OCEANOGRAPHY

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CHAPTER-1

Water and Sea-water Chemistry

Properties of Water

- **Geometry:** Water molecule consists of a central oxygen atom covalently bonded to two hydrogen atoms separated by an angle of about **105°**. The covalent bonds are formed due to the sharing of electrons between oxygen and each hydrogen atom.
- **Polarity:** A slight overall negative charge to the side of the oxygen atom and a slight overall positive charge to the side of the hydrogen atoms are generated due to bent geometry of the water molecule. **Dipolar nature** in water molecule exists due to slight charge separation which gives the water molecule an electrical polarity.
- Universal Solvent: Water behaves as the Universal solvent.
- The water molecule has the ability to stick with other water molecules and polar chemical compounds.
- The water molecule through this process reduces the attraction between ions of opposite charges by as much as **80 times**.
- The electrostatic attraction between oppositely charged ions produces an ionic bond.
- Example: The electrostatic attraction (ionic bonding) between the sodium and chloride ions is reduced by 80 times when solid NaCl is placed in water. This in turn makes both the sodium (Na) and chloride (Cl) ions to separate and dissolve in water easily.
- Heat Capacity and Specific Heat: Heat capacity is the amount of heat energy required to raise the temperature of a substance by 1°C.
- Heat capacity per unit mass of a body is called Specific heat capacity.
- High Heat Capacity of water is due to its ability to acquire more energy to increase the kinetic energy of hydrogen-bonded water molecules than it does for substances where the dominant intermolecular interaction is the much weaker Van der Waals force. Therefore, water gain or lose much more heat than other common substances while undergoing an equal temperature change.

CHARACTERISTICS OF SEAWATER

• Salinity: It is the total amount of solid material dissolved in water including dissolved gases but excluding dissolved organic substances and is expressed in parts per thousand (ppt). Seawater salinity is 35‰.

Salinity (‰) = 1.80655 * Chlorinity (‰)

- Salinometer is used to measure salinity of seawater. It can measure up to an accuracy of 0.003‰ or more.
- Law of Constant Proportion: The principle of constant proportions states that the "major dissolved constituents responsible for the salinity of seawater occur nearly everywhere in the ocean in the exact same proportions, independent of salinity".
- **Seawater has** constancy of composition, so the concentration of a single major constituent can be measured to determine the total salinity of a given water sample.
- Chloride ion occurs in highest abundance and shows the easiest accuracy.
- **Chlorinity**: The weight of chloride ion in a seawater sample is its chlorinity.
- Seawater Density: It is an important property of seawater as density differences determine the vertical position of ocean water and cause water masses to float or sink, thereby creating deep ocean currents. The seawater density averages between 1.022 and 1.030 g/cm3 (depending on its salinity). The density of seawater is 2% to 3% greater than that of pure water.

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SELECTED DISSOLVED MATERIALS IN SEAWATER:

Constituent	Concentration (%)	Ratio of constituent/total salts (%)	
Chloride (CI ⁻)	19.2	55.04	
Sodium (Na*)	10.6	30.61	
Sulfate (SO ₄ ²⁻)	2.7	7.68	
Magnesium (Mg ²⁺)	1.3	3.69	
Calcium (Ca ^{2*})	0.40	1.16	
Potassium (K*)	0.38	1.10	
Total	34.58%	99.28%	

2. Minor Constituents (in parts per million, ppm^a)

	3505	Nutrients		Others		
Constituent	Concentration (ppm)	Constituent	Concentration (ppm)	Constituent	Concentration (ppm)	
Carbon dioxide (CO	90	Silicon (Si)	3.0	Bromide (Br)	65.0	
Nitrogen (N ₂)	14	Nitrogen (N)	0.5	Carbon (C)	28.0	
Oxygen (O ₂)	6	Phosphorus (P)	0.07	Strontium (Sr)	8.0	
		Iron (Fe)	0.002			
	nts (in parts per billi Concentration (ppb)		Concentration (ppb)	Boron (B)	4.6 Concentration (ppb)	
Constituent	Concentration (ppb)	on, ppb ^b)	Concentration	1	Concentration	
	Concentration (ppb) 185 Z	on, ppb ^b) Constituent	Concentration (ppb)	Constituent	Concentration (ppb)	

CONSERVATIVE AND NON-CONSERVATIVE ELEMENTS

- **Conservative elements** are non-reactive. Thus, remain in ocean for long periods (long residence time). Examples: Na, K, S, Cl, Br, Sr, B (conservative major elements).
- Non conservative elements are biologically and/or chemically reactive. Examples: C, P, Fe.
- **Residence Time** is the average length of time something spends somewhere. It is also the length of time it takes to replace the amount in a reservoir.
- **Residence time** (in years) = $\frac{Amount of sodium in the ocean}{Amount of sodium being added}$

(or removed) to the ocean each year

- Residence time of some ions in the ocean:
 - Sodium-68 million yearsChloride-100 million yearsMagnesium-10 million yearsSulphate-10 million yearsPotassium-7 million yearsCalcium-1 million years
- Elements with longer residence time have longer time of ocean accumulation and are well mixed whereas those with short residence time has are quickly removed and do not concentrate and not well mixed.

Component	River Water	Seawater	تې ^ء (1000 yr)
CI-	230	558,000	87.000
Na*	315	479,000	55,000
Mg ⁺⁺	150	54,300	13,000
SO ₄	120	28,900	8700
Ca ⁺⁺	367	10,500	1000
K*	36	10,400	10,000
HEO3	870	2000	83
H4SIO4	170	100	21
NUS	10	20	72
Orthophosphate	0.7	1	50

Sources: Based on Tables 8.1 and 8.2 and data of Meybeck 1979, 1982 for world average river water.

 ${}^{a}\tau_{r} = ([SW]/(RW])\tau_{u}$ where τ_{u} = replacement (residence) time of H₂O = 36,000 yr; RW = river water; SW = seawater, and [] = concentration in µmoles per liter = µM.

NOTE:

If residence time < mixing time of the ocean: non-uniform concentration, not well mixed. If residence time > mixing time of the ocean: uniform concentration, well mixed. All major ions have residence times > 1 million years. Hence major ions are well mixed with respect to each other= Marcet's Principle.

PROCESS AFFECTING SEAWATER SALINITY

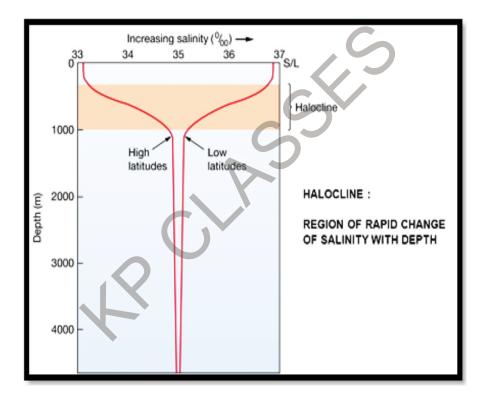
- It changes the amount of water (molecule) or dissolved substances within water.
- Salinity gets lowered by addition of water and further leads to dilution of dissolved components. Conversely, removal of water increases salinity.

The Table below shows the factors that affect the seawater salinity:

Process	How accomplished	Adds or removes	Effect on salt in seawater	Effect on H ₂ O in seawater	Salinity increase or decrease?	Source of freshwater from the sea?
Precipitation	Rain, sleet, hail, or snow falls directly on the ocean	Adds very fresh water	None	More H ₂ O	Decrease	N/A
Runoff	Streams carry water to the ocean	Adds mostly fresh water	Negligible addition of salt	More H ₂ O	Decrease	N/A
Icebergs melting	Glacial ice calves into the ocean and melts	Adds very fresh water	None	More H ₂ O	Decrease	Yes, icebergs from Antarctic have been towed to South America
Sea ice melting	Sea ice melts in the ocean	Adds mostly fresh water and some salt	Adds a small amount of salt	More H ₂ O	Decrease	Yes, sea ice can be melted and is better than drinking seawater
Sea ice forming	Seawater freezes in cold ocean areas	Removes mostly fresh water	30% of salts in seawater are retained in ice	Less H ₂ O	Increase	Yes, through multiple freez- ings, called freeze separation
Evaporation	Seawater evaporates in hot climates	Removes very pure water	None (essentially all salts are left behind)	Less H ₂ O	Increase	Yes, through evaporation of seawater and condensation of water vapor, called <i>distillation</i>

VARIATION OF SEAWATER SALINITY, TEMPERATURE, DENSITY WITH SURFACE AND DEPTH

- The major factors governing the vertical movement of ocean waters are the salinity and temperature of the seawater that together controls the density of seawater.
- Variation of surface salinity with latitude:
- Highest salinity values are recorded in 30°N and 30°S latitudes as evaporation exceeds precipitation in subtropical latitudes.
- Salinity is lower at the **equator** because of higher precipitation and in the **poles** due to less evaporation and melting of ice which adds freshwater to the ocean and hence decreases its salinity.
- Variation of salinity with depth:
- Halocline: It is the layer of rapidly changing salinity.
- Low latitudes: Salinity decreases with depth.
- High latitudes: Salinity increases with depth.
- Deep ocean salinity: Fairly remains constant globally.

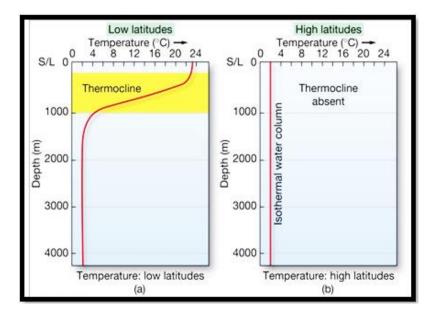


Variation of surface temperature with latitude:

• The highest temperatures occur over tropics and sub-tropics (high insolation). The lowest temperatures occur in polar and sub-polar regions.

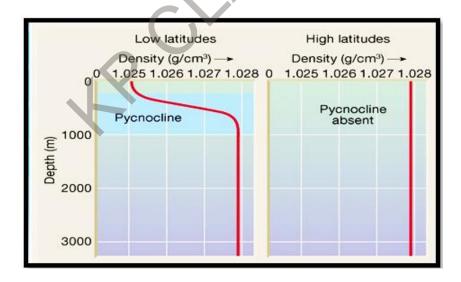
Variation of temperature with depth:

- The boundary region from where there is a rapid decrease of temperature is called the Thermocline. About, 90% of total water volume is found below thermocline in deep oceans. Temperature leads to 0°C.
- Photic or Euphotic Zone: Upper surface to ~200 m.
- Aphotic zone extends from 200 m to the ocean bottom.



Variation of Density with Depth

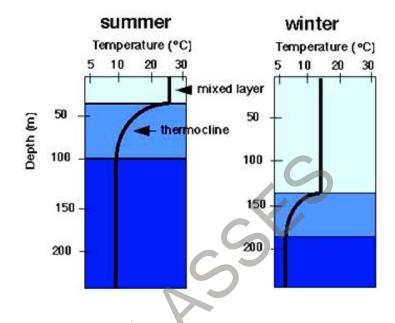
- Below surface, density remains constant until a depth of about **300 meters (980 feet)** due to good surface mixing.
- Density increases below 300 m up to a depth of about 1000 m (3300 feet).
- After exceeding a depth of **1000 m**, density remains constant again.
- Density is relatively high at the surface because surface water temperatures are low.
- Density is low because surface water temperatures are high. (Temperature has the greatest influence on density and temperature is inversely proportional to density).



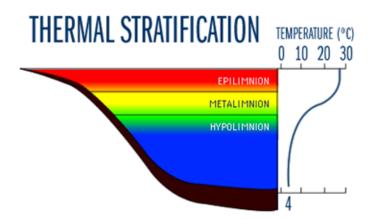
THREE LAYERED OCEAN STRUCTURE:

- **Mixed layer, main thermocline, and deep-water layer** are the three-layered structure of an ocean. Polar region shows no thermocline.
- **Mixed layer** exists at top of ocean model with fairly constant warm temperature.
- In mid-latitudes mixed layer extends from the surface to a maximum depth of about 450 meters.
- Mechanical and Convective Mixing processes give rise to Mix layer.

- **Mechanical mixing** caused by wave action, surface storms etc. The process is important in summer than winter because surface waters are much warmer and less dense than subsurface waters, thereby producing a stable water column.
- **Convective mixing** a temperature decrease of .01°C or a salinity increase of 0.01 ‰, is sufficient to initiate the convective mixing process.
- **Convective mixing** is most noticeable in the **Mediterranean and Red seas**, where evaporation far exceeds precipitation.



- **Main Thermocline** covers the central layer of ocean. Is marked by rapid decrease of water temperature with depth.
- **Seasonal Thermocline** develops in mid-latitudes as summer advances. In summer, the seasonal thermocline is deeper and covers a broader range of depth.
- The mixed layer deeper the seasonal thermocline as autumn advances.
- In **low latitudes**, small seasonal temperature changes make it difficult to distinguish between the seasonal and the permanent thermocline.
- **Deep Water Layer** is the bottom layer of ocean water and exist in the mid-latitudes below 1200 m. Constant cold temperatures <4°C.
- The vertical temperature profile is essentially **isothermal** (no change in temperature with depth).
- Lake Stratification: water is unique as it appears denser as a liquid than a solid, therefore ice floats.
- Water is most dense at 4°C (39°F), and as water warms or cools it gets less dense. It has implication for a lake structure as denser water is heavier and will be at the bottom of a lake while the less dense water is lighter and will generally be at the top of the lake.



- **During summer**, the top layer of lake **Epilimnion** is heated by sun rays to become less dense. The bottom layer of the lake, the **Hypolimnion**, does not receive sunlight and therefore remains cold.
- The **epilimnion** is less dense, it floats on top of the hypolimnion and the two do not mix. The thermocline is the dividing area between the top and bottom layers.
- Hypolimnion can become anoxic during the summer in a **mesotrophic** or **eutrophic** lake.
- **During Fall**, the Epilimnion cools off and becomes more dense sinks to the hypolimnion, mixing the layers. This mixing allows oxygen and nutrients to be distributed across the whole water column.
- In winter, hypolimnion is 4°C (39°F), is colder and less dense. The thin layer of water floats on top of the hypolimnion throughout the winter, but this stratification is not quite as stable as in the summer because the density difference is much smaller. This phenomenon is called inverse stratification because cooler water is sitting on top of warmer water.
- In spring, oxygen and nutrients gets well distributed throughout the water column as the water mixes. With warm weather, the water surface gets warmer and set up summer stratification.
- **Example:** Lakes in Minnesota are **dimictic** as mix twice a year during spring and fall. Shallow lakes behave differently and can mix more often.

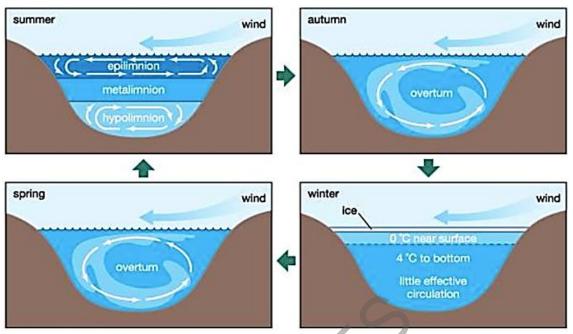


FIGURE: EPILIMNION, HYPOLINION POSITIONS IN DIFFERENT SEASONS

NET TIP:

- Questions from residence time are asked frequent, make sure to remember them.
- Differences between lake stratification and ocean stratification should be clear.
- Variation of density, salinity and temperature with latitude is important.

Practice Questions:

- 1. The relative abundance of elements, in decreasing order, in the Earth is:
 - a) Iron, oxygen, silicon, magnesium
 b) oxygen, silicon, aluminium, iron
 c) Iron, magnesium, silicon, oxygen
 d) oxygen, silicon, aluminium, magnesium
- 2. Which is correct order of abundance of H₂O?
 a) River > groundwater > atmosphere
 b) Groundwater > atmosphere > river
 c) Atmosphere > river > groundwater
 d) Groundwater > river > atmosphere
- 3. Which is the abundant anion in rain water? **[CSIR NET June 2017]** a) SO_4^{2-} b) Cl^- c) HCO_3^- d) CO_{3-}^{2-}
- 4. Identify the correct sequence of freshwater abundance on the Earth. (GP = Glaciers & Polar ice; A = Atmosphere; LR = Lakes & Rivers; UW = Underground Water)

a) $GP > A > LR > UW$	b) $UW > GP > A > LR$
c) $A > GP > UW > LR$	d) GP >UW > LR > A

5. If the relative residence times $\left(\tau_{erl} = \frac{\tau \ subs \tan ce}{\tau \ water}, \tau = residence \ time\right)$ of substances A, B, C in lake

are 0.85, 1.0 & 1.6, respectively. Identify the correct set for behaviors of A, B & C for a steady state lake (c-conservative, nc- non-conservative, a – accumulates in the lake, r- removed from the lake).

a) A – ncr, B – nca, C – c	b) A – ncr, B – c, C – nca
c) A – c, B – nca, C – ncr	d) A – nca, B – ncr, C – c

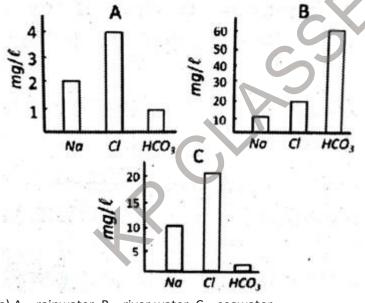
- 6. Which of the following elements have residence times closet to the oceanic stirring time?a) Cu, Ag, Gdb) Hg, Sn, Thc) Cd, Pb, Ced) U, Ga, Ti
- Several plankton precipitate calcium carbonate in the upper ocean. Which of the following is INCORRECT during the formation of CaCO₃?

a) Decrease in pH b) Increase in CO_2 c) Decrease in HCO_3^{2-} d) Decrease in CO_3^{2-}

- 8. Arrange the following ocean basins in the increasing order of surface salinity:
 - 1) Dead Sea
 2) Red Sea

 3) Mediterranean Sea
 4) Arabian Sea

 a) 4, 3, 2, 1
 b) 4, 2, 3, 1
 c) 4, 1, 2, 3
 d) 1, 2, 3, 4
- 9. The relative abundance of dissolved solid load components in A, B and C are given in figures below. Identify A, B and C from their chemistry.



a) A – rainwater, B – river water, C – seawater

- b) A river water, B rainwater, C seawater
- c) A seawater, B rainwater, C river water
- d) A rainwater, B seawater, C river water

10. Which one of the following orders of residence times of the elements in the seawater is correct?

a) Mg < Cl < Ca < Si	b) Cl < Mg < Ca < Si
c) Si < Ca < Mg < Cl	d) Ca < Cl < Mg <si< td=""></si<>

14. Since the beginning of the industrial era, the pH of ocean surface waters has decreased by 0.1 unit. This is ascribed to increase in H⁺ ion concentration by about:

a) 3%	b) 10%	c) 25%	d) 45%
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15. The major atmospheric constituents that are homogeneously distributed in the lower atmosphere are:

17. The order of molar abundance in sea water is in the sequence

a) Na+ > CI- > Mg2+ >
$$SO_4^2$$
 -
b) CI- > Mg2+ > Na+ > SO_4^2 -
c) CI- > Na+ > Mg2+ > SO_4^2 -
d) Na+ > CI- > SO_4^2 - > Mg2+

18. The residence time (τ) of the elements Mg, Ca, Sr and Ba in sea water is in the sequence:

- a) τMg > τCa > τSr > τBa b) τMg > τSr > τCa > τBa c) τCa > τBa > τSr > τMg
- d) $\tau Sr > \tau Mg > \tau Ba > \tau Ca$

19. The most non-co	onservative element in t	the sea is	
a) Lithium	b) Uranium	c) Fluorine	d) Thorium

20. Which of the following elements has the least residence time in sea water?a) Copperb) Molybdenumc) Manganesed) Iron

ANSWERS:

1A, 2B, 3C, 4B, 5D, 6A, 7B, 8C, 9C, 10C, 11A, 12A, 13C, 14C, 15D, 16C, 17C, 18B, 19D, 20D.

Previous Year Questions:

21. Which form of energy molecule is reduced during ice formation of sea water? [CSIR NET June 2019]

a) Chemical energy	b) Hydration energy
c) Kinetic energy	d) Potential energy

22. Select the following elements in the order from higher to lower residence time in the seawater.

a) Sr-Mg-B-Cl	b) Sr-B-K-Cl	[CSIR NET June 2019]
c) Mg-Ba-Ga-Al	d) Na-Cl-Mg-Ca	

23. Concentration of metal ions in seawater is mainly regulated by
a) Remineralization
c) Desorption[CSIR NET June 2019]
b) Biological Uptake
d) Adsorption and Scavenging

24. Under anoxic conditions manganese is expected in water in the form of: [CSIR NET June 2019]

a) Mn 2+ b) Mn 3+

c) Mn 4+ d) Mn 6+ 25. Enrichment of dissolved substances in sea surface microlayer is primarily caused by b) biological productivity. [CSIR NET June 2019] a) aerosol deposition c) bubble transport and bursting d) evaporation 26. Which of the following is a semi-conservative element in seawater? [CSIR NET Dec 2019] a) Ca b) Cl c) Fe d) CO2 27. Which of the following is NOT a major ingredient of photochemical smog? [CSIR NET Dec 2019] b) Hydrocarbons a) NO_x c) SO_x d) Carbon monoxide 28. Which ions are the most abundant in rainwater, river water and seawater respectively? [CSIR NET Dec 2019] b) Cl⁻, HCO3⁻, Cl⁻ a) Na⁺, Cl⁻, Na⁺ c) Cl⁻, Na⁺, Cl⁻ d) Na^{+,} Ca²⁺, Na⁺ 29. Rise in atmospheric CO₂ will NOT lead to [CSIR NET Dec 2019] a) ocean acidification b) ocean warming d) decrease in efficiency of biological pump c) decrease in [CO3²⁻] in ocean 30. The total amount of an element dissolved in the ocean is 10⁷ kg and its removal rate from seawater is 10⁵ g/y. Under steady-state condition, the residence time of the element is [CSIR NET Dec 2019] b) 10⁵ years a) 10¹⁵ years d) 10^{0.5} years c) 10² years 31. Which one of the following gas has the highest solubility in water? [CSIR NET Dec 2019] a) Nitrous oxide b) Oxygen c) Nitrogen d) Carbon dioxide 32. Name the pair of master variables in natural waters [CSIR NET Dec 2019] a) Oxygen and redox potential b) Ph and redox potential d) Temperature and salinity c) Oxygen and temperature 33. Match columns I and II

	I		II
А	Oxygen isotopes	E	Dietary information
В	Phosphorous fractions	F	Climatic conditions in river catchment
С	Carbon isotopes	G	Paleotemperature in ocean
D	Chemical Index of alteration	Н	Palaeoproductivity in oligotrophic

a) A-E, B-F, C-G, D-H c) A-G, B-H, C-E, D-F b) A-F, B-G, C-H, D-E d) A-H, B-E, C-F, D-G

[CSIR NET Dec 2019]

34. Seawater having salinity of 35 psu was subjected to icing in steps as shown below Seawater

A _____ B ____ C 1litre 900 ml 750 ml (lig) (lig) (lig)

Which is the correct sequence of salinity of A, B and C?

a) A > B > C	b) A < B < C
c) A > C > B	d) A < B > C

35. Which one of the following statements is INCORRECT?

[CSIR NET Dec 2019]

[CSIR NET Dec 2019]

a) Water vapour has more global warming potential than CO2

b) Volatile organic compounds are not responsible for ozone production in troposphere

c) N₂O has more global warming potential than CO₂

d) NO_x and N_2O are potential source of nitrogenous species in troposphere and stratosphere, respectively?

36. Pick out the wrong statement: In the Ocean,

[CSIR NET June 2018]

- a) major elements are conservative
- b) a few minor elements are non-conservative

c) non-conservative elements have short residence time

d) all non-conservative elements are bioactive

37. For water mass identification, which of the two parameters are essential? [CSIR NET June 2018]

a) in situ temperature

b) in situ salinity

- c) potential temperature
- d) potential density

i) a and b

iii) b and c

- ii) a and d iv) c and d
- 38. The maximum amount of latent heat is released in a rising saturated parcel of air when it is and at a altitude. [CSIR NET Dec 2018]
 - a) cold, high c) cold, low
 - b) warm high d) warm, low

39. Which of the following has the least residence time in seawater? [CSIR NET Dec 2018]

- a) Uranium b) Molybdenum
- c) Rhenium d) Thorium

40. The conductivities of porous sandstone saturated with rainwater, brackish water, seawater and
brine are σ_{Rw} , σ_{Bw} , σ_{Sw} & σ_{B} respectively, then:[CSIR NET June 2017]

a) o _{Rw} >o _{Bw} >o _{Sw} >o _B	D) σ _B >σ _{Sw} >σ _{Bw} >σ _{Rw}
c) σ _{Sw} <σ _B <σ _{Bw} <σ _{Rw}	d) σ _B <σ _{Sw} <σ _{Rw} <σ _{Bw}

41. Which one of the following represents the correct ascending order of residence times of elements in the ocean? [CSIR NET June 2017]

a) Cl > Na > Mg > Fe	b) Na > Cl > Fe > Mg
c) Cl > Na > Fe > Mg	d) Cl > Mg > Na > Fe

42. Which is the abundant anion in rain water? [CSIR NET June 2017] a) $SO_4^{2^-}$ b) Cl^- c) HCO_3^-

d) CO^{2-}_{3}

43. The deepest mixed layer is found at the [CSIR NET Dec 2016]

- a) Equator b) Northern North Atlantic
- c) Subtropical gyres d) Northern Indian Ocean

R

Answers: 21C, 22C, 23D, 24A, 25C, 26A, 27C, 28B, 29D, 30B, 31D, 32B, 33C, 34B, 35B, 36D, 37iii, 38D, 39D, 40A, 41B, 42B, 43B

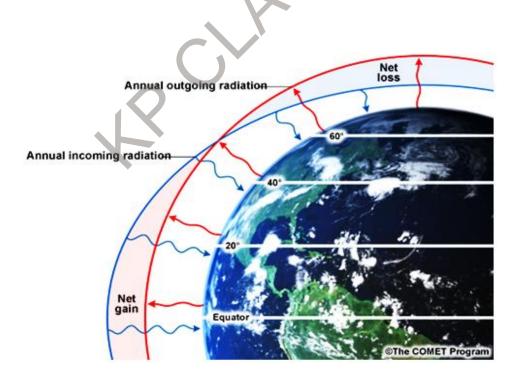
Weightage of the chapter based on competitive exams:

NET Year	Weightage (Marks)
December 2016	2
June 2017	6
June 2018	4
December 2018	4
June 2019	10
December 2019	20
Average	8
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CHAPTER-2 AIR-SEA INTERACTION

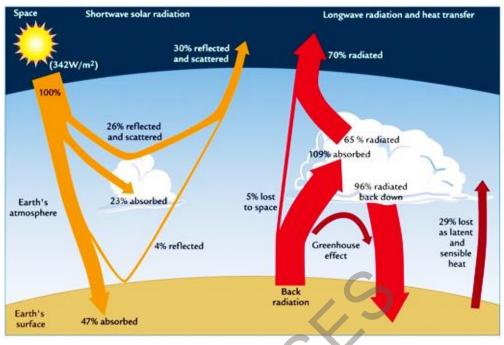
DISTRIBUTION OF TEMPERATURE ON EARTH

- The distribution of differential heat of sun in different regions of the earth is the cause of all climatic features like wind systems, pressure systems, precipitation.
- **Insolation** is the intercepted radiation where the earth intercepts only one in two billion parts of solar radiation.
- During day, earth absorbs **short wave radiation** and reflects back heat as **long wave radiation** (IR) at night.
- Latitudinal Heat Balance: Regions within the equator and 40° N and S latitudes receive abundant sunlight and hence more heat will be gained than lost. Hence, they are energy surplus regions.
- Regions beyond 40° N and S latitudes lose more heat than that gained from sunlight. Hence, they are energy deficit regions (This is because of slant sunlight and high albedo of Polar Regions).
- The atmosphere (planetary winds) and the oceans (ocean currents) transfer excess heat from the tropics (energy surplus region) towards the poles (energy deficit regions) making up for heat loss at higher latitudes. And most of the heat transfer takes place across the midlatitudes (30° to 50°).



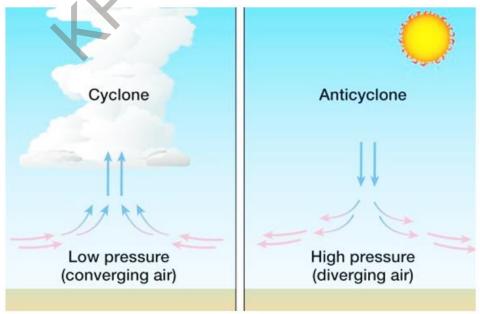
• **Heat Budget:** Earth maintains a constant temperature by receiving a certain amount of insolation (short waves) and giving back heat into space by terrestrial radiation (long wave radiation).

• Earth receives heat from solar radiation by three mechanisms: Radiation, Conduction and Convection.



Pressure Systems:

- Variation in atmospheric pressure results by air expansion (heated) and compression(cooled). Vertical Variation of Pressure:
- Atmospheric pressure decreases at a rate of **34 millibars** every **300 m** of height on average.
- Surface air is denser, with high pressure due to gravity.
- Air pressure is proportional to density, temperature and its variation affects the air pressure.
- A high pressure indicates fine, settled weather, while a low pressure indicates unstable and cloudy weather.



Horizontal Distribution of Pressure: