# The World Ocean - II



## Salt content (salinity) of seawater

- About 3.5% of average seawater consists of dissolved salts
  - If these precipitated, they would form a layer about
    56 m thick on the seafloor
- Average salinity is 33 to 37 per mil
  - Principally sodium, chlorine and six other ions derived from
    - Dissolved load in streams
    - Volcanic volatiles carried by atmospheric water
    - Submarine volcanism
    - Aeolian dust
    - Pollutants

### Salinity of ocean water is related to

- a) Latitude
- b) Evaporation
- c) Precipitation of rain and snow
- d) Inflow of fresh river water
- e) Freezing of sea ice



#### Challenger Expedition 1872 - 1876



### Challenger Expedition (1872~1875)



H.M.S. CHALLENGER UNDER SAIL, 1874.

H.M.S. Challenger sampled the ocean across the globe heralding the beginning of oceanography as a science discipline.



Route of Challenger



William Dittmar analyzed 77 water samples collected during the Challenger expedition.

**Constancy of composition** – the concentrations of the major dissolved ions in seawater vary from place to place in the oceans, but their relative proportions remain virtually constant.

| DITTMAR'S VALUES FOR THE MAJOR CONSTITUENTS OF SEA WATER (Values in grams per kilogram, ‰) |                 |       |                        |                     |             |       |  |
|--------------------------------------------------------------------------------------------|-----------------|-------|------------------------|---------------------|-------------|-------|--|
| lon                                                                                        | Original values |       | Recalculat<br>atomic w | ed, 1940<br>/eights | 1940 values |       |  |
|                                                                                            | CI = 19 ‰       | %     | Cl = 19 ‰              | %                   | CI = 19 ‰   | %     |  |
| C1⁻                                                                                        | 18.971          | 55.29 | 18.971                 | 55.26               | 18.980      | 55.04 |  |
| Br⁻                                                                                        | 0.065           | 0.19  | 0.065                  | 0.19                | 0.065       | 0.19  |  |
| SO4-                                                                                       | 2.639           | 7.69  | 2.635                  | 7.68                | 2.649       | 7.68  |  |
| CO₃⁻                                                                                       | 0.071           | 0.21  | 0.071                  | 0.21                |             |       |  |
| HCO <sub>3</sub> ⁻                                                                         |                 |       |                        |                     | 0.140       | 0.41  |  |
| F-                                                                                         |                 |       |                        |                     | 0.001       | 0.00  |  |
| $H_3BO_3$                                                                                  |                 |       |                        |                     | 0.026       | 0.07  |  |
| Mg <sup>++</sup>                                                                           | 1.278           | 3.72  | 1.292                  | 3.76                | 1.272       | 3.69  |  |
| Ca++                                                                                       | 0 411           | 1 20  | 0 411                  | 1.20                | 0.400       | 1.16  |  |
| Sr++                                                                                       | 0.411           | 1.20  | 0.411                  |                     | 0.013       | 0.04  |  |
| K+                                                                                         | 0.379           | 1.10  | 0.385                  | 1.12                | 0.380       | 1.10  |  |
| Na <sup>+</sup>                                                                            | 10.497          | 30.59 | 10.498                 | 30.58               | 10.556      | 30.61 |  |
| Total                                                                                      | 34.311          |       | 34.328                 |                     | 34.482      |       |  |

Salinity – the total amount in grams of solid material dissolved in 1 kg of seawater when all the carbonate has been converted to oxide, all the iodine and bromine have been replaced by chlorine, and all organic matter has been completely oxidized.

S(%) = 1.80655 CI(%) CI(%) determined by titration

More recently salinity has been determined by electrical conductivity TDS (‰) = 0.073 + 1.8110 CI(%)

Why two different definitions of dissolved solids?

#### **Standard Seawater:**

Seawater with TDS of 35,000 mg/l (ppm) is considered as "standard seawater" since this constitutes by far the largest amount of water worldwide. The composition is nearly the same all over the world (see table 1)

|                                                      | TABLE          | 1: "Standard | Seawater" Comp  | position  | -                        |  |
|------------------------------------------------------|----------------|--------------|-----------------|-----------|--------------------------|--|
| Calcium 410 mg/l Silica<br>Chloride 19,700 mg/l Sodi |                | Silica       | 0.04 - 8.0 mg/l | Magnesium | 1,310 mg/l<br>2,740 mg/l |  |
|                                                      |                | Sodium       | 1,900 mg/l      | Sulphate  |                          |  |
| Potassium                                            | 390 mg/l       | Fluoride     | 1.4 mg/l        | Barium    | 0.05 mg/l                |  |
| Bromide                                              | 65 mg/l        | Strontium    | 13 mg/l         | Nitrate   | < 0.7 mg/l               |  |
| Iron < 0.02 mg/l Bicar                               |                | Bicarbonate  | 152 mg/l        | Manganese | < 0.01 mg/l              |  |
| 6                                                    | TDS = 35,000 m | g/l          |                 | pH = 8.1  |                          |  |

The actual TDS content may, however, vary within wide limits from e.g. the Baltic Sea with 7,000 ppm to the Red Sea with up to 45,000 ppm. The actual composition can be proportionally estimated from the "standard seawater" composition.

Be aware that seashore wells depending on the soil, influx from island, etc. can often have salinity and composition quite different from that of a sample taken from the sea itself.

In seawater treatment the limiting factor is of a physical nature, i.e. the osmotic pressure caused by the high TDS.





### **Density of Seawater**

Density ( $\rho$ ) = mass/volume and specific volume ( $\alpha$ ) = volume/mass

 $\rho_{s,t,p}$  – density as a function of salinity, temperature, and pressure

Determination of seawater density –

- 1. Determine temperature in situ
- 2. Determine salinity of seawater in the lab by titration or conductivity
- 3. Calculate pressure from the hydrostatic equation ( $P = \rho gh$ )

All three values can be determined simultaneously using a Nansen bottle and reversing thermometers.

# Nansen Bottle – simultaneous determination of salinity, temperature, and pressure







Sigma t ( $\sigma_t$ ) – density when the pressure = surface pressure

 $\sigma_{t} = (\rho_{s,t,o} - 1) \times 10^{3}$ 

#### Determination of $\sigma_t$ :

Specific volume =  $\alpha_{s,t,o}$  = 1/  $\rho_{s,t,o}$  when calculating sigma t

The thermosteric anomaly ( $\Delta_{s,t}$ ) is the difference between the specific volume of water at S = 35‰ and T = 0°C and the salinity and temperature of the actual water sample. Pressure is surface pressure.

$$\alpha_{s,t,o} = \alpha_{35,0,o} + \Delta_{s,t} = 0.97264 + \Delta_{s,t}$$

 $\rho_{s,t,o} = 1/\alpha_{s,t,o}$ 

 $\sigma_{t} = (\rho_{s,t,o} - 1) \times 10^{3}$ 

#### Determination of the Thermosteric Anomaly and $\sigma_t$

| Δ <sub>s,t</sub> x 10 <sup>-5</sup> (cm³/g) as a f(T,P) |            |       |       |       |       |        |  |  |
|---------------------------------------------------------|------------|-------|-------|-------|-------|--------|--|--|
|                                                         | Salinity ‰ |       |       |       |       |        |  |  |
| T (°C)                                                  | 30         | 32    | 34    | 35    | 36    | 38     |  |  |
| -1                                                      | 379.4      | 225.6 | 72.2  | -4.4  | -80.8 | -233.5 |  |  |
| 0                                                       | 382.3      | 229.1 | 76.3  | 0.0   | -76.2 | -228.4 |  |  |
| 1                                                       | 386.6      | 233.9 | 81.7  | 5.7   | -70.3 | -221.9 |  |  |
| 2                                                       | 392.1      | 240.1 | 88.3  | 12.6  | -63.1 | -214.2 |  |  |
| 4                                                       | 407.1      | 256.1 | 105.4 | 30.2  | -45.0 | -195.2 |  |  |
| 6                                                       | 426.9      | 276.8 | 127.1 | 52.3  | -22.4 | -171.6 |  |  |
| 8                                                       | 451.2      | 302.0 | 153.2 | 78.8  | 4.5   | -143.9 |  |  |
| 10                                                      | 479.8      | 331.4 | 183.4 | 109.4 | 35.5  | -112.1 |  |  |
| 15                                                      | 568.7      | 422.0 | 275.6 | 202.5 | 129.4 | -16.6  |  |  |
| 20                                                      | 680.5      | 535.1 | 390.0 | 317.5 | 245.1 | 100.3  |  |  |
| 30                                                      | 966.8      | 822.9 | 679.1 | 607.3 | 535.6 | 392.1  |  |  |

#### Example:

Seawater T = 3°C and Salinity = 33.5‰

Determine the thermosteric anomaly by interpolation using the table to the left.

|   | 32    | 32.5  | 33    | 33.5  | 34    |
|---|-------|-------|-------|-------|-------|
| 2 | 240.1 |       |       |       | 88.3  |
| 3 | 248.1 | 210.3 | 172.5 | 134.7 | 96.85 |
| 4 | 256.1 |       |       |       | 105.4 |

 $\alpha_{s,t,o} = \alpha_{35,0,o} + \Delta_{s,t} = 0.97264 + 0.001347 = 0.973987$ 

 $\sigma_{t} = (\rho_{s,t,o} - 1) \times 10^{3} = (1/\alpha_{s,t,o} - 1) \times 10^{3} = (1.02671 - 1) \times 10^{3} = 26.71$ 

#### Water Mass and T-S Diagrams

Water mass - body of ocean water with a distinctive narrow range of temperature and salinity that distinguishes it from other water bodies. Salinity and temperature are determined by the source of the water body.



Mixing of water masses is a linear process. Mixing of A and B results in a water mass that falls on the mixing line between the two water masses.

Caballing – mix two water masses with the same density but different salinities and temperatures. The result is a water mass with a higher density.

#### **T-S Plots for Various Ocean Waters**





#### Diffusivity in seawater – homogenization of seawater

- Diffusion transfer of heat, chemicals, momentum, or dissolved gases along a concentration gradient.
- Controlled by
  - Molecular diffusion very slow
  - Convection generally not important in oceans
  - Turbulence very important in ocean

#### Thermal properties of seawater

- Heat capacity
- Latent heat of vaporization -L = 596 0.52T (°C) cal/g
- Latent heat of fusion = 80 cal/g for fresh water. Decreases with increasing salinity
- Formation of sea ice
  - Salt content lowers freezing temperature
  - Initial solid is pure water further increasing salinity of remaining water
  - Ice acts an thermal insulator



Water is most dense at 3.98 degrees celsius and gets less dense as it cools or warms.



Fig. 7.3 The depression of the initial freezing point and temperature of maximum density of seawater with increasing salinity.

Large water masses in the ocean behave adiabatically Potential temperature =  $t_{in \ situ} - \Delta t_{adiabatic \ temperature \ rise}$ Example: Water collected at 8,000 m has measured t = 2°C Potential t = 2°C - 0.925 = 1.075°C

| Adiabatic temperature rise (Δt x 10 <sup>-2</sup> ) |        |                         |       |       |       |      |      |      |          |
|-----------------------------------------------------|--------|-------------------------|-------|-------|-------|------|------|------|----------|
|                                                     | Depth  | Initial temperature, °C |       |       |       |      |      |      | Salinity |
|                                                     | m      | -2                      | 0     | 2     | 4     | 6    | 8    | 10   | ‰        |
| Salinity                                            | 1000   | 2.6                     | 4.4   | 6.2   | 7.8   | 9.5  | 11.0 | 12.4 | 34.85    |
|                                                     | 2000   | 7.2                     | 10.7  | 14.1  | 17.2  | 20.4 | 23.3 | 26.2 | 34.85    |
|                                                     | 4000   | 21.7                    | 28.4  | 34.7  | 40.6  | 46.3 | 51.9 | 57.2 | 34.85    |
| Constant                                            | 6000   | 42.8                    | 52.2  | 61.1  | 69.4  |      |      |      | 34.85    |
|                                                     | 8000   |                         | 81.5  | 92.5  | 102.7 |      |      |      | 34.85    |
|                                                     | 10,000 |                         | 115.7 | 128.3 | 128.3 |      |      |      | 34.85    |
| Pressure<br>Constant                                | 1000   |                         | 3.5   | 5.3   | 7.0   | 8.7  | 10.3 | 11.8 | 30.00    |
|                                                     | 1000   |                         | 3.9   | 5.7   | 7.3   | 9.0  | 10.6 | 12.1 | 32.00    |
|                                                     | 1000   |                         | 4.3   | 6.0   | 7.7   | 9.4  | 10.9 | 12.4 | 34.00    |
|                                                     | 1000   |                         | 4.7   | 6.4   | 8.1   | 9.7  | 11.2 | 12.7 | 36.00    |
|                                                     | 1000   |                         | 5.1   | 6.8   | 8.4   | 10.0 | 11.6 | 13.0 | 38.00    |

#### Surface tension gives the air-sea boundary its elastic quality

- Controls transfer of ions and molecules across the air-sea interface
- Affects the shape of small waves which is controlled by surface tension

Surface tension (dynes/cm<sup>2</sup>) = 75.54 - 0.144 x t (°C) + 0.399 x Cl%



#### Vertical structure of the ocean

#### Propagation of sound in the ocean

- Velocity of sound greater in water ( $\sim$ 1500 m/s) than air ( $\sim$ 340 m/s)
- Velocity of sound waves,  $V = (elasticity/density)^{1/2}$
- Elasticity =  $C_P/C_V \ge 1/K$

K = compressibility of the transmitting medium

Why is the speed of sound greater in water than in air?

In the ocean the speed of sound increases with increasing salinity, temperature, and pressure. Temperature is the most important factor.



### Determining the temperature – depth (pressure) profile for the ocean

### The bathythermograph









# The wave path bends towards the region of lower velocity



Critical angle for total internal reflection

 $\sin \theta_2 = (V_1/V_2) \sin \theta_1$ where  $V_1 < V_2$ 







Fig. 8.4 Near the surface of the sea the temperature structure (a) will act to produce a sound shadow zone (b) if the salinity is constant. (After L. E. Kinsler and A. R. Frey, *Fundamentals of Acoustics*, 2d ed., Wiley, New York, 1962.)



**Fig. 8.5** The temperature, salinity, and pressure variation with depth combine to produce a minimum sound velocity at about 1000m. Sound generated at this depth can be trapped in a layer known as the SOFAR channel. (After L. E. Kinsler and A. R. Frey, *Fundamentals of Acoustics*, 2d ed., Wiley, New York, 1962.)

### Attenuation of sound in seawater

- Spreading inverse square law
- Absorption

$$I_{x\lambda} = I_{o\lambda} e^{-2\upsilon x}$$

 $I_{x\lambda}$  = intensity of wavelength  $\lambda$  at distance x

 $I_{o\lambda}$  = intensity of wavelength  $\lambda$  at the origin

x = distance

 $v = absorption \ coefficient$ 

Absorption coefficient =  $\upsilon = 8\pi^2 \mu/3\lambda^2 \rho V$ 

 $\mu = \text{viscosity of water}$   $\lambda = \text{wavelength of sound}$   $\rho = \text{density of water}$ V = speed of sound in water

• Scattering

#### Propagation of light in the sea

- Water is essentially opaque to all EM radiation except visible light
- Attenuation of light
  - Spreading
  - Absorption

 $I_{x\lambda} = I_{o\lambda} e^{-\alpha_{\lambda} x}$ 

where  $\alpha_{\lambda}$  = absorption coefficient for light of wavelength  $\lambda$ 

- Scattering
  - Salt and water molecules scatter short wavelengths of light so the ocean appears blue
  - Larger particles (organic molecules, microscopic plants and animals) scatter longer wavelengths and the ocean appears green.

# Absorption coefficients of light in pure water, per meter

| Color       | Wavelength<br>(microns) | Absorption coefficient per<br>meter |
|-------------|-------------------------|-------------------------------------|
| Ultraviolet | 0.30                    | 0.800                               |
| Blue        | 0.40                    | 0.072                               |
| Green       | 0.50                    | 0.016                               |
| Yellow      | 0.60                    | 0.125                               |
| Orange      | 0.70                    | 0.840                               |
| Red         | 0.80                    | 2.400                               |
|             | 0.90                    | 6.550                               |
|             | 1.00                    | 39.700                              |
| Infrared    | 1.10                    | 20.300                              |
|             | 1.20                    | 123.200                             |
|             | 1.30                    | 150.000                             |
|             | 1.40                    | 1600.000                            |
|             | 1.50                    | 1940.000                            |

Heat budget for the oceans:

- $Q_s$  = shortwave radiation absorbed from the sun (0.221 cal/cm<sup>2</sup>·s)
- $Q_b$  = net longwave radiation from oceans to atmosphere (0.090 cal/cm<sup>2</sup>·s)
- $Q_h$  = heat flux from ocean to atmosphere (0.013 cal/cm<sup>2</sup>·s)
- $Q_e$  = heat transferred during the process of evaporation (0.113 cal/cm<sup>2</sup>·s)

Oceans act as thermal buffers and moderate temperature changes