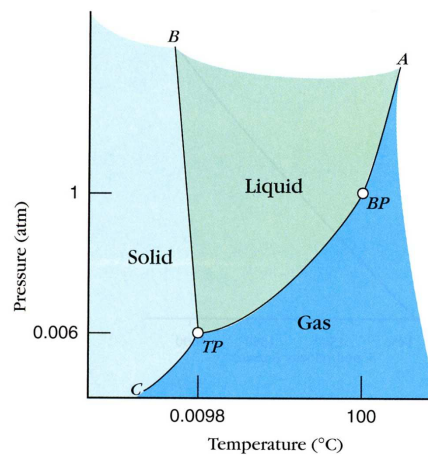


Figure 6-8 Phase Diagram for Water

Temperature and pressure cause changes in the phase or state of water. There is only one combination of temperature and pressure at which water can exist simultaneously as gas, liquid, and solid. This is the triple point (TP). The boiling point (BP) at 1 atm (760 mm) occurs at 100°C and is one point on a curve defining the boundary between liquid and gas (steam). *Thurman & Trujillo, 2003*

## Temperatur

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Thermodynamische Temperatur

Einheiten: Kelvin und Celsius  $T_k = T_c + 273.16$

1 K ist 1/273.16 der thermodynamischen Temperatur am Triplepunkt des Wassers.

Calibration of thermometers

triple point of equilibrium hydrogen at 13.8033 K

triple point of water at 0.060 °C

the melting point of Gallium at 29.7646 °C

freezing point of Indium at 156.5985 °C (Preston-Thomas, 1990).

Oceanic temperature range: -2 to 40 °C

## Temperature

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International Practical Temperature Scale (IPTS)

IPTS-68: polynomial fit of temperature between triple points etc.

IPTS-90: correction to IPTS-68

$$(T_{68}/^{\circ}\text{C}) = 1.00024 (T_{90}/^{\circ}\text{C}) \quad (\text{Saunders, 1990})$$

Polynom 8er Ordnung (Rusby, 1991)

*Difference is <0.001 K in the oceanic temperature range -2 °C to 40 °C*

## Heat

$$dQ = \rho c_p dT$$

$c_p$  – specific heat

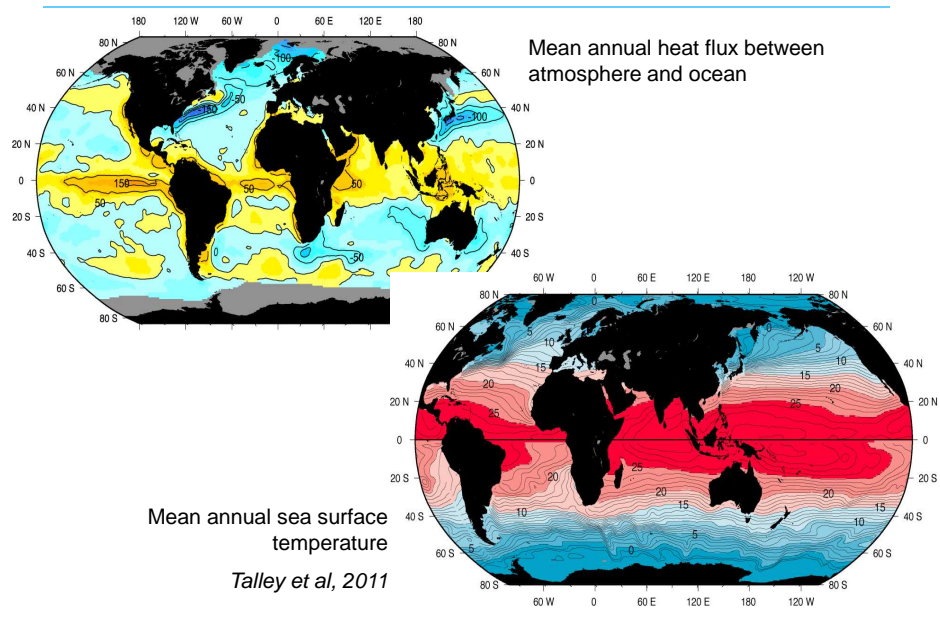
Sea water:  $\rho \sim 1025 \text{ kg / m}^3$ ,  $c_p \sim 4000 \text{ J / kg K}$

1 Joule =  $1 \text{ kg m}^2 / \text{s}^2$       energy

1 Watt = 1 Joule/s      heat change with time

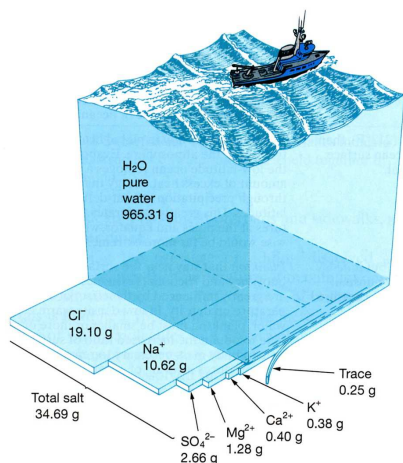
1 Watt/m<sup>2</sup> =  $1 \text{ kg / s}^3$       heat flux

## Heat fluxes and sea surface temperature



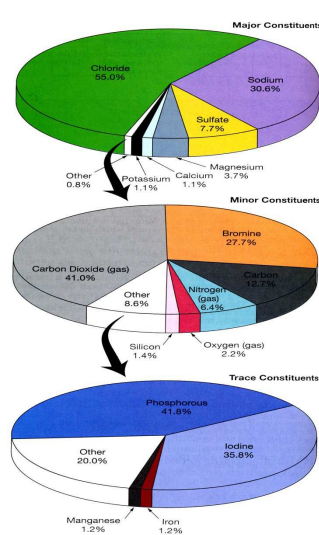


## Dissolved components in sea water



**Figure 5-13 Constituents of ocean salinity.** The composition of 1 kilogram of ocean water in grams (g), showing the concentrations of various dissolved substances. Average seawater salinity is approximately 35‰ or 3.5%.

Thurman & Trujillo, 2003



**Figure 5-14 Major dissolved components in seawater.** The percent of major constituents (top), minor constituents (middle), and trace constituents (bottom) dissolved in 35‰ seawater.

## Solutes

TABLE

Major solutes in seawater

| Salt Ion                                     | Ions in Seawater* (‰) | Ions by Weight (%) | Cumulative (%) |
|--|-----------------------|--------------------|----------------|
| Chloride (Cl <sup>-</sup> )                  | 18.980                | 55.04              | 55.04          |
| Sodium (Na <sup>+</sup> )                    | 10.556                | 30.61              | 85.65          |
| Sulfate (SO <sub>4</sub> <sup>2-</sup> )     | 2.649                 | 7.68               | 93.33          |
| Magnesium (Mg <sup>2+</sup> )                | 1.272                 | 3.69               | 97.02          |
| Calcium (Ca <sup>2+</sup> )                  | 0.400                 | 1.16               | 98.18          |
| Potassium (K <sup>+</sup> )                  | 0.380                 | 1.10               | 99.28          |
| Bicarbonate (HCO <sub>3</sub> <sup>-</sup> ) | 0.140                 | 0.41               | 99.69          |
| Bromide (Br <sup>-</sup> )                   | 0.065                 | 0.19               | 99.88          |
| Boric acid (H <sub>3</sub> BO <sub>3</sub> ) | 0.026                 | 0.07               | 99.95          |
| Strontium (Sr <sup>2+</sup> )                | 0.013                 | 0.04               | 99.99          |
| Fluoride (F <sup>-</sup> )                   | 0.001                 | 0.00               | 99.99          |
| Total  | 34.482                | 99.99              | 99.99          |

\*The gram weight of ions per 1 kg of seawater, or g/kg.

Source: Adapted from H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, *The Oceans* (Englewood Cliffs, N.J.: Prentice-Hall, 1942).

Thurman & Trujillo, 2003

Based on Dittmar's (1884) chemical analysis of 77 samples of sea water collected by the Challenger Expedition and further studies by Carritt and Carpenter (1959).



## Trace elements

TABLE

Examples of trace elements in seawater

| Trace Element   | Concentration (ppb)* |
|-----------------|----------------------|
| Lithium (Li)    | 170                  |
| Iodine (I)      | 60                   |
| Molybdenum (Mo) | 10                   |
| Zinc (Zn)       | 10                   |
| Iron (Fe)       | 10                   |
| Aluminum (Al)   | 10                   |
| Copper (Cu)     | 3                    |
| Manganese (Mn)  | 2                    |
| Cobalt (Co)     | 0.1                  |
| Lead (Pb)       | 0.03                 |
| Mercury (Hg)    | 0.03                 |
| Gold (Au)       | 0.004                |

\*ppb = parts per billion

Thurman & Trujillo, 2003

## Salinity

### Definition:

Total amount of solid materials in grams dissolved in one kilogram of sea water when all the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine and all organic matter completely oxidized. (Knudsen, 1902)

Practical definition: Salinity Based on Chlorinity. Because the above definition was difficult to implement in practice, because salinity is directly proportional to the amount of chlorine in sea water, and because chlorine can be measured accurately by a simple chemical analysis, salinity S was redefined using chlorinity:

$$S = 0.03 + 1.805Cl$$

where chlorinity Cl is defined as "the mass of silver required to precipitate completely the halogens in 0.328 523 4 kg of the sea-water sample.

UNESCO 1964 definition of salinity.  $S = 1.806 55Cl$   
(Wooster, Lee, and Dietrich, 1969)

## Salinity

Salinity Based on Conductivity:

Definition: The Practical Salinity Scale of 1978 : (not psu !!!)

$$S_p = 0.0080 - 0.1692 K15^{1/2} + 25.3851 K15 + 14.0941 K15^{3/2} - 7.0261 K15^2 + 2.7081 K15^{5/2}$$

$$K15 = C(S, 15, 0)/C(KCl, 15, 0) \quad \text{for } 2 \leq S \leq 42$$

where  $C(S, 15, 0)$  is the conductivity of the sea-water sample at a temperature of 14.996 °C on the International Temperature Scale of 1990 (ITS-90) and standard atmospheric pressure of 101 325 Pa.

$C(KCl, 15, 0)$  is the conductivity of the standard potassium chloride (KCl) solution at a temperature of 15 °C and standard atmospheric pressure.

The standard KCl solution contains a mass of 32.435 6 grams of KCl in a mass of 1.0 kg of solution.

Millero (1996) and Lewis (1980) give equations for calculating salinity at other pressures and temperatures.

## Conductivity

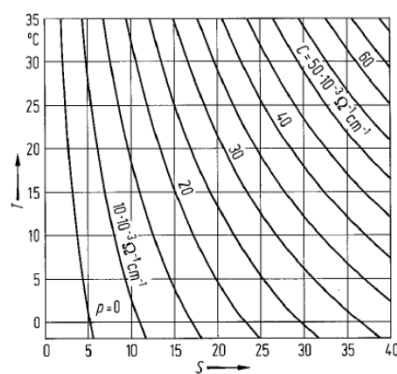


Fig. 1. Electrical conductivity  $C$  in  $[10^{-3} \Omega^{-1} \text{cm}^{-1}]$  as function of practical salinity and temperature at atmospheric pressure using  $C(35, 15, 0) = 42.914 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$ . Contour interval  $5 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$ .

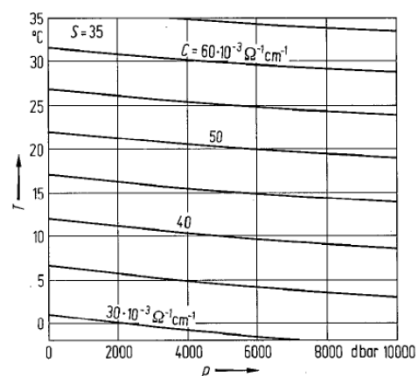


Fig. 2. Electrical conductivity  $C$  in  $[10^{-3} \Omega^{-1} \text{cm}^{-1}]$  as function of pressure and temperature for  $S=35$  using  $C(35, 15, 0) = 42.914 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$ . Contour interval  $5 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$ .

Siedler & Peters, 1989

## Absolute salinity

Practical salinity PSS-78 should be stored in data basis, BUT:

Composition of seawater is NOT constant !

Standard sea water is taken from deep waters in the North Atlantic (40-50 N) and its salinity is „reference salinity“

$$S_R \sim u_{ps} S_P \quad (u_{ps} = 35.16504/35) \text{ g/kg for } 2 < S < 42$$

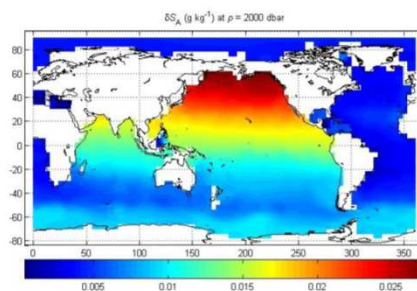
Absolute  $S_A$  salinity takes the non-uniform composition into account.

$S_A$  is the mass fraction of dissolved non- $H_2O$  material in the sea water sample at its pressure and temperature

additional variables:  $CO_2$ ,  $SiO_4$  etc.  $f$  (time, depth, latitude,...)

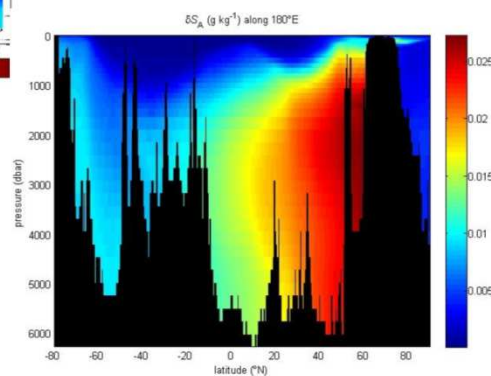
These variables influence the density

## Absolute salinity



$$\Delta S_A = S_A - S_R$$

*McDougall et al., 2010*



## Pressure

z-momentum:  $0 = -\frac{\partial p}{\partial z} - \rho g$

$$p = \int \rho g \, dz$$

Units: 1 Pascal = 1 N/m<sup>2</sup>

1 bar = 10<sup>6</sup> dynes/cm<sup>2</sup> = 10<sup>5</sup> N/m<sup>2</sup>

approximately the atmospheric pressure at sea level

1 atmosphere = 1000 millibar = 1 bar

1 dbar = 0.1 bar

Relation depth and pressure:

$$\rho \sim 1025 \text{ kg/m}^3, \quad g \sim 9.81 \text{ m/s}^2, \quad z = 1 \text{ m}$$

1 metre corresponds to about 1 dbar

## Compressibility

Water (including seawater) is compressible

$$\chi_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

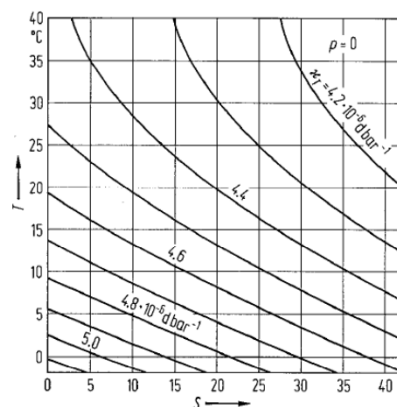


Fig. 7. Isothermal compressibility  $\chi_T$  in [ $10^{-6} \text{ dbar}^{-1}$ ] as function of salinity and temperature at atmospheric pressure. Contour interval  $10^{-7} \text{ dbar}^{-1}$ .

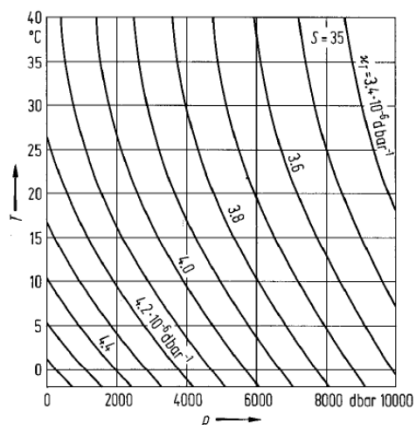


Fig. 8. Isothermal compressibility  $\chi_T$  in [ $10^{-6} \text{ dbar}^{-1}$ ] as function of pressure and temperature at  $S=35$ . Contour interval  $10^{-7} \text{ dbar}^{-1}$ .

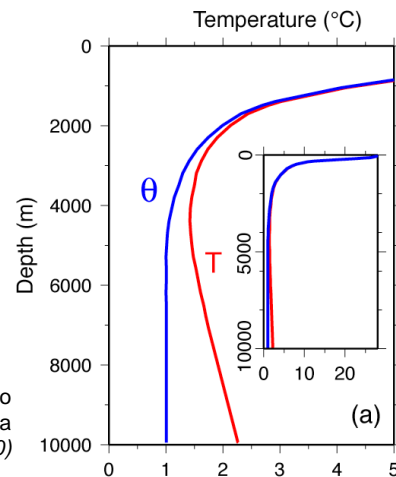
Siedler & Peters, 1989

## Potential temperature

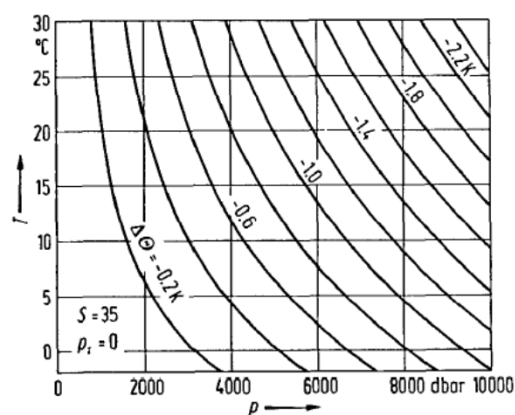
When a volume of water is compressed adiabatically (i.e. with no exchange of heat with its surroundings), its temperature increases.

Define “potential temperature” as the temperature ( $\Theta$ ,  $\Theta_1$ ,  $\Theta_2$ ,  $\Theta_3$  etc.) a parcel of water has if moved adiabatically (without exchanges or mixing) to the sea surface or some other standard (1000dbar, 2000 dbar etc.) level. Potential temperature is conserved following a water parcel.

Temperature and potential temperature referred to the sea surface from a station in the Mariana Trench (from Talley et al., 2010)



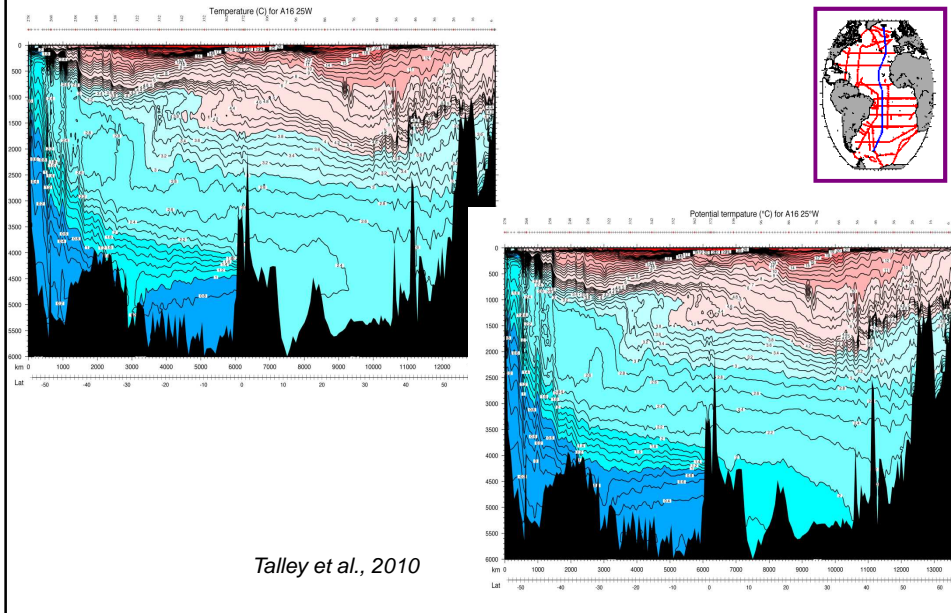
## Potential temperature



**Fig. 16. Difference between potential and in-situ temperature in [K] as function of pressure and in-situ temperature;  $S = 35$ ,  $p_r = 0$ . Contour interval 0.2 K.**

*Siedler & Peters, 1989*

## Atlantic potential temperatures



## Specific heat

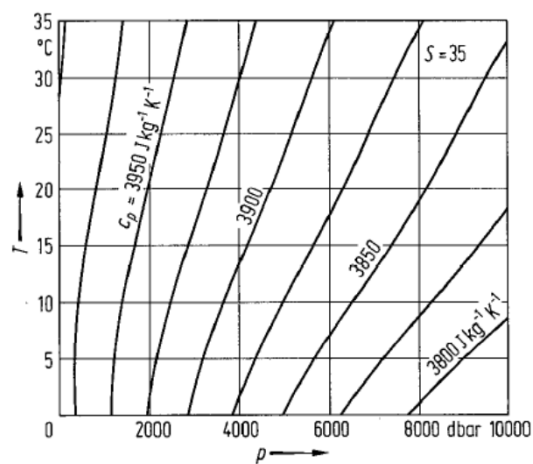
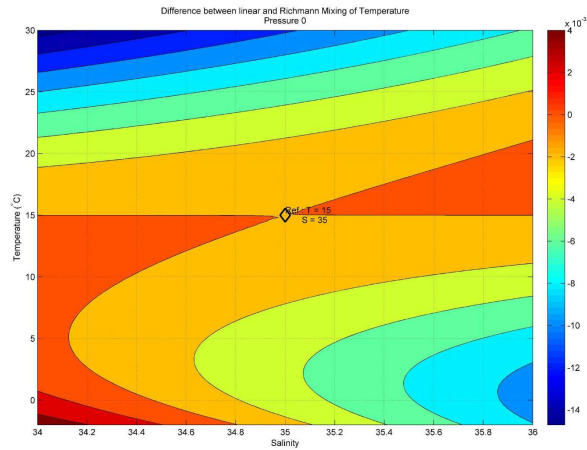


Fig. 13. Specific heat at constant pressure  $c_p$  in  $[\text{J kg}^{-1} \text{K}^{-1}]$  as function of pressure and temperature for  $S=35$ . Contour interval  $25 \text{ J kg}^{-1} \text{K}^{-1}$ .

Siedler & Peters, 1989

## Mixing of water

1:1 mixing<sup>1</sup> of water with different temperature and salinity with reference water ( $T=15^\circ\text{C}$ ,  $S = 35$ ) compared to linear mixing<sup>2</sup> of temperature.



$$(1) T_m = (c_{p1}\rho_1 T_1 + c_{pr}\rho_r T_r) / 2 c_{pm} \rho_m$$

$$(2) T_m = (T_1 + T_r) / 2$$

## Thermal expansion

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

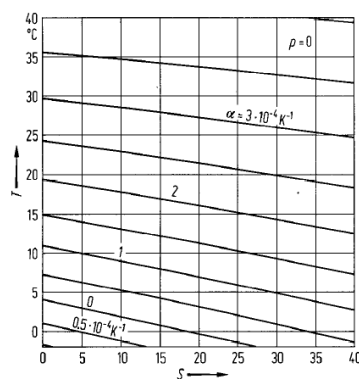


Fig. 9. Thermal expansion coefficient  $\alpha$  in  $[10^{-4} \text{K}^{-1}]$  as function of salinity and temperature at atmospheric pressure. Contour interval  $5 \cdot 10^{-5} \text{K}^{-1}$ .

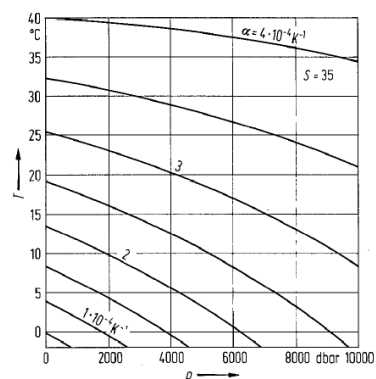
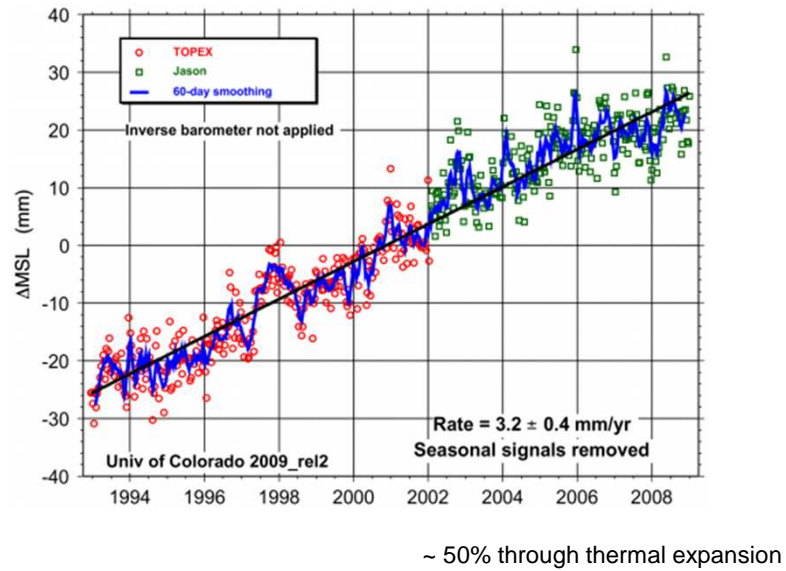


Fig. 10. Thermal expansion coefficient  $\alpha$  in  $[10^{-4} \text{K}^{-1}]$  as function of pressure and temperature for  $S=35$ . Contour interval  $5 \cdot 10^{-5} \text{K}^{-1}$ .

Siedler & Peters, 1989



## Global warming – sea level rise



## Freezing point

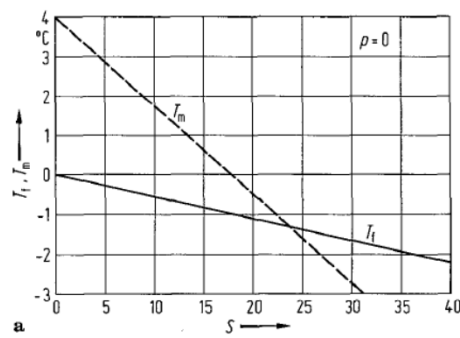


Fig. 19a. Freezing point temperature  $T_f$  as function of salinity at atmospheric pressure and maximum density temperature  $T_m$ .

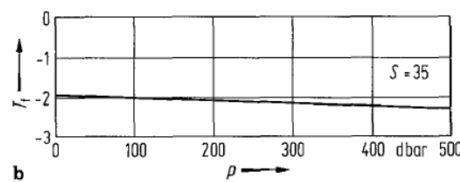


Fig. 19b. Freezing point temperature as function of pressure for  $S=35$ .

Siedler & Peters, 1989

## Sea water density

- Vertical stratification  $N^2 = g/\rho \cdot \partial \rho / \partial z$  Brunt-Väisälä Frequency
- Large scale pressure gradients thermal wind, geostrophy
- Mixing most efficient along isopycnals

Density  $\rho = m/V = \rho(S, T, p)$  [kg/m<sup>3</sup>]  
depends on temperature, salinity and pressure.

Density anomaly  $\sigma(S, T, p) = \rho(S, T, p) - 1000 \text{ kg/m}^3$

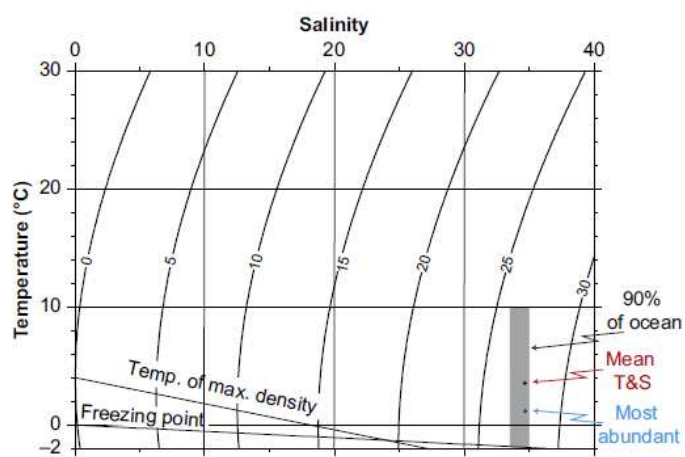
Potential density - reference pressure, potential density

International Thermodynamic Equation Of State

$$\rho = \rho(S, T, 0) / (1 - p/k(S, T, p)) \quad [\text{kg/m}^3]$$

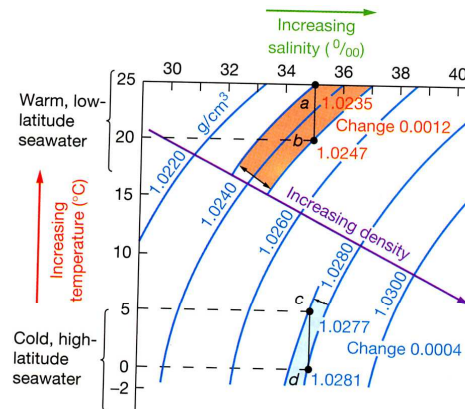
EOS1980 and TEOS 2010 (incl. absolute salinity)

## Sea water density anomaly (EOS80)



Talley et al., 2011

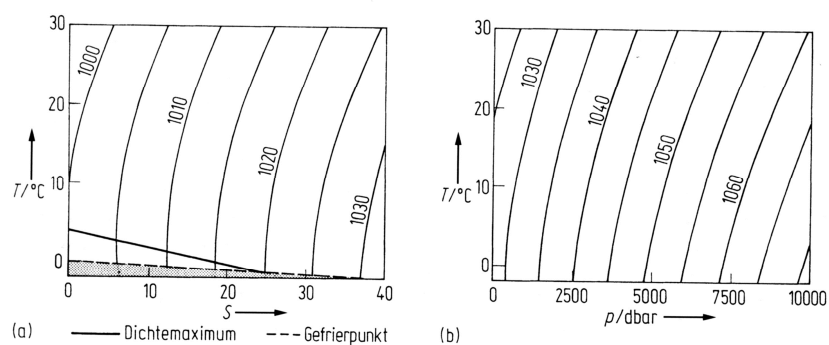
## Sea water density



**Figure 5-23 Seawater density varies with temperature and salinity.** Blue curves show density, which increases with increasing salinity and decreases with increasing temperature. In high-latitude areas of cold water, temperature has less effect on density than in high-temperature, low-latitude areas.

Thurman & Trujillo, 2003

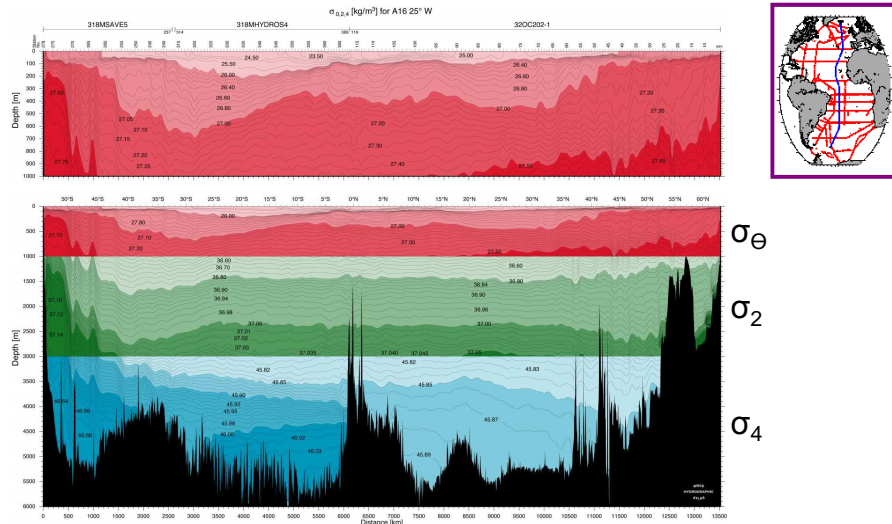
## Sea water density pressure effect



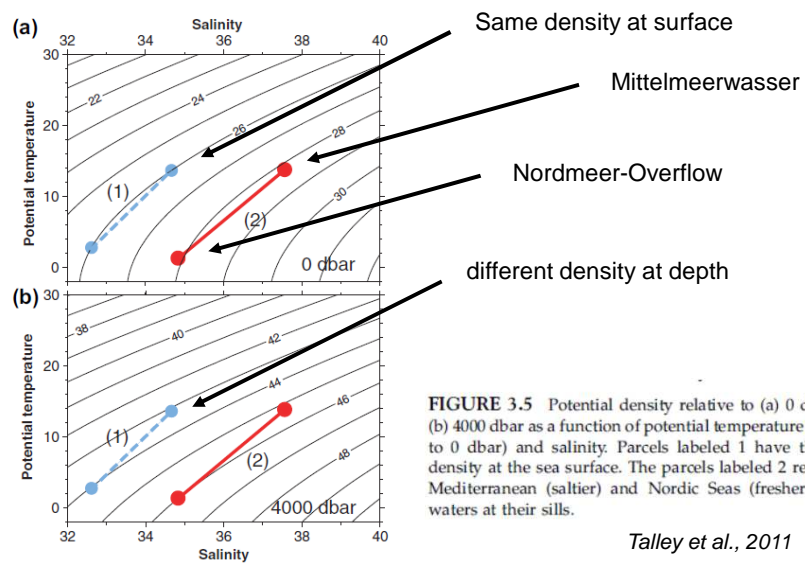
**Abb. 2.1** Isopyknen (Linien gleicher Dichte des Meerwassers) in  $\text{kg m}^{-3}$  (a) bei Atmosphärendruck als Funktion von Salzgehalt und Temperatur und (b) bei einem konstanten Salzgehalt ( $S = 35$ ) als Funktion von Druck und Temperatur.

Kalle & Dietrich, 1975

## Potential density anomaly



## Thermobaric Effect



**FIGURE 3.5** Potential density relative to (a) 0 dbar and (b) 4000 dbar as a function of potential temperature (relative to 0 dbar) and salinity. Parcels labeled 1 have the same density at the sea surface. The parcels labeled 2 represents Mediterranean (saltier) and Nordic Seas (fresher) source waters at their sills.

*Talley et al., 2011*

## Isentropic surfaces and Neutral Density

Isentropic surface:

water moves adiabatically if no external input of heat and freshwater

But:  $\rho = \rho(S, T, p)$  mixing changes temperature and salinity of a parcel and thus its compressibility

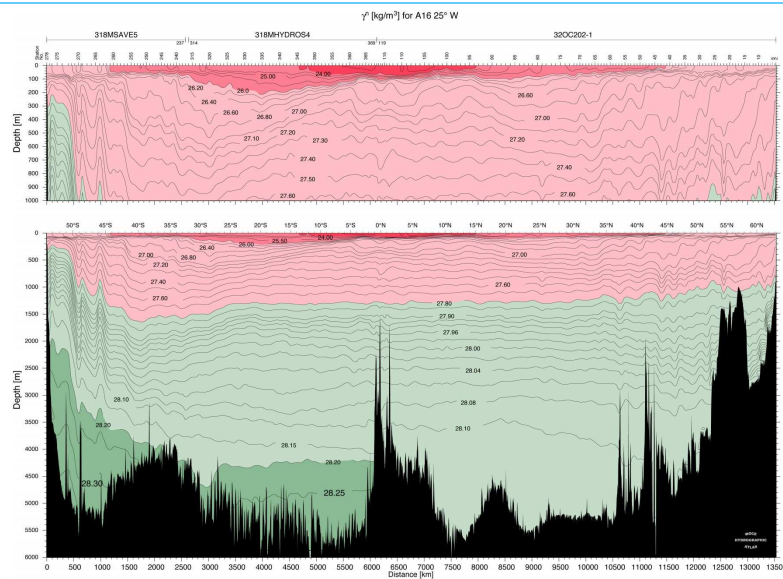
Stratification is different with and without mixing

==> there are no closed isentropic surfaces

Common approximations of isentropic surfaces:

Constant surfaces of: pressure  $P$ , sigma- $t$   $\sigma_t$ , Theta  $\Theta$ , sigma Theta  $\sigma_\Theta$   
sigma-1,2,3 ...  $\sigma_{1,2,3}$  ... or  
neutral surfaces  $\gamma$ : continuously changing reference pressure (not a thermodynamic property)

## Neutral Density



## Linearized equation of state

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$$\rho = \rho(S, T, 0) / (1 - \alpha(T - T_0) - \beta(S - S_0))$$

$$\rho \sim \rho_0 + \alpha(T - T_0) + \beta(S - S_0)$$

with

$$\alpha = \frac{1}{\rho} \frac{\partial \rho}{\partial T}$$
 thermal expansion coefficient

$$\beta = \frac{1}{\rho} \frac{\partial \rho}{\partial S}$$
 haline contraction coefficient

Frequently used in simple theoretical and numerical models

Ranges:

$$\alpha \quad 50 - 300 \times 10^{-6} \text{ K}^{-1}$$
$$\beta \quad 785 - 744 \times 10^{-6}$$

## More topics

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|         |                     |
|---------|---------------------|
| Tracers | - Wassermassen      |
| Sound   | - ???               |
| Light   | - Oberflächenflüsse |
| Ice     | - Oberflächenflüsse |