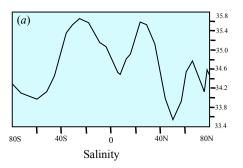
Module 7 Adiabatic Effects in the Ocean

7.1 Introduction

The density of ocean waters is determined mainly by temperature and salinity because pressure effects on density are sensibly negligible. The large scale circulation of ocean is slow and the water parcels which have origin in deep dense waters find their way to the surface of ocean through the path of thermohaline circulation. Cold and dense water primarily reside in the high latitudes and lighter waters in the low latitudes. The variations of density also arise from depth wise lateral changes in temperature and salinity as evident from the equation of state. The surface waters move poleward losing heat during their journey but their salinity increases due to excess evaporation over precipitation. However, rainfall over the ocean decreases salinity of ocean waters and as shown in Fig. 7.1, the salinity variations of seawaters can be directly explained in terms of the difference evaporation minus precipitation (E - P). The regions where evaporation exceeds precipitation, high salinity is obvious. That is why salinity peaks in mid latitudes (Fig. 7.1a) where evaporation exceeds precipitation (Fig. 7.1b), but in the equatorial region low salinity waters are present because seawater constantly mixes with rainwater from deep convective clouds in the intertropical convergence zone (ITCZ). Even in the open sea, the surface freshwater and deeper cool high salinity waters would mix only when sufficiently strong winds force upwelling in such regions. Thus, ocean is in a state of mixing primarily due to surface wind forcing and several processes; as a result, lapse rate in the ocean is constantly altered.



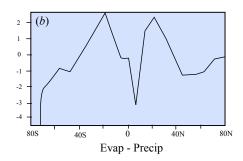


Fig. 7.1 Salinity relation to evaporation minus precipitation. (a) Zonally averaged salinity profile; (b) Zonally averaged curve of difference of evaporation and precipitation.

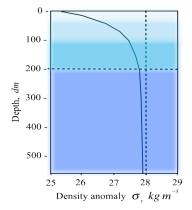


Fig. 7.2 The density profile and water types in the upper oceanic layer.

- (i) Lighter waters occupy the top 50 m of the ocean depth. Density rise with depth is steepest in this layer.
- (ii) The rise in density is relatively slow with depth up to 200 m.
- (iii) Below 200 m there is a very slow rise in density with depth.

The density profile demonstrates that the top layer of 200 m profounder is very active; it interacts and responds to changes in the overlaying atmosphere

We have presented in Fig 7.2, the density profile of ocean waters with depth which shows that seawater density rapidly increases in the top 50 m layer of the ocean. The steeper increase in density is noted from Fig. 7.2 up to a depth of 100 m.

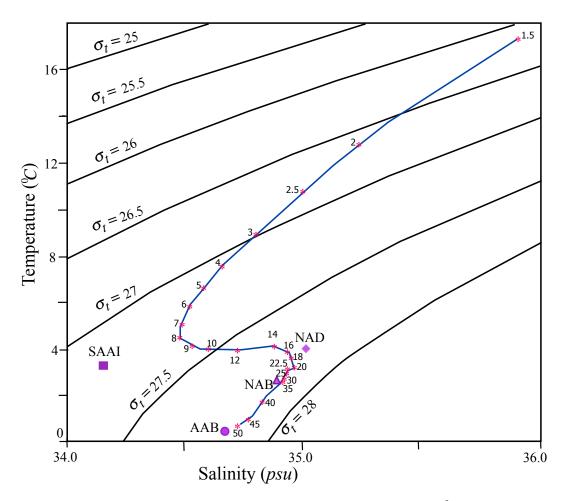


Fig. 7.3 T-S diagram for Atlantic Ocean observation from 150 m to 5000 m at $9^{\circ}S$. Density increase from 150 m to 200 m is steepest. Two inflexion points in the density profile; first at 800 m where seawaters are at $4^{\circ}C$ and second at 2000 m. The rise in density of Atlantic waters from 800 m to 1400 m is due to salinity increase and then due to the combined effect of temperature and salinity up to 2000 m. In the lowest layer from 2000 m to 5000 m the density of Atlantic waters is practically invariant. (To get the depth in meters, multiply the depth indicator number by 100; e.g. the point marked 3 is at $3 \times 100 = 300$ m depth). SAAI: SubAntArctic Intermediate waters; NAD: North Atlantic Deep waters; NAB: North Atlantic Bottom waters; AAB: AntArctic Bottom waters

Fig. 7.3 presents a density profile on the salinity-temperature diagram obtained by plotting the observations at different depths in the Atlantic Ocean at 9^{0} S starting from 150 m to 5000 m. On the salinity-temperature diagram, it is easier to interpret the types of Atlantic waters that occupy the body of the ocean depths. It means that the density profile is very instructive in understanding even the ocean circulation as the Atlantic Ocean spans from North Pole to South Pole. The waters moving along the ocean bottom reach from North Atlantic Ocean to Antarctica in several centuries (~ 2000 years). This kind of

movement of water masses is associated with the thermohaline circulation that has been explained by Stommel and Aorons (1961). Now, let us analyse the density profile in the southern tropical Atlantic Ocean. The σ_t profile in Fig. 7.3 shows that at 150 m, warm high salinity waters are present, and the salinity constantly decreases with depth. The stratification in which higher density waters are arranged in deeper layer is mainly the result of colder temperatures. At a depth of 800 m, the ocean temperatures are at $4^{\circ}C$ (freshwater has maximum density at this temperature) and the density increases with depth as a result of salinity rise from 34.5 psu at 800 m to 34.9 psu at 1.6 km. Then density of deeper waters from 1.4 km to 2.0 km increases due to colder temperatures and slight increase in salinity.

However, most spectacular observation is the existence of two inflexion points in the σ_t profile in Fig. 7.3. The density of seawater rises with the simultaneous fall of temperature and salinity and the first inflexion point occurs at 800 m as further rise in the density happens only due to rise in salinity from 34.5 psu and temperature remains practically constant at about $4^{\circ}C$. The second inflexion point occurs at 2000 m because in the deep ocean density remains almost constant though both temperature and salinity decrease up to a depth of 5000 m. Note that in fresh water, density is maximum at $4^{\circ}C$ and it decrease if temperature further lowers with all the water freezing at $0^{\circ}C$. This means that there is only one inflexion point in the density of fresh water. Naturally, for the ice to form on the top of the sea surface there should be constant brine rejection from the freezing waters. The rejected brine adds to the lower level waters increasing the *in situ* density in the column.

7.2 Adiabatic lapse rate

What causes lapse rate in the sea? The adiabatic lapse rate is generally said to be proportional to the work done on a fluid parcel as its volume changes due to a pressure change (increase/ decrease). According to this definition, the adiabatic lapse rate Γ in the ocean would increase both with pressure and the fluid compressibility, but this is not the case. Indeed, Γ is proportional to thermal expansion coefficient and is independent of the compressibility of seawater. The adiabatic lapse rate Γ for seawater is defined as the rate at which *in situ* temperature (T) changes with pressure (p) while salinity (S) and entropy (η) are held constant, that is

$$\Gamma = \left(\frac{\partial T}{\partial p}\right)_{nS} \tag{7.1}$$

From the "fundamental thermodynamic relation (or Gibb's relation)" given by eqn. (6.45), we have the enthalpy change per unit mass,

$$dh = T d\eta + \alpha dp + \mu dS \tag{7.2}$$

which takes the form

$$dh = C_p dT + \left(\frac{\partial h}{\partial p}\right)_{TS} dp + \left(\frac{\partial h}{\partial S}\right)_{Tp} dS \tag{7.3}$$

Note that in writing eqn. (7.3), it has been assumed that

$$h = h(T, p, S)$$

Hence, specific heat at constant pressure,

$$C_p = \left(\frac{\partial h}{\partial T}\right)_{pS} \tag{7.4}$$

Also, from equation (7.2), we have

$$T = \left(\frac{\partial h}{\partial \eta}\right)_{pS} , \quad \alpha = \left(\frac{\partial h}{\partial p}\right)_{pS}, \quad \mu = \left(\frac{\partial h}{\partial S}\right)_{p\eta}$$
 (7.5)

which on differentiation gives

$$\Gamma = \frac{\partial T}{\partial p} = \frac{\partial}{\partial p} \left[\frac{\partial h}{\partial \eta} \Big|_{pS} \right] = \frac{\partial^2 h}{\partial p \partial \eta} = \frac{\partial^2 h}{\partial \eta \partial p} = \frac{\partial}{\partial \eta} \left(\frac{\partial h}{\partial p} \right)_{\eta S} = \left(\frac{\partial \alpha}{\partial \eta} \right)_{pS} \quad \text{since } \left(\frac{\partial h}{\partial p} \right)_{\eta S} = \alpha .$$

$$\Gamma = \left(\frac{\partial \alpha}{\partial \eta}\right)_{ps} = \frac{\left[\frac{\partial \alpha}{\partial \tau}\right]_{ps}}{\left[\frac{\partial \eta}{\partial \tau}\right]_{ps}} \tag{7.6}$$

In (7.6), the expressions for $\left(\frac{\partial \alpha}{\partial T}\right)_{pS}$ and $\left(\frac{\partial \eta}{\partial T}\right)_{pS}$ are to be obtained from the eqn. (7.3),

which involve some algebra.

Now
$$C_p = \left(\frac{\partial h}{\partial T}\right)_{pS} \Rightarrow C_p = \left(\frac{\partial h}{\partial \eta}\right)_{pS} \left(\frac{\partial \eta}{\partial T}\right)_{pS}$$
 (7.7)

$$C_p = T \left(\frac{\partial \eta}{\partial T} \right)_{pS} \qquad \Rightarrow \qquad \left(\frac{\partial \eta}{\partial T} \right)_{pS} = \frac{C_p}{T}$$
 (7.8)

Hence, the expression for Γ given by (7.6) becomes

$$\Gamma = \frac{T}{C_n} \left(\frac{\partial \alpha}{\partial T} \right)_{pS} \tag{7.9}$$

It immediately follows from equation (7.9) that the lapse rate Γ in the ocean depends not only on the temperature but also on the changes in specific volume α of ocean waters

with temperature. Now, it remains to find out the expression for $\left(\frac{\partial \alpha}{\partial T}\right)_{pS}$ in calculating

the lapse rate Γ ; the rest of the analysis is devoted to this derivation. To begin with salinity and pressure remaining constant, the change of specific volume with respect to temperature is given by

$$\frac{\partial \alpha}{\partial T} = \frac{\partial}{\partial T} \left(\frac{1}{\rho} \right) = -\frac{1}{\rho^2} \frac{\partial \rho}{\partial T} = -\frac{1}{\rho} \left(\frac{1}{\rho} \frac{\partial \rho}{\partial T} \right)_{pS} \tag{7.10}$$

From the equation of state in the differential form, $\frac{1}{\rho}d\rho = \gamma_T dp - \alpha_T dT + \beta dS$, and the thermal expression coefficient α_T

$$\alpha_T = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{pS},\tag{7.11}$$

the expression (7.10) in the light of (7.11) becomes

$$\frac{\partial \alpha}{\partial T} = \frac{\alpha_T}{\rho} \tag{7.12}$$

Therefore, the adiabatic lapse rate Γ can be written from (7.9) using (7.12) as

$$\Gamma = \frac{T\alpha_T}{\rho C_p}$$
 (T in Kelvin) (7.13)

Equation (7.13) is the standard expression for the adiabatic lapse rate $\Gamma = \left(\frac{\partial T}{\partial p}\right)_{pS}$ in the

ocean. The first determination of adiabatic lapse rate Γ , was done by Thompson (1857), who correctly showed the negative nature of Γ in cool fresh waters. The most modern measurements of Γ , made by Rogener and Soll [1980] and Caldwell and Eide [1980: Deep-sea Research 27A, 71-78], have confirmed that Γ is negative in cool fresh waters. A most recent account of Γ has been given by McDougall and Feistel (2003; Deep-Sea Research pt I, Vol 50, 1523-1535); it is a very informative paper which has been referred for preparing the material presented here.

7.3 Potential temperature

The potential temperature with respect to a given reference pressure p_r , is defined as

$$\theta = T + \int_{p}^{p_r} \Gamma(p', \theta[p, T, S; p'], S) dp'$$
(7.14)

Here $\theta = \theta [p, T, S; p_r]$ is the potential temperature and $\Gamma = \Gamma (p, T, S)$ is the lapse rate.

The recent technique of evaluating θ is to solve the equality

$$\eta(p_r, \theta, S) = \eta(p, T, S) \tag{7.15}$$

Substitute for Γ in (7.14) using the expression for Γ from eqn. (7.13); and we obtain

$$\theta = T + \int_{p}^{p_r} \frac{T}{\rho} \frac{\alpha_T}{C_p} dp'$$
 and using the hydrostatic equilibrium $dp' = g\rho dz'$, we can write

$$\theta = T + \int_{z}^{0} \frac{T}{\rho} \cdot \frac{\alpha_{T}}{C_{p}} \cdot g\rho \, dz' \tag{7.16}$$

Limits of integration are set accordingly; that is, z' = z at p' = p; and z' = 0 at $p' = p_r$. By changing the sense of integration from θ to z, the eq. (7.16) can be written as

$$\theta = T - \int_{0}^{z} \frac{T \cdot \alpha_{T}}{C_{p}} g \, dz' \tag{7.17}$$

The potential temperature θ of a layer of thickness δz in the sea may be written as

$$\theta = T - \delta T \quad ; \qquad \delta T = \int_{0}^{\delta z} \frac{T \cdot \alpha_{T}}{C_{p}} g \, dz' = \frac{T \cdot \alpha_{T}}{C_{p}} g \, \delta z \tag{7.18}$$

This derivation is due to Kelvin (1857). In the deep ocean, the potential temperature θ is less than the *in situ* temperature T by amount δT , which is mainly determined by the expansion coefficient α_T . Moreover, α_T can vary over a wider range and could even become negative for cool fresh water near freezing temperature. That is why lapse rate Γ is generally negative in the deep ocean. The correction δT obtained by Thomson (1857)

is indeed a very remarkable finding for deep ocean waters (JJ Thompson later became Lord Kelvin). A notable point from the expression for Γ in (7.13) is that it varies linearly with α_T and T. Consequently if two parcels at same salinity but different temperatures are brought down adiabatically to deeper levels, the warm water parcel will warm up more than the cold water parcel. Such an increase in temperature is due to compression; as a consequence, the temperature of adiabatically moving parcels is not conserved.

This can be further illustrated with an example: Consider a water parcel moving downwards in the ocean to deeper layers from surface at a level where pressure is 500 bar (i.e. about to a depth of 5000 m). Thus $\delta p = 500 \times 10^5 Pa$; if the initial temperature of the water parcel is $T = 288 \ K$, then adiabatically moving parcel will have a change in temperature by δT given by

$$\delta T = \left(\frac{\partial T}{\partial p}\right)_{\eta S} \delta p = \Gamma \delta p = \frac{T \alpha_T}{\rho C_p} \delta p$$
$$= \frac{T \cdot \alpha_T}{C_p} g \delta Z = \frac{288 \times 2.2 \times 10^{-4}}{4200} \times 9.81 \times 5000 = 0.74 K$$

In above calculations, $\alpha_T = 2.2 \times 10^{-4} \, K^{-1}$ and $C_p = 4200 \, J \, kg^{-1} \, K^{-1}$. It is very informative to know that Γ can also be estimated from $\frac{\delta T}{\delta p} = \frac{0.74(K)}{5000(db)} = 0.148 \, K \, / \, (1000 \, db)$. It shows

that essentially Γ is very different from actual vertical gradients of temperature in the ocean. The principal reason for such a large difference is that large scale overturning in the ocean is not allowed; this means, water masses from deep levels at a location do not reach to the surface through direct vertical movements (so common in the atmosphere). Instead, the water masses are formed in cold high latitudes, sink to deeper layer in the ocean along isopycnal surfaces associated with significant lateral movements. The outcropping of isopycnal surfaces in higher latitudes therefore plays a key role in the lateral movement of water masses from higher latitudes back to middle and low latitudes at deeper levels in the ocean. As a result of this lateral movement, large vertical gradients of temperature develop that are indeed observed in low and middle latitude ocean waters. This also explains the low salinity waters at deeper layers in the ocean. From this discussion it is evident that θ as a conserved quantity takes care of the adiabatic changes during vertical movements of water masses. It therefore assumes immense importance because it allows tagging of parcels during their movement.

7.4 Potential density

The adiabatic lapse rate Γ has been used to define the potential temperature θ in equation (7.14); it can also be used to define the potential density in the ocean. It has been averred earlier that the seawater is almost incompressible but in deeper levels pressures are so high that density changes need to be taken in to account. And thus arises the concept of potential density which is be defined as the density a seawater parcel would attain if it were lifted adiabatically from a pressure level p to a reference pressure p_r at z = 0 (i.e. surface of the ocean). Thus, the potential density is defined as

$$\rho_{\theta} = \rho(p_r, \theta, S) \quad (kg/m^3) \tag{7.19}$$

The potential temperature is calculated using the expression given in (7.18).

7.5 Static Stability of Seawater

Under equilibrium conditions, density ρ is a function of depth z alone and a column of seawater can be at rest. But, does this equilibrium stable? Considering the exchange of two water parcels at different levels, the stability of the ocean at rest can be tested. If the displaced parcel finds itself heavier than its surroundings, it will sink back to its original level implying a stable ocean column. Both "adiabatic" and "isentropic" are the words that are used to refer to a process in which "heat content is not changed". Thus, "adiabatic" means "no exchange of heat with surroundings"; whereas "isentropic" means "no change of entropy". From the expression of adiabatic lapse rate Γ given in (7.13), the temperature change dT is related to the pressure change dp by the formula

$$dT = \Gamma dp = \frac{T\alpha_T}{\rho C_p} dp = \frac{\alpha T\alpha_T}{C_p} dp \tag{7.20}$$

Using the hydrostatic equation (7.20) can be written as

$$dT = \frac{T\alpha_T}{\rho C_p} (-g\rho dz) \implies dT = -\frac{gT\alpha_T}{C_p} dz = -\Gamma_a dz$$
 (7.21)

where Γ_a is the adiabatic lapse rate with depth in the ocean.

The parameter Γ_a can be expressed as

$$\Gamma_a = \frac{gT \alpha_T}{C_p} = \frac{T}{H_T} \; ; \quad H_T = \frac{C_p}{\alpha_T g}$$
 (7.22)

The changes in C_p due to salinity changes in the ocean are relatively small (~8% only). Further, for every 10 meter depth, pressure changes by I bar (I0 decibar); hence pressures in the ocean column are generally expressed in decibar which coincide with ocean depths in meters. The changes in α_T (being in the denominator) has larger impact on Γ_a in deeper levels because α_T varies with depth. The temperature scale height $H_T \sim 2000 \ km$ gives a value of Γ_a equal to $0.07 \ K \ km^{-1}$, when the ocean is at rest. Though H_T depends both on C_p and α_T , the value of Γ_a largely depends upon α_T (being in the denominator) which varies with depth. It is worthwhile to remark here that for gases the product $T\alpha_T$ in (7.22) is equal to unity and relation becomes $\Gamma_a = g/C_p$.

Specific Heat C_p : The calculation of adiabatic lapse rate Γ_a requires an accurate evaluation of C_p in eqn. (7.22). The specific heat at the surface of the ocean (where reference pressure is zero) is first calculated for freshwater as

$$C_{p}(0,T,0) = 4217.4 - 3.720283 T + 0.1412855 T^{2} - 2.654387 \times 10^{-3} T^{3} + 2.093236 \times 10^{-5} T^{4} \left[J \ kg^{-1} K^{-1} \right].$$
(7.23)

The specific heat for seawater $C_p(0,T,S)$ at the ocean surface is then calculated as

$$C_{p}(0,T,S) = C_{p}(0,T,0) + S \left[-7.6444 + 0.107276 \ T - 1.3839 \times 10^{-3} T^{2}\right] + S^{3/2} \left[0.17709 - 4.0772 \times 10^{-3} T + 5.3539 \times 10^{-5} T^{2}\right]$$
(7.24)

This formula can be checked against the result $C_p(0,40,40) = 3981.050$. The standard deviation is 0.074 for the algorithm fit (7.24). Finally the values of $C_p(p,T,S)$ are

obtained by integrating the expression of $\left(\frac{\partial C_p}{\partial p}\right)_T$ which one can derive from the thermodynamic relations as shown below.

Expression for $\left(\frac{\partial C_p}{\partial p}\right)_T$: For simplicity the seawater of uniform salinity is assumed so

that dS = 0 in the equation of state of seawater. Neglecting the effect of evaporation (dn = 0), the expression for internal energy change, de from Gibbs relation (6.41) reads

$$de = Td\eta - p \ d\alpha$$
 or $Td\eta = de + p \ d\alpha$ (7.25)

From (7.25) we can write

$$T\left(\frac{\partial \eta}{\partial T}\right)_{p} = \left(\frac{\partial e}{\partial T}\right)_{p} + p\left(\frac{\partial \alpha}{\partial T}\right)_{p} \qquad \text{(Pressure constant)}$$
 (7.26)

$$T\left(\frac{\partial \eta}{\partial p}\right)_{T} = \left(\frac{\partial e}{\partial p}\right)_{T} + p\left(\frac{\partial \alpha}{\partial p}\right)_{T}$$
 (Temperature constant) (7.27)

Differentiating (7.26) with respect to p, we get

$$T\left(\frac{\partial^{2} \eta}{\partial p \partial T}\right)_{p} = \left(\frac{\partial^{2} e}{\partial p \partial T}\right)_{p} + \left(\frac{\partial \alpha}{\partial T}\right)_{p} + p\left(\frac{\partial^{2} \alpha}{\partial p \partial T}\right)_{p}$$
(7.28)

Differentiating (7.27) with respect to T, we get

$$T\left(\frac{\partial^2 \eta}{\partial T \partial p}\right)_T + \left(\frac{\partial \eta}{\partial p}\right)_T = \left(\frac{\partial^2 e}{\partial T \partial p}\right)_T + p\left(\frac{\partial^2 \alpha}{\partial T \partial p}\right)_T$$
(7.29)

At a point (T, p) on thermodynamic diagram, cross-derivatives of a thermodynamical

variable are equal; this implies that
$$\left(\frac{\partial^2 \eta}{\partial T \partial p}\right)_T = \left(\frac{\partial^2 \eta}{\partial p \partial T}\right)_p$$
 and $\left(\frac{\partial^2 e}{\partial p \partial T}\right)_p = \left(\frac{\partial^2 \alpha}{\partial T \partial p}\right)_T$.

Subtracting (7.28) from (7.29) and using the equality of cross-derivatives at a point (T,p) on the thermodynamic diagram, one obtains the so-called Maxwell's relation,

$$\left(\frac{\partial \eta}{\partial p}\right)_T = -\left(\frac{\partial \alpha}{\partial T}\right)_p \quad . \tag{7.30}$$

Maxwell's equations can be derived easily from the thermodynamic equation given in (6.41) without considering the evaporation term; thus, it reads

$$de = Td\eta - p \ d\alpha + \mu dS \tag{7.31}$$

From calculus, one writes the total differential de as

$$de = \left(\frac{\partial e}{\partial \eta}\right)_{\alpha S} d\eta + \left(\frac{\partial e}{\partial \alpha}\right)_{\eta S} d\alpha + \left(\frac{\partial e}{\partial S}\right)_{\eta \alpha} dS \tag{7.32}$$

Comparing (7.31) and (7.32), one obtains

$$T = \left(\frac{\partial e}{\partial \eta}\right)_{\alpha S}; \quad p = -\left(\frac{\partial e}{\partial \alpha}\right)_{\eta S}; \quad \mu = \left(\frac{\partial e}{\partial S}\right)_{\eta \alpha} \tag{7.33}$$

Because the right-hand side of (7.31) is an exact differential, we have

$$\frac{\partial^2 e}{\partial \eta \partial \alpha} = \frac{\partial^2 e}{\partial \alpha \partial \eta} \tag{7.34}$$

Thus the First Maxwell Equation can be obtained from (7.33) and (7.34) as

$$-\left(\frac{\partial p}{\partial \eta}\right)_{\alpha} = \left(\frac{\partial T}{\partial \alpha}\right)_{\eta} \tag{7.35}$$

The specific heat for seawater C_p has been defined in eq. (7.8), which can be used to obtain the derivative of C_p with the pressure as follows,

$$C_{p} = T \left(\frac{\partial \eta}{\partial T} \right)_{p} \implies \left(\frac{\partial C_{p}}{\partial p} \right)_{T} = \left\{ \frac{\partial}{\partial p} \left[T \left(\frac{\partial \eta}{\partial T} \right)_{p} \right] \right\}_{T}$$
 (7.36)

This gives $\left(\frac{\partial C_p}{\partial p}\right)_T = \left\{T \frac{\partial}{\partial T} \left[\left(\frac{\partial \eta}{\partial p}\right)_T\right]\right\}_T$ on interchanging the orientation of the

differentiation with respect to p and T; and now substitute for $\left(\frac{\partial \eta}{\partial p}\right)_T$ from (7.30) we get,

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 \alpha}{\partial T^2}\right)_p \tag{7.37}$$

Equation (7.37) permits us to obtain values of C_p at higher pressures while temperature remains constant, from its initial value $C_p(0,T,S)$ that is calculated from relation (7.24). For the computation of C_p at higher pressures in the ocean, it is required to write Taylor expansion for $C_p(\delta p,T,S)$ as follows,

$$C_{p}(\delta p, T, S) = C_{p}(0, T, S) + \left(\frac{\partial C_{p}}{\partial p}\right)_{T} \delta p.$$
(7.38)

The second term on the right hand side of (7.38) involves second derivatives of α , that is $\frac{\partial^2 \alpha}{\partial T^2}$; and it can be evaluated by putting δp for p in eq. (6.5), which gives

$$\alpha(\delta p, T, S) = \alpha(0, T, S) \left[1 - \frac{\delta p}{K_T(\delta p, T, S)} \right]. \tag{7.39}$$

On obtaining $\left(\frac{\partial^2 \alpha}{\partial T^2}\right)$ from eqn. (7.39) keeping δp fixed and S constant, C_p at a depth (at pressure δp), is obtained from eqn. (7.38). The value of $C_p(\delta p, T, S)$ gives the adiabatic lapse rate Γ_a . The calculation of second derivative of α is given in what follows.

Expression for α : Since $\alpha(\delta p, T, S)$ is a product of two functions, we can apply the differentiation of product of functions using the Leibniz rule in the following manner

$$\frac{\partial^2}{\partial T^2} \left\{ f(T) g(T) \right\} = f''(T) g(T) + 2f'(T) g'(T) + f(T) g''(T) .$$

We obtain the following expression for $\frac{\partial^2 \alpha}{\partial T^2}$,

$$\frac{\partial^{2} \alpha}{\partial T^{2}} = \frac{\partial^{2} \alpha(0, T, S)}{\partial T^{2}} \left[1 - \frac{\delta p}{K_{T}(\delta p, T, S)} \right] + 2 \frac{\partial \alpha(0, T, S)}{\partial T} \cdot \frac{\delta p}{K_{T}^{2}(\delta p, T, S)} \frac{\partial K_{T}(\delta p, T, S)}{\partial T} + \alpha(0, T, S) \left[\frac{1}{K_{T}^{2}(\delta p, T, S)} \frac{\partial^{2} K_{T}(\delta p, T, S)}{\partial T^{2}} - \frac{2}{K_{T}^{2}(\delta p, T, S)} \left(\frac{\partial K_{T}(\delta p, T, S)}{\partial T} \right)^{2} \right]$$
(7.40)

Further $\alpha(0,T,S)$ and $K_T(\delta p,T,S)$ are evaluated from the following expressions,

$$\frac{1}{\alpha(0,T,S)} = A + BS + CS^{3/2} + DS^2 = \frac{1}{\alpha_0}$$
 (7.41)

$$K_T(\delta p, T, S) = E + F \times S + G \times S^{3/2} + (H + I \times S + J \times S^{3/2}) \delta p + (M + N \times S) \delta p^2$$
 (7.42)

From the expressions in (7.41) and (7.42), we can calculate $\frac{\partial^2 \alpha_0}{\partial T^2}$, $\frac{\partial \alpha_0}{\partial T}$, $\frac{\partial K_T}{\partial T}$ and $\frac{\partial^2 K_T}{\partial T^2}$. On substituting their values in (7.40), one obtains the value of $\frac{\partial^2 \alpha}{\partial T^2}$, which allows determining $\left(\frac{\partial C_p}{\partial p}\right)_T$ from eqn. (7.37); and using this value of the derivative of C_p we obtain the value of C_p at the level $p = \delta p$. Finally the adiabatic lapse rate in the ocean is obtained at the level $p = \delta p$ as

$$\Gamma_a = \frac{gT \,\alpha_T}{C_p(\delta p, T, S)} \tag{7.43}$$

7.6 Gibbs function

The thermodynamic relation (7.31) for $de = Td\eta - p \ d\alpha + \mu dS$ may be written as $de = d(T\eta) - d(p\alpha) - \eta dT + \alpha dp + \mu dS$ (7.44)

On rearranging this equation, we get the following relation

$$d(e-T\eta+p\alpha) = -\eta dT + \alpha dp + \mu dS \tag{7.45}$$

Define the Gibbs potential (also called the Gibbs Function and Gibbs Free Energy) as $G = e - T\eta + p\alpha$ (7.46)

The eqn. (7.45) takes the form,

$$dG = -\eta dT + \alpha dp + \mu dS. \tag{7.47}$$

Since we formally have,

$$dG = \left(\frac{\partial G}{\partial T}\right) dT + \left(\frac{\partial G}{\partial p}\right) dp + \left(\frac{\partial G}{\partial S}\right) dS , \qquad (7.48)$$

we may write from a comparison of (7.47) and (7.48) the following definitions,

$$\left(\frac{\partial G}{\partial T}\right)_{p,s} = -\eta \quad ; \qquad \left(\frac{\partial G}{\partial p}\right)_{T,S} = \alpha \quad \text{and} \quad \left(\frac{\partial G}{\partial S}\right)_{T,\eta} = \mu \, .$$
 (7.49)

Oceanographers have obtained a highly accurate equation of state of seawater and relations for evaluating other physical properties of seawater. The form of the Gibbs function that accurately reproduces the properties of seawater with certain degree of economy has been given by Vallis (2006). Though the expression is rather complicated yet it offers sufficient ease in computations; the expression for the Gibbs function is

$$G = G_o - \eta_o(T - T_o) + \mu(S - S_o) - C_{po}T \left[\ln\left(\frac{T}{T_o}\right) - 1 \right] \left[1 + \beta_s^*(S - S_o) \right]$$

$$+ \alpha_o(p - p_o) \left[1 + \beta_T(T - T_0) - \beta_s(S - S_0) - \frac{\beta_p}{2}(p - p_0) \right]$$

$$+ \alpha_o(p - p_o) \left[\frac{\beta_T \gamma^*}{2}(p - p_0)(T - T_0) + \frac{\beta_T^*}{2}(T - T_0)^2 \right]$$

$$(7.50)$$

The specific volume $\alpha = \left(\frac{\partial G}{\partial p}\right)_{T,S}$ is given by the following expression

$$\alpha = \alpha_o \left[1 + \beta_T (1 + \gamma^* p) (T - T_o) + \frac{\beta_T^*}{2} (T - T_o)^2 - \beta_S (S - S_o) - \beta_p p \right]. \tag{7.51}$$

The parameters appearing in (7.50) have the following meaning and values:

$egin{array}{c} ho_o \ lpha_o \ T_o \end{array}$	Reference density Reference specific volume Reference temperature	$1.027 \times 10^{3} \text{ kg/m}^{3}$ $9.738 \text{ E-4 m}^{3}/\text{kg}$ 283 K
$egin{array}{c} S_o \ C_{so} \ oldsymbol{eta}_T \end{array}$	Reference salinity Reference sound speed First Thermal expansion coefficient	$35 \ psu \approx 35\%$ $1490 \ m/s$ $1.67 \ E-4 \ K^{-1}$
$egin{array}{c} oldsymbol{eta}_T^* \ oldsymbol{eta}_S \ oldsymbol{eta}_p \end{array}$	Second thermal expansion coefficient Haline contraction coefficient Compressibility coefficient $(=\alpha_o / C_{so}^2)$	$1.00 E-5 K^{-2}$ $0.78 E-3 psu^{-1}$ $4.39 E-10 ms^{2}/kg$
$egin{array}{c} oldsymbol{\gamma}^* \ oldsymbol{C}_{po} \ oldsymbol{eta}_s^* \end{array}$	Thermobaric parameter Specific heat capacity at constant pressure Haline heat capacity coefficient	1.1 E-8 Pa ⁻¹ 3986 J/kg/K 1.5 E-3 psu ⁻¹
$P_o=0$	Pressure at sea surface	0.0 Pa

The expression of entropy $\eta = -\left(\frac{\partial G}{\partial T}\right)_{p,S}$ is given by

$$\eta = \eta_o + C_{po} \ln \left(\frac{T}{T_o} \right) \left[1 + \beta_s^* (S - S_o) \right] - \alpha_o p \left[\beta_T + \beta_T \gamma^* \frac{p}{2} + \beta_T^* (T - T_o) \right]$$
 (7.52)

The specific heat capacity, $C_p = T \left(\frac{\partial \eta}{\partial T} \right)_n$ is given by

$$C_{p} = C_{po} \left[1 + \beta_{S}^{*} (S - S_{o}) \right] - \alpha_{o} p \beta_{T}^{*} T.$$
 (7.53)

To a first approximation C_p is a constant that varies mildly with salinity and also depends weakly on temperature and pressure. The thermal expansion coefficient,

$$\alpha_{T} = \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_{p,S} \text{ is given by}$$

$$\alpha_{T} = \left(\frac{\alpha_{o}}{\alpha} \right) \left[\beta_{T} + \beta_{T} \gamma^{*} p + \beta_{T}^{*} (T - T_{o}) \right]$$
(7.54)

where α , the specific volume, has been calculated using the expression (7.51). Finally, the adiabatic lapse rate Γ is obtained by substituting $\left(\frac{\partial \alpha}{\partial T}\right)_{\alpha,\beta}$ from (7.54) as

$$\Gamma_{a} = \left(\frac{\partial T}{\partial p}\right)_{n} = \frac{T}{C_{p}} \left(\frac{\partial \alpha}{\partial T}\right)_{p,S} = \frac{T}{C_{p}} \alpha_{o} \left[\beta_{T} (1 + \gamma^{*} p) + \beta_{T}^{*} (T - T_{o})\right]$$
(7.55)

This is a simpler expression to obtain Γ_a , but accuracy of the lapse rate nevertheless depends on the accuracy of C_p . Note that all the expressions derived here are approximate. Though there are some errors involved, yet their magnitudes are small enough, so the final values can be confidently used in calculations.

For obtaining an expression for adiabatic lapse rate we can also use the following expression for entropy change $d\eta$ which is largely determined by temperature and pressure changes in the ocean,

$$d\eta = \left(\frac{\partial \eta}{\partial T}\right)_{pS} dT + \left(\frac{\partial \eta}{\partial p}\right)_{TS} dp$$

On setting $d\eta = 0$ in the above equation, we get the following relation for the lapse rate,

$$\left(\frac{\partial T}{\partial p}\right) = -\left(\frac{\partial \eta}{\partial p}\right)_{TS} \left(\frac{\partial \eta}{\partial T}\right)_{pS}^{-1} ; \left(\frac{\partial \eta}{\partial T}\right)_{pS} = -\frac{C_p}{T} ; \left(\frac{\partial \eta}{\partial p}\right)_{TS} = -\left(\frac{\partial \alpha}{\partial T}\right)$$

The above relations give

$$\left(\frac{\partial T}{\partial p}\right) = \frac{T}{C_p} \times \left(\frac{\partial \alpha}{\partial T}\right) = \frac{T\alpha}{C_p} \times \left(\frac{1}{\alpha} \frac{\partial \alpha}{\partial T}\right)$$

Hence the expression of Γ_a is obtained as

$$\Gamma_a = \left(\frac{\partial T}{\partial p}\right) = \frac{T\alpha_T}{\rho C_p}$$

This expression for Γ_a is same as (7.13) but obtained in much simpler manner.

7.7 Double-diffusion

In the preceding module and the sections above, it has been discussed at length that the ocean columns are stably stratified because density increases with depth and the changes in density of seawater are mainly determined by the changes in temperature and salinity. It has also been emphasized that different water masses, be of same density but having different temperatures and salinities, produce denser waters after mixing under the mechanical forcing of winds at the surface. However, a counterintuitive physical phenomenon was observed by M.E. Stern (The "salt fountain" and thermohaline convection, Tellus, vol.12, 1960), which arises due to the differences in the molecular

diffusivities of salt and temperature. This is known as the "double-diffusion" phenomenon. Why the mixing caused by double-diffusion is counterintuitive? Because, due this kind of mixing, dense waters become denser and light waters become lighter. If one considers a warm and salty water layer above a relatively colder and less salty water layer in the ocean, then due to the phenomenon of double-diffusion, the interface becomes unstable even though the density of the upper layer is lesser than that of the lower. The main reason being that molecular diffusion of heat is 100 times more than that of the salt, and the interfacial instability is caused by this difference in molecular diffusivities of the two important components of seawater viz., heat and salt. Ocean circulation is dominated both by large scale motions and eddies. Therefore, at this point, two important questions arise:

- (i) Does the large-scale dynamics of ocean circulation affect double-diffusion?
- (ii) Does double-diffusion affect the large-scale ocean circulation and thereby produce consequences of interest to the sensitivity of climate system?

Answer to the first question is relatively clear because the instability associated with double-diffusion is mostly confined to the interface, hence the scales of inhomogeneity that dominate the large-scale flow would hardly affect the dynamics operating at the double-diffusion. However, an answer to the second question has been investigated in recent years theoretically, numerically and also observationally. New observations from "Salt Finger Tracer Release Experiment" have thrown new light on the mixing induced by double-diffusion in transformation of water masses. When water mass transformation happens due to salt fingering, it impacts the climate system. The early view that doublediffusion has an important role in the maintaining the thermocline, also favours the argument that double-diffusion has tangible influence on large-scale phenomena in the ocean. Finally, it may be mentioned that the adiabatic mechanisms that control the stratification and limit overturning of water masses would inevitably reduce the mixing induced by turbulence or salt fingering. This has been observed for the Antarctic Circumpolar Current (ACC), where adiabatic effects control stratification and overturning, because any land barrier does not obstruct it; consequently, the flow reenters into the same region after completing the latitude circle.

7.8 Potential temperature definition in numerical models

The expression derived for various terms of thermodynamical variables that appear in the equation of state, allow calculation of lapse rate, enthalpy and potential temperature that are computationally complex. The efficiency of computations can however be achieved with a simplified equation of state. The ocean numerical models also use potential temperature as one of the thermodynamic variables, which can be obtained at a given instant solving the equation (7.15), i.e.

$$\eta(p_r, \theta, S) = \eta(p, T, S)$$

In the above equation, $\eta(p_r, \theta, S)$ is obtained from (7.52) by putting $p = p_r$ and we have

$$\eta(p_r, \theta, S) = \eta_o + C_{po} \ln \left(\frac{\theta}{T_o}\right) \left[1 + \beta_s^*(S - S_o)\right] - \alpha_o p_r \left[\beta_T + \beta_T \gamma^* \frac{p_r}{2} + \beta_T^*(\theta - T_o)\right]$$
(7.56)

By taking $p_r = 0$, the above equation becomes

$$\eta(0,\theta,S) = \eta_o + C_{po} \ln\left(\frac{\theta}{T_o}\right) \left[1 + \beta_s^*(S - S_o)\right]$$
(7.57)

Equation (7.15) implies that (7.57) must be equated to (7.52), which gives

$$C_{po} \ln \left(\frac{\theta}{T_o}\right) \left[1 + \beta_s^* (S - S_o)\right] = C_{po} \ln \left(\frac{T}{T_o}\right) \left[1 + \beta_s^* (S - S_o)\right] - \alpha_o p \left[\beta_T + \beta_T \gamma^* \frac{p}{2} + \beta_T^* (T - T_o)\right]$$

The above expression can be put in the following concise form,

$$C_{po}\left[1+\beta_s^*(S-S_0)\right]\ln\left(\frac{\theta}{T}\right) = -\alpha_o\beta_T p \left[1+\frac{\gamma^*}{2}p+\frac{\beta_T^*}{\beta_t}(T-T_0)\right]$$
(7.58)

From the above expression, we can write the most amenable form of the potential temperature for numerical computations as,

$$\theta = T \exp \left\{ -\frac{\alpha_o \beta_T p}{C_{po} \left[1 + \beta_S^* (S - S_o) \right]} \left[1 + \frac{\gamma^*}{2} p + \frac{\beta_T^*}{\beta_t} (T - T_0) \right] \right\}$$
(7.59)

The equation (7.59) is much like the definition of θ in the atmospheric thermodynamics. In writing (7.59), the deviations of T and θ from T_0 are presumed to be small and that the exponential term itself is small. The quantity $C'_p = C_{po} \left[1 + \beta_s^* (S - S_o) \right]$ is nearly constant; therefore a simplified form (7.59) for θ could be derived.

If we write $T' = T - T_o$; $\theta' = \theta - T_o$ with $\theta_o \equiv T_o$ at the sea surface, then from eq. (7.59) we have

$$T = \theta \left\{ 1 + \frac{\alpha_o \beta_T p}{C_p'} \left(1 + \frac{\gamma^* p}{2} \right) + \frac{\alpha_o \beta_T^* p}{C_p'} T' + \frac{\alpha_o^2 \beta_T^{*2} p^2}{C_p'^2} T'^2 + \frac{\alpha_o^2 \beta_T^{*2} p^2}{C_p'^2} \left(1 + \gamma^* p \right)^2 + \dots \right\}$$

Substitute $T = T_o + T'$; $\theta = T_o + \theta'$, then we obtain a relation between the perturbations of T and θ as

$$T'\left(1 - \frac{\alpha_o \beta_T^* p}{C_{po}}\right) \approx \frac{\alpha_o T_o \beta_T}{C_{po}} p\left(1 + \frac{\gamma^* p}{2}\right) + \theta'\left(1 + \frac{\alpha_o \beta_T^*}{C_{po}} p\right). \tag{7.60}$$

The above expression can be approximated as

$$T' = \frac{\alpha_o T_o \beta_T}{C_{po}} p + \theta' \quad \text{or} \quad \theta' = T' - \frac{\alpha_o T_o \beta_T}{C_{po}} p \quad . \tag{7.61}$$

The coefficient of p in (7.61) is same as the lapse rate Γ , defined earlier in this lecture.

The numerical models use potential temperature as a thermodynamic variable, though the potential enthalpy should be a preferable choice like in the compressible models of atmosphere in motion. The main advantage of using potential enthalpy as a variable is its interpretation as a useful measure of heat content and also a conserved quantity. For numerical models, the simplified form of the equation of state is given as

$$\alpha = \alpha_o \left[1 + \frac{\alpha_o p}{C_{So}^{\prime 2}} + \beta_T \left(1 + \tilde{\gamma}^* p \right) \theta' + \frac{1}{2} \beta_T^* \theta'^2 - \beta_s (S - S_o) \right]$$
(7.62)

$$\tilde{\gamma}^* = \gamma^* + \frac{\alpha_o \beta_T^* T_o}{C_{po}} \approx \gamma^*, \qquad \tilde{C}_{so}^{-2} = C_{so}^{-2} - \frac{\beta_T^2 T_o}{C_p} \approx C_{so}^{-2}$$

The equation (7.62) can be approximated further with the use of hydrostatic pressure,

$$p = -\frac{g(z - z_0)}{\alpha_0}$$
; at $z = z_0$, $p = 0$. Thus one may write (7.62) as

$$\alpha = \alpha_o \left[1 + \frac{g(z - z_o)}{C_{so}^2} + \beta_T \left(1 - \tilde{\gamma}^* \frac{g(z - z_o)}{\alpha_o} \right) \theta' + \frac{1}{2} \beta_T^* \theta'^2 - \beta_s (S - S_o) \right]$$
(7.63)

Thus, we may use either (7.62) or (7.63) as the equation of the state, which is simplified but it involves quadratic terms in the perturbation of potential temperature.

A final word about inclusion of various mixing mechanisms in numerical models should be in order. The mixing-driven circulation is certainly a correction to adiabatically controlled modes of circulation; therefore, numerical ocean models include various mixing mechanisms for simulating realistically the ocean currents. Double-diffusion has also been included in some models mainly to isolate microstructures developing due to its mixing effects in large-scale flows that are dynamically distinct from those arising due to turbulent mixing. In this manner, the relative roles of these processes could be identified in the large scale dynamics of ocean currents.