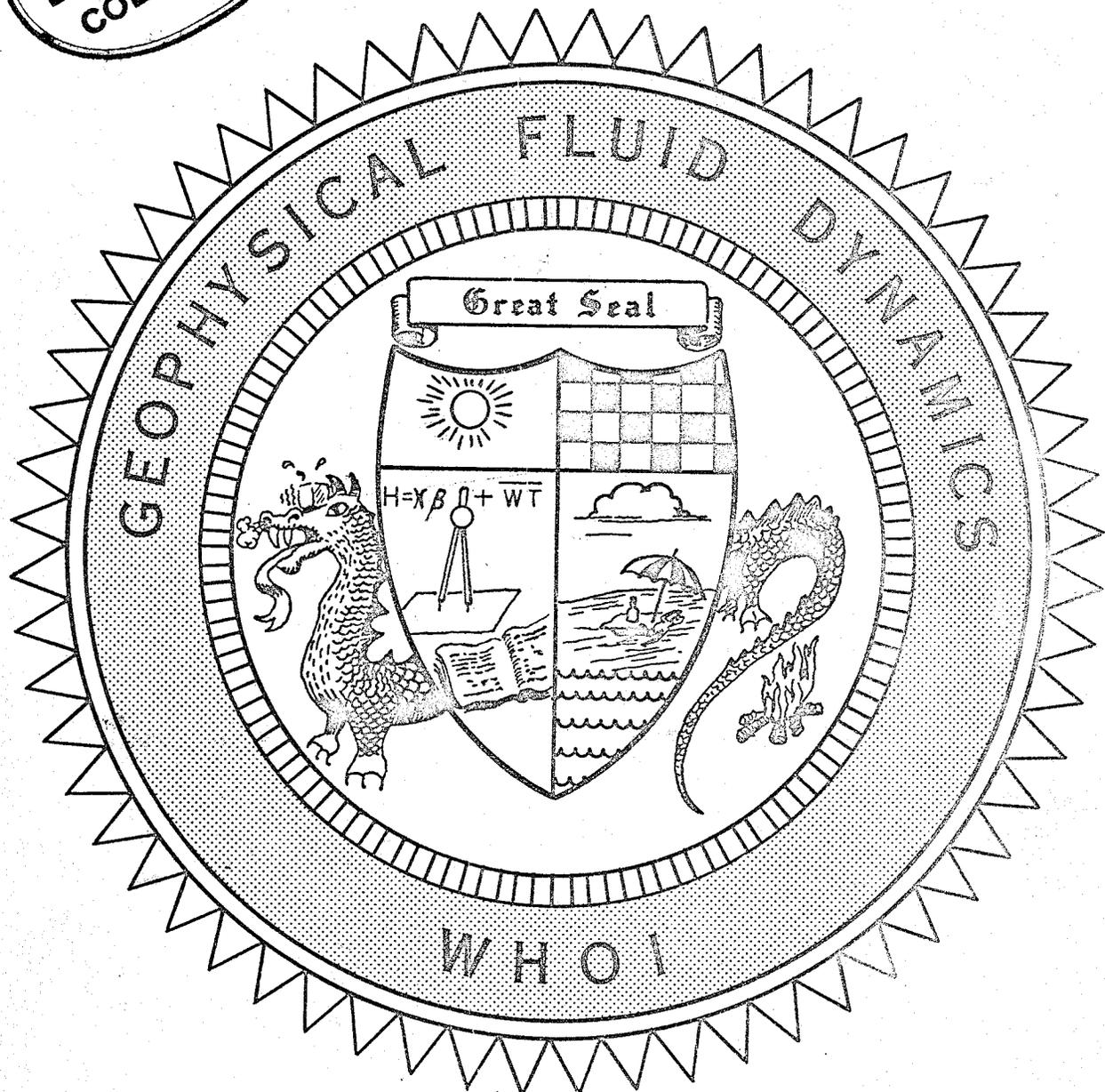


61-39

vol. II ~~copy 2.~~
copy 2
~~Archer~~

WHOI
DOCUMENT
COLLECTION



Lectures by N.P. Fofonoff



MBL/WHOI
0 0301 0092189 6

Energy Transformations in the Ocean

N. P. Fofonoff

Fisheries Research Board of Canada

Pacific Oceanographic Group, Nanaimo, B. C.

Part I

The purpose of the following series of lectures is to examine a specific area of geophysical hydrodynamics and to discuss the questions that might be asked in the course of scientific investigations. For a specific topic, I have chosen to examine the energy balance in oceanic circulation, including the various modes of interconversion of kinetic, potential and internal energies. We shall look particularly closely at the effects of non-linearity of the equation of state of sea water on energy conversions and try to determine the consequences in terms of observable effects on the distributions of temperature, salinity and currents in the ocean.

The ideas to be presented in these lectures are not entirely new - even in their oceanographic applications. Most of them can be found scattered in the oceanographic literature. However, no systematic treatment of the energy transformations has been made for an ocean system. I shall attempt to present such a treatment and to draw as many conclusions of potential importance as I can. We shall have to rely on our collective scientific judgement to evaluate these conclusions.

In the course of the lectures, we shall consider briefly some of the earlier oceanographic concepts that contributed to the development of the present treatment of energy transformations.

We will consider the concepts in their most elementary form to gain a thorough familiarity with their content. Then, we shall interpret the general conservation equations for fluid motion in terms of these concepts, and finally, derive results that can be compared directly with those obtained from observations of the real ocean.

The study of energy transformations and particularly the dynamical effects of non-linearity of the equation of state of sea water got its start shortly after the appearance of Knudsen's tables of sea water density in 1901. Prof. Emil Witte (1902) found from the tables that a slight decrease of total volume took place when two masses of sea water of different temperatures and salinities were mixed together. This effect - contraction on mixing - is well-known in the study of solutions. The contraction is extremely small - about 2 parts in 10^4 for a temperature difference of 10°C - and its effect on dynamical processes in the ocean has been frequently discounted but never thoroughly investigated.

Because of the contraction, mixing between two masses of sea water of equal, or nearly equal, density results in a mixture that is slightly more dense than either of the constituents being mixed. Witte argued that if two such masses of sea water were side by side in the ocean the mixtures formed along their mutual boundary would sink and form a convergence line along the surface of the ocean with opposing currents (Stromkabelung) on either side. The density differences involved are extremely small and it is difficult to assess the effectiveness of Witte's mechanism. No one, including

Witte, has been able to come up with convincing evidence to show that the mechanism contributes significantly to the formation of convergence zones or lines. Still, the mechanism is intriguing and it continued to attract the attention of oceanographers during the past 60 years.

Contraction on Mixing

Pure water has many anomalous properties and the anomalies are present, though usually to a lesser extent, in sea water. Of particular interest in the study of energy transformations is the rapid change of the coefficient of thermal expansion with temperature and pressure. The coefficient increases with temperature, pressure and salinity. On the other hand, both the coefficients of compressibility and saline contraction* decrease in magnitude with temperature, pressure and salinity. The variation of the coefficients with temperature and salinity implies that volume is not conserved in mixing. We shall examine this effect in detail.

Let us consider two bodies of sea water of masses m_1 , m_2 , temperatures ν_1^l , ν_2^l and salinities S_1 , S_2 respectively. Mixed together, these yield a homogeneous mass m of sea water of temperature ν^l and salinity S . We assume that the pressure p remains constant throughout the mixing.

Applying conservation of mass, we obtain

$$\Delta m = m - (m_1 + m_2) = 0 \quad 1.1$$

*The term 'coefficient of saline contraction' was introduced by R.O. Reid (1958) for the coefficient $-\frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial S} \right)_{\nu, p}$.

$$m \Delta S = mS - (m_1 S_1 + m_2 S_2) = 0 \quad 1.2$$

The change of volume ΔV is

$$\Delta V = m\alpha - (m_1 \alpha_1 + m_2 \alpha_2), \quad 1.3$$

where α_1, α_2 and α are the specific volumes of the two initial masses and of the final mixture respectively. Conservation of energy requires that

$$m\Delta e = me - (m_1 e_1 + m_2 e_2) = -p\Delta V, \quad 1.4$$

*No heat flow
no work done by
shears, body forces.*

where e_1, e_2 and e are the specific internal energies of the initial and final masses. Substitution for ΔV in (1.4) yields

$$m\Delta(e + p\alpha) = m(e + p\alpha) - [m_1(e_1 + p\alpha_1) + m_2(e_2 + p\alpha_2)] = 0 \quad 1.5$$

or

$$m\Delta h = mh - (m_1 h_1 + m_2 h_2) = 0. \quad 1.6$$

where h_1, h_2 and h are the corresponding specific enthalpies for the initial and final masses.

If we assume that the temperatures and salinities and, hence, enthalpies, of the two initial masses differ only slightly from each other, we can expand the specific volume as a Taylor series in h and S about a suitably chosen reference point

h_0, S_0 . The expansion is of the form

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial h}\right)_0 (h - h_0) + \left(\frac{\partial \alpha}{\partial S}\right)_0 (S - S_0) + \frac{1}{2} \left[\left(\frac{\partial^2 \alpha}{\partial h^2}\right)_0 (h - h_0)^2 + 2 \left(\frac{\partial^2 \alpha}{\partial h \partial S}\right)_0 (h - h_0)(S - S_0) + \left(\frac{\partial^2 \alpha}{\partial S^2}\right)_0 (S - S_0)^2 \right] + \dots \quad 1.7$$

Substitution of (1.7) into (1.3) yields

$$\Delta V = -\frac{m_1+m_2}{2} \left[\frac{m_1 m_2}{(m_1+m_2)^2} \right] \left[\left(\frac{\partial^2 \alpha}{\partial h^2} \right)_0 (h_2-h_1)^2 + 2 \left(\frac{\partial^2 \alpha}{\partial h \partial S} \right)_0 (h_2-h_1)(S_2-S_1) + \left(\frac{\partial^2 \alpha}{\partial S^2} \right)_0 (S_2-S_1)^2 \right] + \dots$$

$$= -\frac{m_1+m_2}{2} \left[\frac{m_1 m_2}{(m_1+m_2)^2} \right] \Delta_{hS}^2 \alpha, \quad 1.8$$

where $\Delta_{hS}^2 \alpha$ is a shorthand notation introduced for the differential form in (1.8). Conversion of the derivatives from enthalpy to temperature yields

$$\Delta V = -\frac{(m_1+m_2)}{2} \left[\frac{m_1 m_2}{(m_1+m_2)^2} \right] \left[\Delta_{\rho S}^2 \alpha - \frac{1}{C_p} \frac{\partial \alpha}{\partial \rho} \Delta_{\rho S}^2 h \right], \quad 1.9$$

where

$$\Delta_{\rho S}^2 h = \frac{\partial C_p}{\partial \rho} (\rho_2 - \rho_1)^2 + 2 \frac{\partial C_p}{\partial S} (\rho_2 - \rho_1)(S_2 - S_1) + \frac{\partial^2 h}{\partial S^2} (S_2 - S_1)^2 \quad 1.10$$

and C_p is specific volume at constant pressure.

The additional term $\frac{1}{C_p} \Delta_{\rho S}^2 h$ represents departure of temperature from the linear mixing law because of variation of specific heat with temperature and salinity and of heat absorbed or released on mixing water of different salt concentrations (heat of dilution). The contribution of this temperature departure to the total contraction is small and may usually be neglected. The contraction per unit mass for a small mass ϵm mixed into a large mass m of sea water is given approximately by

$$\delta \alpha = \lim_{\epsilon \rightarrow 0} \left\{ \frac{\Delta V}{\epsilon m} \right\} = -\frac{1}{2} \left[\Delta_{hS}^2 \alpha \right] \approx -\frac{1}{2} \left[\Delta_{\rho S}^2 \alpha \right] \quad 1.11$$

The contraction on mixing will depend on the slope of the

line joining the points representing the two initial water masses on a T-S diagram. Letting

$$\begin{aligned} \nu_2 - \nu_1 &= \gamma \sin \theta \\ S_2 - S_1 &= \gamma \cos \theta, \end{aligned}$$

we can convert (1.11) to

$$\begin{aligned} d\alpha &= -\frac{\gamma^2}{2} \left\{ \frac{\frac{\partial^2 \alpha}{\partial \nu^2} + \frac{\partial^2 \alpha}{\partial S^2}}{2} + \sqrt{\frac{(\frac{\partial^2 \alpha}{\partial \nu^2} + \frac{\partial^2 \alpha}{\partial S^2})^2}{4}} - D \cos 2(\theta - \theta_m) \right\} \\ &= -\gamma^2/2 F(\theta; \nu, S, p) \end{aligned} \tag{1.12}$$

where

$$\tan 2\theta_m = -\frac{2 \frac{\partial^2 \alpha}{\partial \nu \partial S}}{\frac{\partial^2 \alpha}{\partial \nu^2} - \frac{\partial^2 \alpha}{\partial S^2}} \tag{1.13}$$

$$D = \frac{\partial^2 \alpha}{\partial \nu^2} \frac{\partial^2 \alpha}{\partial S^2} - \left(\frac{\partial^2 \alpha}{\partial \nu \partial S} \right)^2 \tag{1.14}$$

Contraction will occur for all θ if D is positive. Typical dependence of $F(\theta; \nu, S, p)$ on θ is shown in Figure 1 for the Knudsen-Ekman (1901, 1908) and the Eckart (1958) equations of state. The discriminant D is positive for all values of temperature, salinity and pressure encountered in the ocean for the Knudsen-Ekman equation. In contrast, it is negative for the Eckart equation except at the high-temperature, low-pressure part of the range in the ocean. The two equations of state yield qualitatively similar results and provide us with at least an order of magnitude of the contraction on mixing. A more precise series of measurements of density, thermal expansion and other physical properties of sea water would be very welcome. The Knudsen-Ekman equation has been used for the remainder of the calculations.

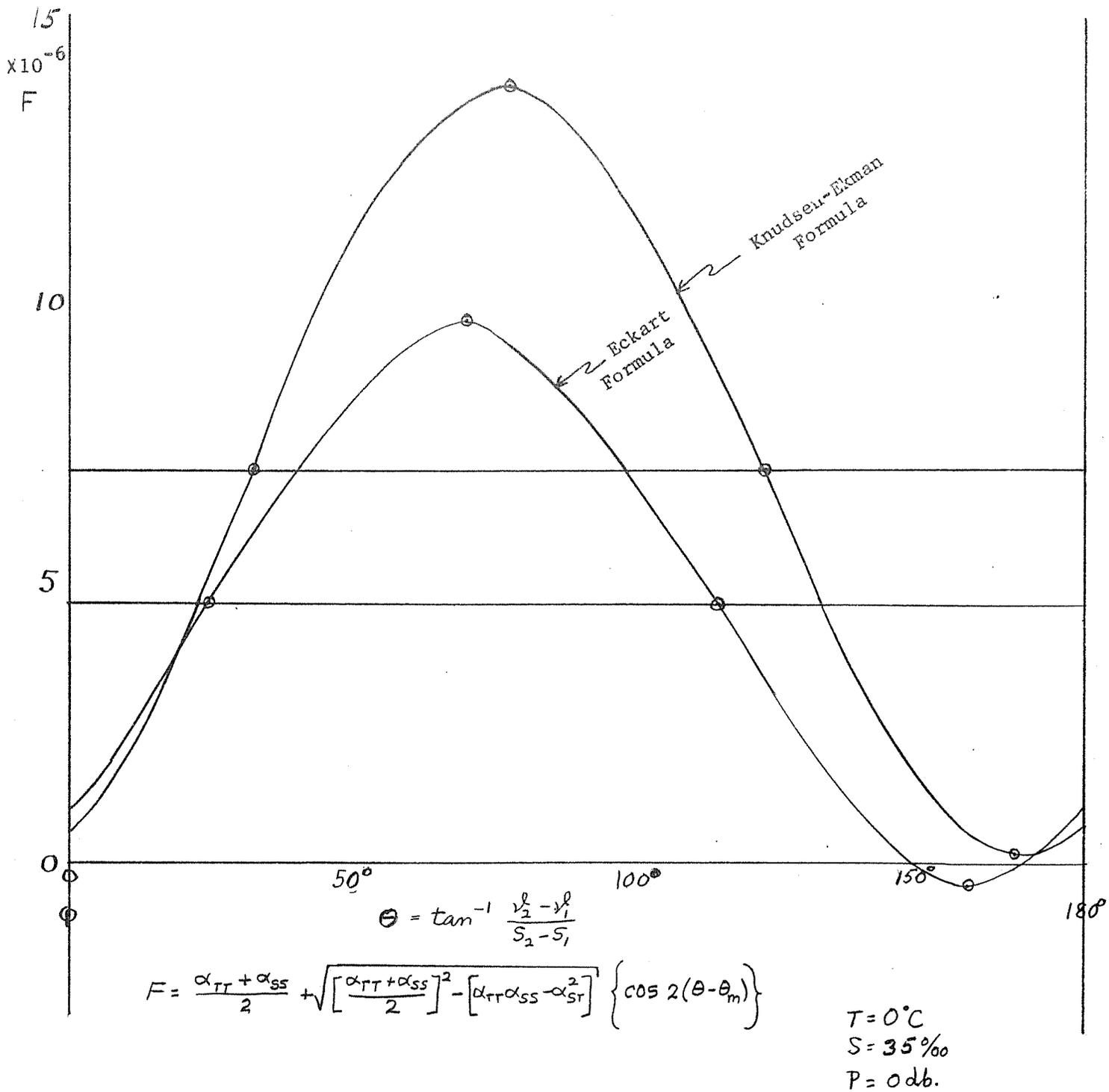


Figure 1. Contraction on mixing as a function of the slope of the T-S relationship between mixing elements.

The contraction on mixing at constant pressure is due largely to the variation of thermal expansion with temperature. The contraction is greatest for pure water at atmospheric pressure near freezing temperatures and, for a given temperature and salinity difference, decreases with temperature, pressure and salinity.

Studies of the dynamical effects of the contraction on mixing have been made by Eckel (1949a, 1949b), Fofonoff (1956) and Subov (1957, 1958).

General equations

Changes of other properties (entropy, internal energy, etc.) denoted by the general property ϕ can be obtained in a form similar to (1.11). The general formula for the change of the property ϕ per unit mass accompanying the mixing is

$$\Delta\phi = -\frac{1}{2} \left\{ \Delta_{rs}^2 \phi \right\} = -\frac{1}{2} \left\{ \Delta_{rs}^2 \phi - \frac{\partial \phi}{\partial r} \frac{\Delta_{rs} h}{c_p} \right\} \quad 1.15$$

Static Stability

If the density increases with depth in such a way that work is necessary to deform the structure, the ocean is considered to be stratified in a stable configuration. The degree of stratification is expressed in terms of a stability parameter introduced into oceanography by Hesselberg and Sverdrup (1915). The stability parameter has often been computed from routine oceanographic data but has not been of much value in interpreting the processes occurring

in the ocean because of the lack of an adequate theory of the formation of structure in the ocean. The parameter enters into studies of internal waves and turbulence. Discussions of stability and stability parameters have been given by Hesselberg (1918, 1929), Schubert (1935), Ivanov-Frantskevich (1953, 1956), and Pollack (1954).

The static stability parameter is usually defined as the buoyant force per unit mass (acceleration) acting on an element of sea water displaced vertically without loss of heat or salt, i.e., isentropically, a unit distance from its initial equilibrium level.

If the initial density is ρ^i , the final density ρ^f after a vertical displacement dz , will be

$$\rho^f = \rho^i + \left(\frac{\partial \rho}{\partial z} \right)_{\eta} dz \quad 1.16$$

where the subscript η denotes differentiation at constant entropy.

The density of the surrounding water at the final level is

$$\rho = \rho^i + \frac{d\rho}{dz} dz \quad 1.17$$

where $\partial \rho / \partial z$ is the vertical gradient of density in situ.

The buoyant force per unit mass is therefore

$$\begin{aligned} \frac{g(\rho^f - \rho^s)}{\rho} &= -g/\rho \left[\frac{d\rho}{dz} - \left(\frac{\partial \rho}{\partial z} \right)_{\eta} \right] dz = \rho g \left[\frac{d\alpha}{dz} - \left(\frac{\partial \alpha}{\partial z} \right)_{\eta} \right] dz \\ &= \rho g \left[\frac{\partial \alpha}{\partial \nu} \left[\frac{d\nu}{dz} - \left(\frac{\partial \nu}{\partial z} \right)_{\eta} \right] + \frac{\partial \alpha}{\partial s} \frac{ds}{dz} \right] dz \\ &= E_{f\eta} dz \end{aligned} \quad 1.18$$

where $E_{f\eta}$ is the stability parameter. The gradient $-\left(\frac{\partial \alpha}{\partial z} \right)_{\eta}$ is called the adiabatic lapse rate (approximately 0.1°C/1000 meters) and is usually denoted by Γ . The stability parameter is given

most frequently in units of 10^{-8} dynes per gram per centimetre and values range from about 10 in deep water to 10^5 and higher near the surface. Negative values are occasionally found in the ocean but almost certainly represent transient conditions. More often than not, a negative stability value is an indication of observational error.

If we multiply the average buoyant force $\frac{1}{2}E_{f\eta} dz$ by the distance dz , we obtain the work per unit mass $\frac{1}{2}E_{f\eta} dz^2 = \frac{1}{2}E_{w\eta} dz^2$ required to produce the vertical displacement. Thus, we can interpret $\frac{1}{2}E_{w\eta}$ as the work (ergs per gram per centimetre) required to displace isentropically a unit mass a unit vertical distance. If the work required to produce the displacement is positive, the stratification is stable. If negative, the stratification is unstable and will undergo spontaneous degeneration of structure by the action of the buoyant forces. In the unstable case, the buoyant forces will act away from the equilibrium level and will not restore the equilibrium.

As the displacement of a single element of fluid does not specify clearly the motion of the remainder of the fluid, we shall consider the interchange of two fluid elements of equal mass separated by a distance dz . The work required to produce the interchange is twice that required for the single element. Hence, we can interpret $E_{w\eta}$ as the work per unit mass required to interchange isentropically two elements of fluid separated by a unit vertical distance.

The interchange of two fluid elements is accompanied by changes of enthalpy, internal energy and potential energy. We shall

compute these changes to obtain a complete picture of the energy transformations that take place.

Enthalpy

As we have seen from (1.6), if no heat or salt is added to a mass of water from external sources and the pressure remains constant, the total enthalpy of the system remains constant. If only a change of pressure occurs, as in the interchange of two fluid elements of equal mass, the change of enthalpy must equal the work done on the system. In the isentropic interchange of two fluid elements separated by a distance dz , the change of enthalpy per unit mass is given by

$$\Delta h = \frac{1}{2}(\alpha_1^f + \alpha_1^i) \Delta P_1 + \frac{1}{2}(\alpha_2^f + \alpha_2^i) \Delta P_2, \quad 1.19$$

where the superscripts refer to the final and initial values of the specific volume and the subscripts to the lower (1) and the upper (2) fluid element.

Substituting

$$\alpha_1^f = \alpha_1^i + \left(\frac{\partial \alpha}{\partial z}\right)_\eta dz + \dots \quad 1.20$$

$$\alpha_1^i = \alpha_0 - \frac{1}{2} \frac{d\alpha}{dz} dz + \dots \quad 1.21$$

and

$$\alpha_2^f = \alpha_2^i - \left(\frac{\partial \alpha}{\partial z}\right)_\eta dz + \dots \quad 1.22$$

$$\alpha_2^i = \alpha_0 + \frac{1}{2} \frac{d\alpha}{dz} dz + \dots \quad 1.23$$

$$\Delta P_2 = -\Delta P_1 \approx \rho_0 g dz \quad 1.24$$

into (1.19) and neglecting all higher order terms, we obtain

$$\begin{aligned} \Delta h &= \rho g \left[\frac{d\alpha}{dz} - \left(\frac{\partial \alpha}{\partial z} \right)_\eta \right] dz^2 \\ &= E_{h\eta} dz^2 = E_{w\eta} dz^2 \end{aligned} \tag{1.25}$$

Hence, the parameter $E_{h\eta}$ giving the change of enthalpy involved in the interchange of the two elements is identical with the static stability parameter $E_{w\eta}$, i.e., equal to the work required to produce the interchange.

Potential Energy

In the interchange of the two fluid elements of equal mass, there is a change of potential energy of the system. The two elements of fluid have different volumes and consequently the fluid between the elements of thickness dz will be displaced vertically by a distance δz such that

$$\delta z = \alpha_2^f - \alpha_1^i = -(\alpha_1^f - \alpha_2^i) \tag{1.26}$$

for each unit of mass of an element interchanged. The potential energy change $\Delta \chi$ per unit mass within the system is therefore

$$\begin{aligned} \Delta \chi^{int.} &\simeq \rho dz \cdot g \delta z = \rho g (\alpha_2^f - \alpha_1^i) dz \\ &= \rho g \left[\frac{d\alpha}{dz} - \left(\frac{\partial \alpha}{\partial z} \right)_\eta \right] dz^2 \\ &= E_{p\eta}^{int.} dz^2 \\ &= E_{h\eta} dz^2 = E_{w\eta} dz^2 \end{aligned} \tag{1.27}$$

Hence, the potential energy change of the fluid between the elements interchanged is equal to the change of enthalpy and to the work done on the system to produce the interchange.

Equation (1.27) does not give the total change of potential energy. The two fluid elements interchanged do not have the same temperatures and salinities. Hence, their compressibilities will differ. As each element undergoes the same change of pressure, the difference in compressibilities will yield a net change of volume of the system. The volume change per unit mass is

$$\begin{aligned} \Delta\alpha &= \alpha_1^f - \alpha_1^i + \alpha_2^f - \alpha_2^i = \left(\overline{\frac{\partial\alpha}{\partial p}}\right)_{\eta_1} \Delta P_1 + \left(\frac{\partial\alpha}{\partial p}\right)_{\eta_2} \Delta P_2 \\ &= \rho g \left\{ \frac{d}{dz} \left(\frac{1}{\gamma} \frac{\partial\alpha}{\partial p} \right) - \left[\frac{\partial}{\partial z} \left(\frac{1}{\gamma} \frac{\partial\alpha}{\partial p} \right) \right]_{\eta} \right\} dz^2 \\ &= V_{\alpha\eta} dz^2, \end{aligned} \tag{1.28}$$

where $\gamma = C_p/C_v$ is the ratio of specific heats.

The net change of volume $\Delta\alpha$ of the system in which the interchange of fluid elements takes place (internal system) produces a change of potential energy of the remainder of the ocean (external system) of an amount $\rho\Delta\alpha$ such that

$$\begin{aligned} \Delta\chi^{ext} &= \rho\Delta\alpha = \rho V_{\alpha\eta} dz^2 \\ &= \rho g \left\{ \frac{d}{dz} \left(\frac{P}{\gamma} \frac{\partial\alpha}{\partial p} \right) - \left[\frac{\partial}{\partial z} \left(\frac{P}{\gamma} \frac{\partial\alpha}{\partial p} \right) \right]_{\eta} \right\} dz^2 \\ &= E_{\chi\eta}^{ext} dz^2 \end{aligned} \tag{1.29}$$

and a change of internal energy Δe of the internal system of

$$\begin{aligned}
 \Delta e &= -p\Delta\alpha = -pV_{\alpha\eta} dz^2 \\
 &= \rho g \left\{ \frac{d}{dz} \left(\frac{p}{\gamma} \frac{\partial\alpha}{\partial p} \right) - \left[\frac{\partial}{\partial z} \left(\frac{p}{\gamma} \frac{\partial\alpha}{\partial z} \right) \right]_{\eta} \right\} dz^2 \\
 &= E_{e\eta} dz^2 = -E_{\eta}^{\text{ext}} dz^2
 \end{aligned}
 \tag{1.30}$$

The change of internal energy of the internal system could also be obtained by considering the change for each element involved in the interchange. The same expression for the internal energy parameter is obtained.

Changes of other thermodynamic potentials can be calculated by the procedure outlined above. The change of a general thermodynamical property ϕ is given by

$$\begin{aligned}
 \Delta\phi &= (\phi_1^f - \phi_1^i) + (\phi_2^f - \phi_2^i) = \left(\overline{\frac{\partial\phi}{\partial p}} \right)_{\eta_1} \Delta p_1 + \left(\overline{\frac{\partial\phi}{\partial p}} \right)_{\eta_2} \Delta p_2 \\
 &= \rho g \left\{ \frac{d}{dz} \left(\frac{\partial\phi}{\partial p} \right)_{\eta} - \left[\frac{\partial}{\partial z} \left(\frac{\partial\phi}{\partial p} \right)_{\eta} \right]_{\eta} \right\} dz^2 \\
 &= E_{\phi\eta} dz^2
 \end{aligned}
 \tag{1.3}$$

where $E_{\phi\eta}$ may be interpreted as the parameter giving the change of a property ϕ per unit mass for the isentropic interchange of two elements of fluid separated by a unit vertical distance.

The changes of enthalpy, internal energy, potential energy and the work done on the system are summarized in Table 1 for the isentropic deformation that we have considered.

Table I

Energy parameters giving the changes per unit mass of enthalpy internal energy and potential energy for the isentropic interchange of two elements of equal mass separated by a unit vertical distance

	Energy change (internal system)	Energy change (external system)	Total energy change
Work required to produce inter- change	$E_{w\eta}$	0	$E_{w\eta}$
Enthalpy	$E_{h\eta} = E_{w\eta}$	0	$E_{h\eta} = E_{w\eta}$
Internal energy	$E_{e\eta}$	0	$E_{e\eta}$
Potential energy	$E_{z\eta}^{int} = E_{h\eta}$	$E_{z\eta}^{ext} = -E_{e\eta}$	$E_{z\eta} = E_{h\eta} - E_{e\eta}$

$$E_{w\eta} = E_{e\eta} = E_{z\eta}^{int} = \rho g \left[\frac{d\alpha}{dz} - \left(\frac{\partial \alpha}{\partial z} \right)_{\eta} \right]$$

$$= \rho g \left[\frac{\partial \alpha}{\partial x} \left(\frac{dx}{dz} + \Gamma \right) + \frac{\partial \alpha}{\partial s} \frac{ds}{dz} \right], \Gamma = - \left(\frac{\partial x}{\partial z} \right)_{\eta, s}$$

$$E_{z\eta}^{ext} = -E_{e\eta} = \rho g \left\{ \frac{d}{dz} \left(\frac{p}{\gamma} \frac{\partial \alpha}{\partial p} \right) - \left[\frac{\partial}{\partial z} \left(\frac{p}{\gamma} \frac{\partial \alpha}{\partial p} \right) \right]_{\eta} \right\}$$

$$= \rho g \left[\frac{\partial}{\partial x} \left(\frac{p}{\gamma} \frac{\partial \alpha}{\partial p} \right) \left(\frac{dx}{dz} + \Gamma \right) + \frac{\partial}{\partial s} \left(\frac{p}{\gamma} \frac{\partial \alpha}{\partial p} \right) \frac{ds}{dz} \right]$$

$$E_{h\eta} = E_{e\eta} + E_{z\eta}$$

Exercises (Part 1)

1. Show that

$$\Delta \varphi = -\Delta_{hs}^2 \varphi = -\Delta_{vs}^2 \varphi + \frac{1}{c_p} \frac{\partial \varphi}{\partial v} \Delta_{vs}^2 h.$$

2. Show that the change of entropy $\Delta \eta$ is given by

$$\Delta \eta = \frac{c_p}{T^2} \Delta T^2 + \frac{\mu}{T} \Delta S^2$$

where T is absolute temperature and μ is introduced for $(\frac{\partial h}{\partial s})_{v,p}$.

3. Show that the change of enthalpy for the isentropic interchange of two elements of mass can be expressed in the alternative form

$$E_{h\eta} = c_p \Delta v + \left(\frac{\partial c_p}{\partial p}\right)_\eta \frac{d\theta}{dz} + \left(\frac{\partial h_s}{\partial p}\right)_\eta \frac{ds}{dz},$$

where Δv is the change of temperature of the system per unit distance, c_p is specific heat, h_s is introduced for $(\frac{\partial h}{\partial s})_{v,p}$ and $d\theta/dz$ for the potential temperature gradient $dv/dz + \Gamma$.

References

- Eckart, C., 1958. Properties of water. Part III. The equation of state of water and sea water at low temperatures and pressures. Amer.J.Sci. 256, 225-240.
- Eckel, O., 1949a. Über die mechanischen Arbeitsgrößen der Binnenseen. Arch.Met., Wien, Ser. A, 1, 108-126.
- 1949b. Über die Mischungsarbeit von stabil geschichteten Wassermassen. Ibid., 264-269.
- Ekman, V.W., 1908. Die Zusammendrückbarkeit des Meerwassers nebst einigen Werten für Wasser und Quecksilber. Publ.Circ.Explor. Mer, No. 43, 1-47.
- 1914. Der adiabatische Temperaturgradient im Meere. Ann.Hydrog., Berlin 42, Heft 6, 340-344.
- Fofonoff, N.P., 1956. Some properties of sea water influencing the formation of Antarctic bottom water. Deep-Sea Res. 4, 32-35.
- Hesselberg, Th. and H.U. Sverdrup, 1915. Die Stabilitätsverhältnisse des Seewassers bei vertikalen Verschiebungen. Bergens Mus. Aarb. 1914-15, No. 15, 1-16.
- Hesselberg, Th., 1918. Über die Stabilitätsverhältnisse bei vertikalen Verschiebungen in der Atmosphäre und im Meer. Ann. Hydrog., Berlin 46, 118-129.
- 1929. Die Stabilitätsbeschleunigung in Meere und in der Atmosphäre. Ann.Hydrog., Berlin 57, 273-282.
- Ivanov-Frantzkevich, G.N., 1953. Vertical stability of water layers as an important oceanological characteristic. (In Russian). Trudi Inst.Oceanol., Akad.Nauk SSSR 7, 91-110.
- 1956. On the problem of vertical stability of water layers. Trudi Inst.Oceanol., Akad.Nauk SSSR 19, 3-45.
- Knudsen, M., 1901. Hydrographische Tabellen. Copenhagen, 1-63.
- Pollack, M., 1954. Static stability parameters in oceanography. J.Mar.Res. 13, 101-112.
- Reid, R.O., 1959. Influence of some errors in the equation of state or in observations on geostrophic currents. Conference on physical and chemical properties of sea water. Natl.Acad.Sci.-Natl.Res.Council, Publ. 600, 10-29.
- Schubert, O.V., 1935. Quantitative Untersuchungen zur Statik und Dynamik des Atlantischen Ozeans. 1.Lieferung: Die Stabilitätsverhältnisse. Wiss.Ergebn.dtsch Atlant.Exped.'Meteor' 6, Zweiter Teil, 1-54.

Subov, N.N., 1957. Contraction on mixing of sea waters of different temperature and salinity. (In Russian) Gidro-Meteo-Izdat.

----- and K.D.Sabinin, 1958. Calculation of contraction on mixing of sea waters. (In Russian). Gidro-Meteo-Izdat. 1-38.

Witte, E., 1902. Zur Theorie der Stromkabelungen. Gaea, Köln, 484ff.

Part II

Thermodynamics of a sea-water system

In order to define more precisely what is meant by the entropy, internal energy, enthalpy and so on, we shall consider the thermodynamical relationships for an element of sea water at some level within the ocean. This element will be considered as a part, or sub-system, of a larger system consisting of a vertical column of sea water extending from the bottom to the surface of the ocean. The column, in turn, can be considered as a part of the total system encompassing the entire ocean.

We shall refer to an element, or a pair of elements and the water between, as the internal system and we shall examine the changes of variables that can take place. The remainder of the column will be referred to as the external system.

Because of gravity the pressure within the column increases monotonically with depth. Hence, a phase within the system cannot have finite vertical extent. Thermodynamical potentials (energies) of a finite portion of the column have to be expressed as integrals over the phases included in the system. Each phase within the system is free to exchange heat, water and salt with adjacent phases. Changes of volume of a phase will affect the location of phases in the external system with respect to the gravitational field. Hence, in addition to the usual thermodynamical relationships, we have equations relating the changes of thermodynamic potentials to changes of potential energy.

Sea water contains a large number of dissolved constituents forming ionic components. These components are in relatively constant

ratios to each other in the open ocean. Changes of salinity are due primarily to the variation in the water content of sea water. If we assume that the relative proportions of ions is not affected by the processes that we will be considering, we can combine all the dissolved constituents into one component expressed in terms of salinity.

The general equation for the change of internal energy E of a multi-constituent system of mass M is

$$dE = TdN - pdV + \sum_i \mu_i dm_i \quad 2.1$$

where T is absolute temperature, N entropy, p pressure, V volume, and μ_i the specific chemical potential of the i -th constituent of mass m_i .

In order to apply the general equation to the sea water system, we convert it into an equation for a system of unit mass. Introducing the intensive quantities

$$e = E/M \text{ specific internal energy,}$$

$$\eta = N/M \text{ specific entropy,}$$

$$\alpha = V/M \text{ specific volume,}$$

$$x_i = m_i/M \text{ mass fraction of the } i\text{-th constituent,}$$

and substituting into (2.1), we obtain the equations

$$de = Td\eta - pd\alpha + \sum_i \mu_i dx_i \quad 2.2$$

$$e = T\eta - p\alpha + \sum_i \mu_i x_i \quad 2.3$$

and the Gibbs-Duhem equation

$$-\eta dT + \alpha dp - \sum_i x_i d\mu_i = 0 \quad 2.4$$

Assuming that the ratios of dissolved ionic constituents is constant, we may write

$$x_i = \lambda_i S \quad 2.5$$

where S is salinity and λ_i the ratio of mass of the i -th constituent to the total mass of dissolved salts. We also introduce a combined chemical potential μ_S for the dissolved salts such that

$$\mu_S = \sum_i \lambda_i \mu_i \quad 2.6$$

and a specific chemical potential μ_w for water in sea water. Using these quantities, we can rewrite (2.2), (2.3) and (2.4) in the form

$$de = Td\eta - pd\alpha + \mu dS \quad 2.7$$

$$e = T\eta - p\alpha + \mu S + \mu_w \quad 2.8$$

$$d\mu_w = -\eta dT + \alpha dp - S d\mu \quad 2.9$$

where

$$\mu = \mu_S - \mu_w \quad 2.10$$

is the difference of chemical potentials of the dissolved salts and water.*

The Gibbs-Duhem equation (2.9) can be written in the form

$$\begin{aligned} d\mu_w &= -\left(\eta + S \frac{\partial \mu}{\partial T}\right) dT + \left(\alpha - S \frac{\partial \mu}{\partial p}\right) dp - S \frac{\partial \mu}{\partial S} dS \\ &= -\eta_w dT + \alpha_w dp - S \frac{\partial \mu}{\partial S} dS \end{aligned} \quad 2.11$$

where η_w and α_w can be interpreted as the partial entropy and partial specific volume of water in sea water.

* See Craig (1960) for a discussion of the disadvantages of introducing the difference of chemical potentials.

The system of equations (2.7) to (2.9) can be applied to an open or closed system and, provided μ can be determined, describes the thermodynamical behaviour of a sea-water system within the limits set by the assumption of constant ionic ratios.

As we shall see, the difference of chemical potentials μ is not completely defined by the equilibrium properties of sea water. If we assume that specific volume α and specific heat C_p are known as a function of temperature, pressure and salinity, we can obtain the derivatives

$$\partial\mu/\partial p = \partial\alpha/\partial s \quad 2.12$$

$$\partial^2\mu/\partial T^2 = -1/T \frac{\partial C_p}{\partial s} \quad 2.13$$

Furthermore, $\partial\mu/\partial s$ can be expressed in terms of the colligative properties of sea water, e.g., vapour pressure lowering. Hence, only $\partial\mu/\partial T$ is not specified completely and is arbitrary to the extent of an unknown constant. The difference μ is therefore arbitrary to the extent of a linear function of temperature.

The derivative $\partial\mu_w/\partial s$, or from (2.11) $-s \partial\mu/\partial s$, can be expressed in terms of the fractional lowering of vapour pressure over sea water as compared with pure water. If sea water is in equilibrium with water vapour at a given temperature, pressure and salinity, the specific chemical potential μ_w of the water in sea water must equal the chemical potential of the vapour μ_v . If we compare two such equilibrium systems of slightly differing salinities, we must have for the differences of chemical potential

$$\Delta\mu_w = \Delta\mu_v = \frac{\partial\mu_v}{\partial p} \Delta p = \alpha_v \Delta p_v \quad 2.14$$

where p_v is the vapour pressure and α_v is the specific volume of the vapour. From (2.11) we have

$$\Delta\mu_w = \alpha_w \Delta p - s \frac{\partial\mu}{\partial s} \Delta s$$

Hence,

$$s \frac{\partial\mu}{\partial s} = -(\alpha_v - \alpha_w) \Delta p / \Delta s \quad 2.15$$

Defining r to be the fractional lowering of vapour pressure

$p^\circ - p/p^\circ$, where p° is the vapour pressure of pure water at the same temperature, we have

$$\begin{aligned} s \frac{\partial\mu}{\partial s} &= p^\circ (\alpha_v - \alpha_w) \frac{\partial r}{\partial s} \\ &\approx \frac{p^\circ \alpha^\circ}{1-r} \frac{\partial r}{\partial s} \approx \frac{RT}{1-r} \frac{\partial r}{\partial s} = - \frac{\partial\mu_w}{\partial s} \end{aligned} \quad 2.16$$

where we have assumed that α_w is negligible ($\alpha_v \gg \alpha_w$) and have introduced the perfect-gas law for the vapour phase.

From (2.16) we obtain

$$\mu_w = \mu_w^\circ + RT \ln(1-r) \quad 2.17$$

or

$$\frac{\partial\mu}{\partial s} = -\frac{1}{s} \frac{\partial\mu_w}{\partial s} = \frac{RT}{s(1-r)} \frac{\partial r}{\partial s} > 0 \quad 2.18$$

Hence, $\partial\mu/\partial s$ can be evaluated from experimental determinations of vapour pressure lowering over sea water.

The interpretation of the arbitrary linear function of temperature in μ is relatively simple if we formulate the expression for entropy in terms of the thermodynamic potential g , where

$$\begin{aligned}
 g &= e^{-T\eta} + p\alpha \\
 &= \mu_s + \mu_w \\
 &= s\mu_s + (1-s)\mu_w
 \end{aligned}
 \tag{2.19}$$

Differentiating with respect to temperature at constant pressure and salinity, we obtain

$$\begin{aligned}
 \frac{\partial g}{\partial T} = -\eta &= s \frac{\partial \mu_s}{\partial T} + (1-s) \frac{\partial \mu_w}{\partial T} \\
 &= - [s\eta_s + (1-s)\eta_w]
 \end{aligned}
 \tag{2.20}$$

where η_s and η_w are the partial specific entropies of the dissolved salts and water respectively. If $\partial\mu/\partial T$ contains an arbitrary constant, then from the relation

$$\frac{\partial \mu}{\partial T} = - \frac{\partial \eta}{\partial s}
 \tag{2.21}$$

the entropy η must contain an arbitrary linear function of salinity. Consequently, from (2.20), η_s and η_w contain arbitrary constants. The arbitrary constants can be eliminated by defining zero-entropy reference phases for the salts and water.

Having obtained the necessary equations to describe the thermodynamical system, we shall examine briefly the conditions of equilibrium in the ocean. In thermodynamical equilibrium, the temperature of two phases in contact with each other must be equal and the differences on chemical potential equal to the work required to move a unit mass from one phase to the other. Hence, for equilibrium

$$\Delta T = 0,$$

$$\Delta \mu_s = \Delta \mu_w = -d\phi,$$

$$\Delta \mu = 0$$

2.22

As the vertical gradient of μ must vanish in equilibrium, we have

$$\frac{d\mu}{dz} = \frac{\partial \mu}{\partial p} \frac{dp}{dz} + \frac{\partial \mu}{\partial s} \frac{ds}{dz} = 0$$

$$\left(\frac{\partial s}{\partial p}\right)_\mu = - \frac{\partial \mu / \partial p}{\partial \mu / \partial s} = - \frac{\partial x / \partial s}{\partial \mu / \partial s}$$

2.23

$$\left(\frac{ds}{dz}\right)_\mu = -\Gamma_s = 89 \frac{\partial x}{\partial s} / \frac{\partial \mu}{\partial s} \sim 3-4\% / 1000 \text{ m.}$$

The salinity increases slightly with pressure in the equilibrium state to offset the effect of gravity.

Conduction and Diffusion

If the distribution of temperature and salinity deviates from the equilibrium, heat conduction and salt diffusion will tend to restore the equilibrium gradients. The flux of heat and salt will depend on the difference between actual and equilibrium gradients. In the absence of turbulent motion, the molecular transport processes will reduce the vertical temperature gradient to zero and the salinity gradient to $-\Gamma_s$, i.e., reduce the gradient of μ to zero.

Assuming the flux of heat and salt to be proportional to the gradients, we may express the fluxes in the form

$$F^Q = -k_Q \frac{dT}{dz} \text{ (heat)}$$

2.24

and

$$F^S = -k_s \left[\frac{dS}{dz} + \Gamma_s \right] \quad (\text{salt}) \quad 2.25$$

If turbulence is present, turbulent transport processes will tend to equalize salinity and entropy rather than temperature and chemical potential difference. Hence, under the 'mixing-length' hypothesis, the turbulent fluxes would be of the form

$$F^Q = -k'_Q \left(\frac{dT}{dz} + \Gamma \right) \quad 2.26$$

$$F^S = -k_s \left(\frac{dS}{dz} \right) \quad 2.27$$

where k'_Q and k_s are eddy coefficients of conductivity and diffusivity respectively.

Values of the molecular conductivity k , diffusivity D and viscosity μ for sea water are not accurately known. Montgomery (1957) gives the values

$$\begin{aligned} k_Q / \rho C_p = K &= 0.00139 \text{ (0}^\circ\text{C, 35\%.)} \\ &= 0.00149 \text{ (20}^\circ\text{C, 35\%.)} \end{aligned}$$

$$\begin{aligned} k_s / \rho &= D = 0.0000068 \text{ (0}^\circ\text{C, 35\%.)} \\ &= 0.0000129 \text{ (20}^\circ\text{C, 35\%.)} \end{aligned}$$

$$\begin{aligned} \mu / \rho &= \nu = 0.01826 \text{ (0}^\circ\text{C, 35\%.)} \\ &= 0.01075 \text{ (20}^\circ\text{C, 35\%.)} \end{aligned}$$

The Prandtl number ν/k for sea water is 13.1 at 0°C and 7.0 at 20°C for a salinity of 35%. To a very rough order of approximation, we can take the ratios of salt and heat diffusivity and viscosity to be

$$D : K : \nu = 1 : 100 : 1000 \quad 2.28$$

The values of the coefficients for turbulent transport are apparently much higher and show considerable variability (Sverdrup et al, 1942).

Summary of thermodynamical definitions and relationships

The variables normally measured in the ocean are temperature, salinity and pressure. We shall regard these as the independent variables.

General Definitions (After Guggenheim, 1950)

The thermodynamic functions (internal energy, entropy, specific volume, etc.), denoted by the general function ϕ , are related to the partial functions, ϕ_s and ϕ_w , by

$$\phi = s\phi_s + (1-s)\phi_w$$

where

$$\phi_s = \phi + (1-s) \frac{\partial \phi}{\partial s}$$

$$\phi_w = \phi - s \frac{\partial \phi}{\partial s}$$

By subtraction

$$\frac{\partial \phi}{\partial s} = \phi_s - \phi_w$$

Thermodynamic Potential g

$$g = e - T\eta + p\alpha$$

$$= \mu_s + \mu_w$$

$$= s\mu_s + (1-s)\mu_w = sg_s + (1-s)g_w$$

$$dg = -\eta dT + \alpha dp + \mu ds$$

Internal energy e

$$\begin{aligned}
 e &= g + T\eta - p\alpha = g - T \frac{\partial g}{\partial T} - p \frac{\partial g}{\partial p} \\
 &= se_s + (1-s)e_w \\
 de &= Td\eta - pd\alpha + \mu ds \\
 &= \left(C_p - p \frac{\partial \alpha}{\partial T}\right) dT - \left(p \frac{\partial \alpha}{\partial p} + T \frac{\partial \alpha}{\partial T}\right) dp + \left(\mu - T \frac{\partial \mu}{\partial T} - p \frac{\partial \mu}{\partial p}\right) ds
 \end{aligned}$$

Enthalpy h

$$\begin{aligned}
 h &= e + p\alpha = g + T\eta = g - T \frac{\partial g}{\partial T} \\
 &= sh_s + (1-s)h_w \\
 dh &= Td\eta + \alpha dp + \mu ds \\
 &= C_p dT + \left(\alpha - T \frac{\partial \alpha}{\partial T}\right) dp + \left(\mu - T \frac{\partial \mu}{\partial T}\right) ds
 \end{aligned}$$

Free energy f

$$\begin{aligned}
 f &= e - T\eta = g - p\alpha = g - p \frac{\partial g}{\partial p} \\
 &= sf_s + (1-s)f_w \\
 df &= -\eta dT - pd\alpha + \mu ds \\
 &= -\left(\eta - p \frac{\partial \eta}{\partial p}\right) dT - p \frac{\partial \alpha}{\partial p} dp + \left(\mu - p \frac{\partial \mu}{\partial p}\right) ds
 \end{aligned}$$

Entropy η

$$\begin{aligned}
 \eta &= - \frac{\partial g}{\partial T} \\
 &= s\eta_s + (1-s)\eta_w \\
 d\eta &= \frac{1}{T} de + \frac{p}{T} d\alpha - \frac{\mu}{T} ds \\
 &= \frac{C_p}{T} dT - \frac{\partial \alpha}{\partial T} dp - \frac{\partial \mu}{\partial T} ds
 \end{aligned}$$

Specific Volume α

$$\begin{aligned}\alpha &= \partial g / \partial p \\ &= s\alpha_s + (1-s)\alpha_w \\ \alpha_s &= \alpha + (1-s) \frac{\partial \alpha}{\partial s} \\ \alpha_w &= \alpha - s \frac{\partial \alpha}{\partial s}\end{aligned}$$

Derived relationships

$$\begin{aligned}\frac{\partial^2 g}{\partial T \partial s} &= - \frac{\partial \eta}{\partial s} = \frac{\partial \mu}{\partial T} \\ \frac{\partial^2 g}{\partial T \partial p} &= \frac{\partial \alpha}{\partial T} = - \frac{\partial \eta}{\partial p} \\ \frac{\partial^2 g}{\partial s \partial p} &= \frac{\partial \mu}{\partial p} = \frac{\partial \alpha}{\partial s}\end{aligned}$$

Specific Heat C_p

$$\begin{aligned}C_p &= T \frac{\partial \eta}{\partial T} = - T \frac{\partial^2 g}{\partial T^2} \\ \frac{\partial C_p}{\partial p} &= - T \frac{\partial^2 \alpha}{\partial T^2} \\ \frac{\partial C_p}{\partial s} &= - T \frac{\partial^2 \mu}{\partial T^2}\end{aligned}$$

Isometric heating ($d\alpha = ds = 0$)

$$\begin{aligned}Td\eta &= C_p dT - T \frac{\partial \alpha}{\partial T} dp = C_v dT \\ d\alpha &= \frac{\partial \alpha}{\partial T} dT + \frac{\partial \alpha}{\partial p} dp = 0\end{aligned}$$

For $dT \neq 0$, the determinant of the coefficients must vanish, i.e.,

$$\begin{vmatrix} C_p - C_v & - T \frac{\partial \alpha}{\partial T} \\ \frac{\partial \alpha}{\partial T} & \frac{\partial \alpha}{\partial p} \end{vmatrix} = 0$$

therefore,

$$C_p - C_v = -T \left(\frac{\partial \alpha}{\partial T} \right)^2 / \frac{\partial \alpha}{\partial p} > 0$$

Adiabatic pressure changes ($d\eta = ds = 0$)

$$d\eta = \frac{C_p dT}{T} - \frac{\partial \alpha}{\partial T} dp = 0$$

$$\left(\frac{\partial T}{\partial p} \right)_\eta = T / C_p \frac{\partial \alpha}{\partial T}$$

Adiabatic compressibility ($d\eta = ds = 0$)

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

$$d\eta = \frac{C_p}{T} dT - \frac{\partial \alpha}{\partial T} dp = 0$$

for $dp \neq 0$, the determinant of the coefficients of dp and dT must vanish, i.e.

$$\begin{vmatrix} \frac{\partial \alpha}{\partial T} & - \left[\left(\frac{\partial \alpha}{\partial p} \right)_\eta - \frac{\partial \alpha}{\partial p} \right] \\ \frac{C_p}{T} & - \frac{\partial \alpha}{\partial T} \end{vmatrix} = 0 =$$

$$\begin{aligned} \therefore \left(\frac{\partial \alpha}{\partial p} \right)_\eta &= \frac{\partial \alpha}{\partial p} + \frac{T}{C_p} \left(\frac{\partial \alpha}{\partial T} \right)^2 \\ &= \frac{C_v}{C_p} \frac{\partial \alpha}{\partial p} = \frac{1}{\sigma} \frac{\partial \alpha}{\partial p} \end{aligned}$$

References:

- Craig, H., 1960. The Thermodynamics of Sea Water. Proc.Natl. Acad.Sci.; 46, (9); 1221-1225.
- Guggenheim, E.A. Thermodynamics. An advanced treatment for chemists and physicists. North-Holland Publ. Co., Amsterdam; Interscience Publ., Inc., New York, 1950.
- Montgomery, R.B. Oceanographic data. American Institute of Physics handbook. Sec. 2, Mechanics, 115-124. McGraw-Hill Book Co., New York, 1957.
- Sverdrup, H.V., M.W.Johnson, and R.H.Fleming. The Oceans. Prentice-Hall Inc. New York, 1942.

Total energies for a column of sea water

We can define the total energy of a column of sea water to be equal to the sum of the energies in each phase even though equilibrium between phases does not exist. The total energy can then be expressed as an integral over depth of the specific energy content.

Thus, the total internal energy E is given by

$$E = \int_{z_B}^{z_S} \rho e dz = \int_0^M e dm \quad 3.1$$

where z_S and z_B are the surface and bottom of the ocean respectively,

ρ is density, M the total mass of the column (of unit cross section) and m a mass coordinate defined by

$$m(z) = \int_{z_B}^z \rho dz, \quad z - z_B = \int_0^m \alpha dm. \quad 3.2$$

The total enthalpy H is given by

$$\begin{aligned} H &= \int_0^M h dm = \int_0^M (e + p\alpha) dm \\ &= E + p \left(\alpha dm \right)_0^M - \int_0^M \frac{dp}{dm} \alpha dm \\ &= E + P_s z_s + \int_0^M g (z - z_B) dm \\ &= E + P_s z_s + \chi \end{aligned} \quad 3.3$$

where χ is the potential energy relative to the bottom of the ocean z_B . If we neglect the contribution to (3.3) by atmospheric pressure, we obtain the simple relationship

$$H = E + \chi \quad 3.4$$

Changes of total enthalpy for which the total mass of the column is constant, are given by

$$\begin{aligned}
\Delta H = \Delta E + \Delta X &= \Delta \int_0^M h dm = \int_0^M \Delta h dm \\
&= \int_0^M \Delta e dm + \int_0^M \Delta(p\alpha) dm
\end{aligned}
\tag{3.5}$$

We have already seen that (3.5) is true for the isentropic interchange of fluid elements (Table I).

If a change or deformation takes place in a portion of the column centered about m_0 corresponding to a level z_0 , and extending from $m_0 - m/2$ to $m_0 + m/2$, the change of potential energy is given by

$$\begin{aligned}
\Delta X &= \Delta H - \Delta U = \int_0^M \Delta(p\alpha) dm \\
&= \int_{m_0 - m/2}^{m_0 + m/2} \Delta(p\alpha) dm
\end{aligned}
\tag{3.6}$$

as no change of $p\alpha$ occurs outside of the subsystem m .

Thus, the total potential energy change can be determined from (3.5) by integrating only over the portion of the system in which the deformation takes place.

Non-isentropic and Isenthalpic Deformations

Having obtained and reviewed some of the necessary thermodynamical concepts, we can examine the energy transformations associated with non-isentropic or irreversible deformations. We have derived and listed in Table I the energy changes associated with the isentropic interchange of two elements of sea water of equal mass separated by a unit vertical distance. We now let the heat and salt from these elements diffuse into the surrounding fluid.

The diffusion is assumed to take place at constant pressure so that no further change of enthalpy takes place. However, a change of volume and hence, of internal and potential energy, accompanies the diffusion. As enthalpy does not change, the change of internal energy must be equal and opposite to the change of potential energy (Equation 3.5). Adding these additional energy changes to the changes derived previously, we obtain the parameters

$$E_h = E_{h\eta} \quad 3.7$$

$$E_e = E_{e\eta} - pV\alpha \quad 3.8$$

$$E_x = E_{x\eta} + pV\alpha \quad 3.9$$

where, from (1.11),

$$V_\alpha = - \left[\delta_{\nu s}^2 \alpha - \frac{\partial \alpha}{\partial \nu} \frac{\delta_{\nu s}^2 h}{c_p} \right] \approx - \delta_{\nu s}^2 \alpha \quad 3.10$$

The deformation, consisting of an isentropic interchange followed by diffusion, can be regarded as rudimentary form of turbulent mixing. Elements of fluid are displaced mechanically and diffused into their new surroundings. The energy for the displacement must come from the kinetic energy of the motion. As the total deformation is irreversible, there is a conversion of kinetic energy into internal and potential energy.

Let us assume that the energy for the vertical displacement comes entirely from the vertical component of velocity and that the horizontal component of momentum is conserved throughout the deformation. Under these conditions, some kinetic energy of

the horizontal motion is converted into other forms. If a mass m_1 with horizontal velocity v_1 is mixed with a mass m_2 with velocity v_2 , momentum is conserved if the final velocity v is such that

$$mv - (m_1 v_1 + m_2 v_2) = 0 \quad 3.11$$

The total kinetic energy changes by an amount

$$\Delta K = \frac{1}{2} m v^2 - \left(\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \right) = -\frac{1}{2} m \left(\frac{m_1 m_2}{m^2} \right) (v_2 - v_1)^2 \quad 3.12$$

In the deformation that we have considered, the difference of velocities between the two elements of fluid is

$$v_2 - v_1 = \frac{dv}{dz} dz \quad 3.13$$

so that the kinetic energy change per unit mass is

$$\Delta K = - \left(\frac{dv}{dz} \right)^2 dz^2 = - E_K dz^2 \quad 3.14$$

The work required to produce the interchange is E_h and the kinetic energy converted from horizontal motion is E_K . It can be argued that if the loss of kinetic energy by the deformation is greater than the energy required to produce the deformation, the system is unstable and the deformation will occur spontaneously. Richardson (1920) introduced a parameter similar to the ratio

$$R_i = E_h / E_K = \frac{E_h}{\left(\frac{dv}{dz} \right)^2} \quad 3.15$$

as a criterion for the development of turbulence. If the ratio is greater than unity, turbulence will decay or be absent. The ratio (3.15) is called the Richardson number. It is generally very

large in the ocean with values of the order of 10^5 in weak currents but may approach unity in strong currents such as the Gulf Stream.

It does not provide an unambiguous index for the development of turbulence and attempts have been made without much success to make it more meaningful by including eddy viscosity and diffusivity. It may be more meaningful in discussing the stability of more highly organized motion such as internal waves.

Isenthalpic Deformations

A deformation similar to that described above can take place by molecular diffusion. We shall consider a segment of water of mass m . In the general case there will be a diffusion of heat, salt, and water into and within the segment. Assuming no lateral exchange, we may write the conservation equations

$$\Delta \int_{M_0 - m/2}^{M_0 + m/2} dm = 0 \quad (3.16)$$

$$\Delta \int_{M_0 - m/2}^{M_0 + m/2} S dm = -(F_s^2 - F_s') \Delta t \quad (3.17)$$

$$\Delta \int_{M_0 - m/2}^{M_0 + m/2} h dm = -(F_h^2 - F_h') \Delta t \quad (3.18)$$

where F_s and F_h are the salt and enthalpy fluxes, and Δt is a time interval for the deformation.

Expanding in a Taylor Series about M_0 , we obtain

$$-(F_s^2 - F_s') \Delta t = \Delta S_0 m + \frac{1}{24} \Delta \frac{d^2 S}{dm^2} m^3 + \dots \quad (3.19)$$

$$-(F_h^2 - F_h') \Delta t = \Delta h_0 m + \frac{1}{24} \Delta \frac{d^2 h}{dm^2} m^3 + \dots \quad (3.20)$$

Applying these basic conservation laws, we obtain the change for a general property φ

$$\Delta \int_{m_0 - m/2}^{m_0 + m/2} \varphi dm = \Delta \varphi_0 m + \frac{1}{24} \Delta \varphi_{mm} m^3 + \left(\frac{\partial \varphi}{\partial h} \Delta h_0 + \frac{\partial \varphi}{\partial S} \Delta S_0 \right) m + \frac{1}{24} \Delta \varphi_{mm} m^3 + \quad 3.21$$

Substituting for ΔS_0 and Δh_0 from (3.13) and (3.14), we have

$$\begin{aligned} \Delta \int \varphi dm &= -\frac{\partial \varphi}{\partial h} (F_n^2 - F_n^1) \Delta t - \frac{\partial \varphi}{\partial S} (F_s^2 - F_s^1) \Delta t + \frac{1}{24} \Delta \left(\frac{d^2 \varphi}{dm^2} - \frac{\partial \varphi}{\partial h} \frac{d^2 h}{dm^2} - \frac{\partial \varphi}{\partial S} \frac{d^2 S}{dm^2} \right) m^3 \\ &= - \left[\frac{\partial \varphi}{\partial h} (F_h^2 - F_h^1) + \frac{\partial \varphi}{\partial S} (F_s^2 - F_s^1) \right] \Delta t + \frac{1}{12} \left\{ \frac{d}{dm} \left(\frac{\partial \varphi}{\partial h} \right) \Delta \frac{dh}{dm} + \frac{d}{dm} \left(\frac{\partial \varphi}{\partial S} \right) \Delta \frac{dS}{dm} \right\} m^3 \end{aligned} \quad 3.22$$

Case 1 $(F^2, F^1) \neq 0$, open system

From the Taylor expansion, we obtain

$$\begin{aligned} \Delta \int_{m_0}^{m_0 + m/2} h dm - \Delta h_0 m/2 + \frac{1}{8} \Delta h_{mm} m^2 + \frac{1}{48} \Delta h_{mmm} m^3 + \dots &= -(F_n^2 - F_n^1) \Delta t \\ \Delta \int_{m_0 - m/2}^{m_0} h dm = \Delta h_0 m/2 - \frac{1}{8} \Delta h_{mm} m^2 + \frac{1}{48} \Delta h_{mmm} m^3 - \dots &= -(F_n^1 - F_n^2) \Delta t \end{aligned} \quad 3.23$$

so that

$$\begin{aligned} \frac{1}{4} \Delta h_{mm} m^2 &= -(F_n^2 + F_n^1 - 2F_0) \Delta t \\ &\approx -\frac{1}{4} \frac{d^2 F_n}{dm^2} m^2 \Delta t \end{aligned} \quad 3.24$$

Hence

$$\Delta h_m \approx - \frac{d^2 F_h}{dm^2} \Delta t$$

A similar expression is obtained for ΔS_m .

Approximating $F_h^2 - F_h^1$ by dF_h/dm and $F_s^2 - F_s^1$ by $\frac{\partial F_s}{\partial m} m$

we obtain

$$\Delta(\varphi dm) = - \left\{ \frac{\partial \varphi}{\partial h} \frac{dF_h}{dm} + \frac{\partial \varphi}{\partial s} \frac{dF_s}{dm} \right\} m \Delta t + o(\Delta t m^2) \quad 3.25$$

Hence the rate of change of φ per unit mass per unit time is

$$\frac{\partial \varphi}{\partial t} = - \frac{\partial \varphi}{\partial h} \frac{dF_h}{dm} - \frac{\partial \varphi}{\partial s} \frac{dF_s}{dm} \quad 3.26$$

Case II $F^2 = F^1 = 0$ (isolated system)

In the case of an isolated system,

$$\Delta h_m = + 8 F_h^0 \Delta t / m^2 \quad 3.27$$

$$\Delta s_m = + 8 F_s^0 \Delta t / m^2 \quad 3.28$$

and

$$\Delta(\varphi dm) = + 2/3 \left\{ \frac{d}{dm} \left(\frac{\partial \varphi}{\partial h} \right) F_h^0 + \frac{d}{dm} \left(\frac{\partial \varphi}{\partial s} \right) F_s^0 \right\} m \Delta t. \quad 3.29$$

Neglecting the numerical coefficient, we obtain for the rate of change of φ per unit mass and time the expression

$$\frac{\partial \varphi}{\partial t} = + \left[\frac{d}{dm} \left(\frac{\partial \varphi}{\partial h} \right) F_h + \frac{d}{dm} \left(\frac{\partial \varphi}{\partial s} \right) F_s \right] = q\varphi \quad 3.30$$

As we are considering an isolated system, we can consider $q\varphi$ as the internal source of φ due to diffusion. The open system

(3.26) can be written

$$\begin{aligned} \frac{\partial \varphi}{\partial t} &= - \frac{d}{dm} \left(\frac{\partial \varphi}{\partial h} F_h + \frac{\partial \varphi}{\partial s} F_s \right) + \left[\frac{d}{dm} \left(\frac{\partial \varphi}{\partial h} \right) F_h + \frac{d}{dm} \left(\frac{\partial \varphi}{\partial s} \right) F_s \right] \\ &= - \frac{dF_\varphi}{dm} + q\varphi \end{aligned} \quad 3.31$$

Hence, we can consider the change of a general property φ due to diffusion as being equivalent to a diffusive flux F_φ and an internal source q_φ . In general, all properties, except enthalpy and salt content, will have a non-zero source in diffusion processes.

The explicit expressions for the fluxes and sources for entropy and internal energy are

1. Entropy flux F_η

$$F_\eta = \frac{\partial \eta}{\partial h} F_h + \frac{\partial \eta}{\partial s} F_s = \frac{F_h}{T} + \left(\frac{\partial \eta}{\partial s} \right)_h F_s \quad 3.32$$

Substituting

$$\begin{aligned} \left(\frac{\partial \eta}{\partial s} \right)_h &= \left(\frac{\partial \eta}{\partial s} \right)_T + \left(\frac{\partial \eta}{\partial T} \right)_s \left(\frac{\partial T}{\partial s} \right)_h = \left(\frac{\partial \eta}{\partial s} \right)_T - \frac{h_s}{T} \\ &= -\frac{\partial \mu}{\partial T} - \frac{\mu - T \partial \mu / \partial T}{T} = -\mu / T \end{aligned} \quad 3.33$$

we obtain

$$F_\eta = \frac{F_h}{T} - \frac{\mu}{T} F_s = \frac{F_q}{T} - \frac{\partial \mu}{\partial T} F_s \quad 3.34$$

where $F_q = F_h - h_s F_s$ is interpreted as a "heat" flux.

2. Entropy source q_η

$$\begin{aligned} q_\eta &= \frac{d}{dm} \left(\frac{\partial \eta}{\partial h} \right) F_h + \frac{d}{dm} \left(\frac{\partial \eta}{\partial s} \right) F_s \\ &= -\frac{1}{T^2} \frac{dT}{dm} F_q - \frac{1}{T} \frac{\partial \mu}{\partial s} \left[\frac{ds}{dm} + \Gamma_s \right] F_s \end{aligned} \quad 3.35$$

where

$$\Gamma_s = -g \frac{\partial \mu / \partial p}{\partial \mu / \partial s} = g \frac{\partial \sigma / \partial s}{\partial \mu / \partial s} = - \left(\frac{\partial s}{\partial m} \right)_\mu$$

3. Internal energy flux F_e

$$\begin{aligned}
 F_e &= \left(1 - p \frac{\partial \alpha}{\partial h}\right) F_h - p \frac{\partial \alpha}{\partial s} F_s \\
 &= F_h - \frac{p}{c_p} \frac{\partial \alpha}{\partial T} F_q - p \frac{\partial \alpha}{\partial s} F_s
 \end{aligned}
 \tag{3.36}$$

4. Internal energy source q_e

$$\begin{aligned}
 q_e &= \frac{d}{dm} \left(\frac{de}{dh} \right) F_h + \frac{d}{dm} \left(\frac{\partial e}{\partial s} \right) F_s \\
 &= - \left[\frac{d}{dm} \left(p \frac{\partial \alpha}{\partial h} \right) \right] F_q + \left[\frac{d}{dm} \left(p \frac{\partial \alpha}{\partial s} \right) \right] F_s \\
 &= - \left\{ \left[\frac{d}{dm} \left(p \frac{\partial \alpha}{\partial T} \right) \right] \frac{F_q}{c_p} + \left[\frac{d}{dm} \left(p \frac{\partial \alpha}{\partial s} \right) \right] F_s \right\} \\
 &\quad + \frac{p}{c_p} \frac{\partial \alpha}{\partial T} \left[\frac{dc_p}{dm} \frac{F_q}{c_p} + \frac{dh_s}{dm} F_s \right]
 \end{aligned}
 \tag{3.37}$$

Exercises

1. Show that the parameter E_x giving the total change of potential energy for an isentropic interchange followed by diffusion can be expressed in the form, similar to (3.30),

$$E_x = E_{h\eta} - E_{e\eta} - pV_\alpha$$
$$= - \left\{ \frac{d}{dz} \left[p \frac{\partial \alpha}{\partial \eta} \right] \left[\frac{dh}{dz} - \left(\frac{\partial h}{\partial z} \right)_\eta \right] + \frac{d}{dz} \left[p \frac{\partial \alpha}{\partial s} \right] \frac{ds}{dz} \right\} + p \frac{\partial \alpha}{\partial h} E_h.$$

2. Derive an expression for the entropy change for the deformation considered in Exercise 1.

The Navier-Stokes Equations

We have examined in detail the various energy transformations that occur if a stratified fluid such as a layer of sea water is deformed in a simple and completely specified way. Non-linearities in the dependence of specific volume on temperature and salinity result in internal "sources" of kinetic energy leading to changes of potential energy of the layer and the surrounding medium.

Having examined the energy transformations in simple deformations, we can now interpret them in a more general form in the Navier-Stokes equations for momentum and energy conservation. We shall also try to assess the possible importance of the energy changes in geophysical systems.

The general conservation equations for momentum and energy for a sea-water system are complicated by the presence of the dissolved salts. We shall, therefore, examine briefly the derivation of the general equations.

The momentum balance in a finite volume fixed relative to the earth is expressed by

$$\frac{\partial}{\partial t} \int_V \rho u_i dV = - \int_S \rho u_i u_j n_j dA - \int_V 2\epsilon_{ijA} \Omega_j \rho u_A dV$$

Rate of change of momentum Convection of momentum by current u_i Momentum change due to Coriolis force

$$- \int_S p \delta_{ij} n_j dA - \int_V \rho \frac{\partial \phi}{\partial x_i} dV$$

Momentum change due to net pressure force Momentum change due to gravity

$$+ \int_S \tau_{ij} n_j dA \tag{4.1}$$

Momentum change due to net viscous force.

The unit vector n_i is directed outward and perpendicular to the surface of integration.

Applying the divergence theorem

$$\int_S \phi_j n_j dA = \int_V \frac{\partial \phi_j}{\partial x_j} dV \tag{4.2}$$

to (4.1) to reduce all integrals to volume integrals and assuming that the volume can be chosen arbitrarily we obtain the momentum conservation equations

$$\frac{\partial \rho u_i}{\partial t} + \frac{\partial \rho u_i u_j}{\partial x_j} - 2\epsilon_{ijA} \Omega_j \rho u_A = - \frac{\partial p}{\partial x_i} - \rho \frac{\partial \phi}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} \tag{4.3}$$

that must be satisfied at every point of the fluid.

For the kinetic and internal energies, we have

$$\begin{aligned}
 \frac{\partial}{\partial t} \int_V \rho(e+k) dV &= - \int_S \rho(e+k) u_j n_j dA - \int_V \rho u_j \frac{\partial \phi}{\partial x_j} dV \\
 &\quad \text{convection by} \qquad \qquad \qquad \text{rate of work} \\
 &\quad \qquad \qquad \qquad \qquad \qquad \text{current} \qquad \qquad \qquad \text{against gravity} \\
 &\quad - \int_S \rho u_j n_j dA \qquad + \int_S u_i \tau_{ij} n_j dA \\
 &\quad \text{rate of work} \qquad \qquad \qquad \text{rate of work} \\
 &\quad \text{against pressure} \qquad \qquad \text{against viscous forces} \\
 &\quad - \int_S F_j n_j dA \qquad \qquad \qquad 4.4 \\
 &\quad \text{net diffusion of} \\
 &\quad \text{internal energy}
 \end{aligned}$$

Transforming to volume integrals, we obtain

$$\frac{\partial \rho(e+k)}{\partial t} + \frac{\partial \rho(e+k)u_j}{\partial x_j} = - \frac{\partial \rho u_j}{\partial x_j} - \rho u_j \frac{\partial \phi}{\partial x_j} - \frac{\partial F_j}{\partial x_j} + \frac{\partial u_i \tau_{ij}}{\partial x_j} \qquad 4.5$$

for the conservation of kinetic and internal energy at a point.

In addition to the momentum and energy conservation equations, we have two equations expressing the conservation of mass and salt. These equations have the form

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_j}{\partial x_j} = 0 \qquad 4.6$$

or

$$\rho \frac{D\alpha}{Dt} = \frac{\partial u_j}{\partial x_j} \alpha \qquad 4.7$$

where

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u_j \frac{\partial}{\partial x_j} \qquad 4.8$$

for the conservation of mass and

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \rho s u_j}{\partial x_j} = - \frac{\partial F_j^s}{\partial x_j} \quad 4.9$$

for the conservation of salt, the flux of salt relative to the motion of the fluid is denoted by F_j^s .

Using (4.6), we obtain the transformation

$$\frac{\partial \rho \phi}{\partial t} + \frac{\partial \rho \phi u_j}{\partial x_j} = \rho \frac{D\phi}{Dt} \quad 4.10$$

for a general property ϕ .

From the momentum equation, we obtain by contraction

with u_i :

$$\rho \frac{D(\kappa + \phi)}{Dt} = - u_j \frac{\partial P}{\partial x_j} + u_i \frac{\partial \tau_{ij}}{\partial x_j} \quad 4.11$$

for the rate of change of "mechanical" energy.

Subtracting (4.11) from (4.5), we find that the internal energy change is given by

$$\rho \frac{De}{Dt} = - \rho \frac{\partial u_j}{\partial x_j} - \frac{\partial F_j^i}{\partial x_j} + \tau_{ij} \frac{\partial u_i}{\partial x_j} \quad 4.12$$

The term $\tau_{ij} \frac{\partial u_i}{\partial x_j}$ is the dissipation function for kinetic energy and is assumed to be positive definite.

Enthalpy Equation

Substituting (4.7) for the velocity divergence, we obtain the enthalpy equation

$$\rho \frac{Dh}{Dt} = \rho \frac{D(e + p\alpha)}{Dt} = \frac{DP}{Dt} - \frac{\partial F_j^i}{\partial x_j} + q_k \quad 4.13$$

where q_k is introduced for the dissipation function $\tau_{ij} \frac{\partial u_i}{\partial x_j}$.

For an isentropic flow

$$\left(\frac{Dh}{Dt}\right)_\eta = \alpha \frac{DP}{Dt}, \quad 4.14$$

hence, we may write (4.13) in the form

$$\rho \left[\frac{Dh}{Dt} - \left(\frac{Dh}{Dt}\right)_\eta \right] = -\frac{\partial F_i}{\partial x_j} + q_k \quad 4.15$$

From (4.15), we see that the enthalpy change by non-isentropic processes consists of the diffusion of enthalpy into the region and the creation of enthalpy by the dissipation of kinetic energy. The dissipation of kinetic energy is the only internal source of enthalpy.

From the thermodynamical relationship

$$\frac{Dh}{Dt} = T \frac{D\eta}{Dt} + \alpha \frac{DP}{Dt} + \mu \frac{DS}{Dt} \quad 4.16$$

we can derive the relationship

$$\begin{aligned} \rho \left[\frac{Dh}{Dt} - \left(\frac{Dh}{Dt}\right)_\eta \right] &= \rho C_p \left[\frac{DY}{Dt} - \eta \frac{DP}{Dt} \right] + \rho h_s \frac{DS}{Dt} \\ &= -\frac{\partial F_i}{\partial x_j} + q_k \end{aligned} \quad 4.17$$

Substituting for $\rho \frac{DS}{Dt}$ from (4.9) and rearranging terms, we obtain

$$\begin{aligned} \rho C_p \left[\frac{DY}{Dt} - \left(\frac{DY}{Dt}\right)_\eta \right] &= -\frac{\partial (F_j - h_s F_j^s)}{\partial x_j} - \frac{\partial h_s}{\partial x_j} F_j^s + q_k \\ &= -\frac{\partial F_j^q}{\partial x_j} - \frac{\partial h_s}{\partial x_j} F_j^s + q_k \end{aligned} \quad 4.18$$

where

$$\left(\frac{D\eta}{Dt}\right)_\eta = \Gamma \frac{DP}{Dt} \quad 4.19$$

$$F_i^{\eta} = F_i^h - h_s F_i^s \quad 4.20$$

The flux F_i^{η} can be interpreted as a heat flux. The term $\frac{\partial h_s}{\partial x_j} F_j^s$ is of the form of a source and represents the heat of mixing of the fluid. For zero temperature and pressure gradients, it reduces to the more usual form of the heat of mixing (heat of dilution $\frac{\partial h_s}{\partial s} \frac{\partial s}{\partial x_j} F_j^s$).

Entropy Equation

The entropy equation can be formulated from the equation

$$\frac{D\eta}{Dt} = \frac{1}{T} \frac{Dh}{Dt} - \frac{\alpha}{T} \frac{DP}{Dt} - \frac{\mu}{T} \frac{Ds}{Dt} \quad 4.21$$

Multiplying through by the density ρ and substituting the fluxes for enthalpy and salt, we have

$$\rho \frac{D\eta}{Dt} = -\frac{1}{T} \frac{\partial F_j^h}{\partial x_j} + \frac{q_k}{T} + \frac{\mu}{T} \frac{\partial F_j^s}{\partial x_j} \quad 4.22$$

Writing (4.22) in the form of a flux and a source, we obtain

$$\rho \frac{D\eta}{Dt} = -\frac{\partial}{\partial x_j} \underbrace{\left[\frac{F_j^h}{T} - \frac{\mu}{T} F_j^s \right]}_{\text{Flux } F_\eta} - \underbrace{\left[\frac{1}{T^2} \frac{\partial T}{\partial x_j} F_j^h - \frac{\partial \mu / T}{\partial x_j} F_j^s + \frac{q_k}{T} \right]}_{\text{Source } g_\eta} \quad 4.22(a)$$

The source or rate of entropy production g_η can be further transformed to

$$g_\eta = \frac{q_k}{T} - \left[\frac{1}{T^2} \frac{\partial T}{\partial x_j} F_j^h + \frac{1}{T} \frac{\partial \mu}{\partial s} \left(\frac{\partial s}{\partial x_j} - \Gamma_s \frac{\partial P}{\partial x_j} \right) F_j^s \right] \quad 4.23$$

where

$$\Gamma_s \frac{\partial P}{\partial x_j} = \left(\frac{\partial s}{\partial x_j} \right)_\mu \quad 4.24$$

is the equilibrium salinity gradient in the presence of a pressure gradient $\partial P / \partial x_j$.

The entropy production is positive definite if we assume phenomenological laws for heat and salt flux of the form

$$F_i^q = -k \frac{\partial T}{\partial x_i} \quad 4.25$$

$$F_i^s = -D \left(\frac{\partial s}{\partial x_i} - \Gamma_s \frac{\partial P}{\partial x_i} \right) \quad 4.26$$

More generally, we can assume

$$F_i^q = -k \frac{\partial T}{\partial x_i} - l_{qs} \left(\frac{\partial s}{\partial x_i} - \Gamma_s \frac{\partial P}{\partial x_i} \right) \quad 4.27$$

$$F_i^s = -l_{sq} \frac{\partial T}{\partial x_i} - D \left(\frac{\partial s}{\partial x_i} - \Gamma_s \frac{\partial P}{\partial x_i} \right) \quad 4.28$$

In this case, the requirement for $q\eta$ to be positive definite implies

$$\left(l_{qs} + T \frac{\partial \mu}{\partial s} l_{sq} \right)^2 < 4T \frac{\partial \mu}{\partial s} kD \quad 4.29$$

The phenomenological laws relating fluxes to potentials or "forces" refer, strictly speaking, to molecular transport processes. The separation of the flow of energy, momentum or matter into convective and diffusive flux terms implies an averaging process at some microscopic scale. The velocity represents a mean velocity, weighted according to the mass of various molecules involved in the flow. Motion of particular molecules

relative to the mean represents diffusion.

On a macroscopic scale, the total flow of a property S , can be separated by averaging into convection, representing the flow $\bar{\rho} \bar{u} \bar{S}$ associated with the mean flow of mass $\bar{\rho} \bar{u}_i$, and a "diffusive" flux $\overline{(\rho u_i)' S'} + F_{i, mol}^S$, representing the flow relative to the mean flow of mass, where $(\rho u_i)'_i S'$ are deviations having zero average with respect to the particular averaging process chosen.

The macroscopic flux of heat and salt may be written

$$F_i^Q = \overline{(\rho u_i)' c_p (T' - T_p')} \approx \bar{\rho} \bar{c}_p \overline{(u_i' T')} \quad 4.30$$

$$F_i^S = \overline{(\rho u_i)' S'} \approx \bar{\rho} \overline{(u_i' S')} \quad 4.31$$

Eddy coefficients for heat and salt flux can be defined to be

$$K_i^Q = -F_i^Q / \bar{\rho} \bar{c}_p \partial T / \partial x_i = -\overline{(u_i' T')} / \partial T / \partial x_i \quad 4.32$$

$$K_i^S = -F_i^S / \bar{\rho} \partial S / \partial x_i = -\overline{(u_i' S')} / \partial S / \partial x_i \quad 4.33$$

For molecular processes, the flow of heat is more rapid than the flow of salt, i.e., $K^Q \gg K^S$. In many parts of the ocean, particularly in deep water, the spacial variation of temperature and salinity appears to be closely correlated so that the ratio $(\partial T / \partial S)$ is constant.

If the ratio is constant for the fluctuations also, we must have $K^Q = K^S$. Under certain conditions, the more rapid molecular thermal conduction can produce gravitational

instability resulting in salt convection by "salt fingers".
Viewed macroscopically, this process can imply $K^s > K^q$.
Hence, in interpreting the effects of the flux of heat and salt on energy conversion it is necessary to examine the relative effects of each type of flux.

Kinetic Energy Equation

The equation for conservation of mechanical energy (4.11), written in the form of a flux and a source, is

$$\rho \frac{D(K+\phi)}{Dt} = -\frac{\partial}{\partial x_j} (P u_j + u_i \tau_{ij}) + \rho \frac{\partial u_i}{\partial x_j} - q_k \quad 4.34$$

The term $\rho \frac{\partial u_i}{\partial x_j}$ is further transformed to

$$\begin{aligned} \rho \frac{\partial u_i}{\partial x_j} &= \rho \frac{D\alpha}{Dt} = \rho \left[\frac{\partial \alpha}{\partial h} \frac{Dh}{Dt} + \frac{\partial \alpha}{\partial P} \frac{DP}{Dt} + \frac{\partial \alpha}{\partial S} \frac{DS}{Dt} \right] \\ &= \rho \left\{ \frac{\partial \alpha}{\partial h} \left[\frac{Dh}{Dt} - \left(\frac{Dh}{Dt} \right)_\eta \right] + \frac{\partial \alpha}{\partial S} \frac{DS}{Dt} + \left[\alpha \frac{\partial \alpha}{\partial \eta} + \frac{\partial \alpha}{\partial P} \right] \frac{DP}{Dt} \right\} \quad 4.35 \end{aligned}$$

Substituting the enthalpy and salt flux, we obtain

$$\begin{aligned} \rho \frac{\partial u_i}{\partial x_j} &= \rho \left\{ \frac{\partial \alpha}{\partial h} \left(-\frac{\partial F_j^q}{\partial x_j} + q_k \right) - \frac{\partial \alpha}{\partial S} \frac{\partial F_j^s}{\partial x_j} \right\} + \rho \left(\frac{\partial \alpha}{\partial P} \right)_\eta \rho \frac{DP}{Dt} \\ &= -\frac{\partial}{\partial x_j} \left[\rho \frac{\partial \alpha}{\partial h} F_j^q + \rho \frac{\partial \alpha}{\partial S} F_j^s \right] + \left[\frac{\partial}{\partial x_j} \left(\rho \frac{\partial \alpha}{\partial h} \right) \right] F_j^q + \left[\frac{\partial}{\partial x_j} \left(\rho \frac{\partial \alpha}{\partial S} \right) \right] F_j^s - \rho \left(\frac{D\alpha}{Dt} \right)_\eta \\ &\quad + \rho \frac{\partial \alpha}{\partial h} q_k \quad 4.36 \end{aligned}$$

Converting further to temperature, we have

$$\begin{aligned} \rho \frac{\partial u_i}{\partial x_j} &= -\frac{\partial}{\partial x_j} \left[\rho \frac{\partial \alpha}{\partial T} \frac{F_j^q}{c_p} + \rho \frac{\partial \alpha}{\partial S} F_j^s \right] - \rho \left(\frac{D\alpha}{Dt} \right)_\eta \\ &\quad + \left[\frac{\partial}{\partial x_j} \left(\rho \frac{\partial \alpha}{\partial T} \right) \right] \frac{F_j^q}{c_p} + \left[\frac{\partial}{\partial x_j} \left(\rho \frac{\partial \alpha}{\partial S} \right) \right] F_j^s \\ &\quad + \frac{\rho}{c_p} \frac{\partial \alpha}{\partial T} \left[q_k - \left(\frac{\partial c_p}{\partial x_j} \frac{F_j^q}{c_p} + \frac{\partial h_s}{\partial x_j} F_j^s \right) \right] \quad 4.37 \end{aligned}$$

The final form of the mechanical energy equation can be obtained by substituting (4.37) for $p \partial u_j / \partial x_j$ in (4.34).

Part V.

Interpretation of the energy parameters

The energy parameters $E_h, E_{xy}, E_{e\eta}$ for isentropic and E_h, E_x, E_e for nonisentropic processes can be interpreted as unit deformations that indicate the direction of energy exchange in mixing processes. Multiplied by a diffusion coefficient, these parameters indicate the rates of energy conversion. As the parameters have been determined in terms of an isentropic exchange of unit masses of sea water, the exchange coefficients for heat and salts are equal. We can remove this restriction by introducing more general enthalpy and potential energy parameters of the form

$$\rho K_Q E_{hi}^* = -\rho g \left[\frac{\partial x}{\partial h} F_i + \frac{\partial x}{\partial s} F_i^s \right] \quad 5.1$$

$$\rho K_Q E_x^* = + \left[\frac{\partial}{\partial y_j} \left(\rho \frac{\partial x}{\partial z} \right) F_j + \frac{\partial}{\partial x_j} \left(\rho \frac{\partial x}{\partial s} \right) F_j^s \right] \quad 5.2$$

These parameters reduce to the one-dimensional form previously considered for

$$F_1 = F_2 = 0, \quad F_3 = -K_Q \left(\frac{dT}{dz} + \rho \right) - K_S \frac{ds}{dz} \quad 5.3$$

$$F_1^s = F_2^s = 0, \quad F_3^s = -K_S \frac{ds}{dz} \quad 5.4$$

and $K_Q = K_S$

Using the generalized parameters, we may write the equation for mechanical energy in the form

$$\rho \frac{D(K+\epsilon)}{Dt} = -\frac{\partial}{\partial x_j} (u_j T_{ij}) - (1 - \rho \frac{\partial x}{\partial h}) g_k - \rho \left(\frac{D\epsilon}{Dt} \right)_{ij}$$

$$\frac{\partial}{\partial x_j} \left[\rho K_a \left(\frac{p}{\rho g} \right) E_{h_j}^* \right] + \rho K_a E_x^* \quad 5.5$$

By adding $\frac{\partial P}{\partial t}$ to both sides of (5.5), we can transform the equation to

$$\rho \left[\frac{D(K+\epsilon + P)}{Dt} + \left(\frac{D\epsilon}{Dt} \right)_{ij} \right] = \frac{\partial P}{\partial t} + \frac{\partial}{\partial x_j} u_j T_{ij} - (1 - \rho \frac{\partial x}{\partial h}) g_k$$

$$+ \frac{\partial}{\partial x_j} \left[\rho K_a \hat{z} E_{h_j}^* \right] + \rho K_a E_x^* \quad 5.6$$

where

$$\left(\frac{D\epsilon}{Dt} \right)_{ij} = -\rho \frac{\partial x}{\partial p} \frac{DP}{Dt} \quad 5.7$$

$$\hat{z} = p/\rho g$$

Hydrostatic approximation

If we introduce the hydrostatic approximation

$$d\phi = -\alpha dp = g dz \quad 5.8$$

we can write

$$\phi = \phi_s - \int_{p_s}^p \alpha dp$$

$$= \phi_s + p_s \alpha_s - p \alpha - \int_{z_s}^z p \frac{\partial \alpha}{\partial z} dz \quad 5.9$$

where $\phi_s = \phi_0 + g z_s$ is the geopotential at the free surface $z = z_s$, and p_s, α_s the pressure (atmospheric) and specific volume at the surface. For convenience, we shall neglect atmospheric pressure, and neglect the term $p_s \alpha_s$ in (5.9).

We may write

$$\int_z^{z_s} p \frac{\partial x}{\partial z} dz = \int_z^{z_s} p \left[\frac{\partial x}{\partial r} \left(\frac{r}{\partial z} + \eta \right) + \frac{dx}{\partial s} \frac{\partial s}{\partial z} \right] dz + \int_z^{z_s} \frac{p}{\gamma} \frac{\partial x}{\partial p} \frac{\partial p}{\partial z} dz$$

$$= \int_z^{z_s} \hat{z} E_{\eta} dz - \int_0^p \frac{p}{\gamma} \frac{\partial x}{\partial p} dp \quad 5.10$$

Substitution of (5.9) and (5.10) into (5.6) yields

$$p \left[\frac{D}{Dt} (k + \phi_s - \int_z^{z_s} \hat{z} E_{\eta} dz) \right] = \frac{\partial p}{\partial t} + \frac{\partial u_i \bar{L}_j}{\partial x_j} - \bar{L}_R$$

$$+ \frac{\partial}{\partial x_j} (p K_Q \hat{z} E_{\eta j}^*) + p K_Q E_x^* \quad 5.11$$

where

$$\frac{D}{Dt} \int_0^p \frac{p}{\gamma} \frac{\partial x}{\partial p} dp - p/\gamma \frac{\partial x}{\partial p} \frac{Dp}{Dt} \quad 5.12$$

is assumed to be negligible. This is equivalent to assuming that the adiabatic compressibility $1/\gamma \frac{\partial x}{\partial p}$ is a function of pressure only, i.e., that no changes of internal energy can occur in isentropic processes. In the ocean, $E_{e\eta}$ is usually much less than E_{η} or $E_{x\eta}$, and the assumption seems reasonable. The term $\frac{p}{\gamma} \frac{\partial x}{\partial p}$ in the factor multiplying \bar{L}_R in (5.6) is also neglected. Its magnitude does not exceed 10^{-2} .

If we assume that the motion at some depth \bar{z}_m in the ocean is small so that horizontal pressure gradients can be neglected, we can evaluate ϕ_s .

As the kinetic energy at such a depth would be small, we have

$$\phi_s = \int_{\bar{z}_r}^{\bar{z}_m} \hat{z} E_{\eta} dz \quad 5.13$$

provided, of course, that strong fluxes of heat and salt do not occur at z_r . Hence, at every other layer in which the diffusive terms are negligible, steady flow must satisfy a Bernoulli equation of the form

$$K + \int_{z_i}^z E_h dz = \text{constant} \quad 5.14$$

along each streamline. Thus, the flow is sensitive to any processes that affect the stability E_h of deeper layers, and to changes of the elevation \hat{z} of the free surface.

For the hypothetical two-layer ocean,

$$(E_h = \frac{\Delta \rho}{\rho} g \delta(z - z_i), \delta - \text{delta function}),$$

(5.14) becomes zero for $z < z_i$ (lower layer) and

$$K + \frac{\Delta \rho}{\rho} g \hat{z}_i = K + \frac{\Delta \rho}{\rho} g h = \text{constant} \quad 5.15$$

for the upper layer, where $\hat{z}_i = h$ is the thickness of the upper layer.

Because the compressibility of sea water is slight, \hat{z} can be interpreted as the geometric distance to the free surface ($z_s - z$).

A simpler form of (5.11) can be obtained by assuming that only vertical diffusive fluxes are important. Assuming further that the diffusion coefficients for heat and salt are equal and constant, and that viscous stresses are of the form

$$\tau_{ij} = \tau_{iz} = -K_m \frac{\partial u_i}{\partial z} \quad 5.16$$

we obtain the energy equation

$$\frac{\partial}{\partial t} (\bar{K} + \bar{\phi}') = -\frac{\partial \bar{K}}{\partial z} + K_m \frac{\partial^2 \bar{K}}{\partial z^2} - \rho g \bar{K} + K_G \frac{\partial^2 \bar{\phi}'}{\partial z^2} + K_G E_y \quad 5.17$$

where

$$\bar{\phi} = \int_0^z E_y dz \quad 5.18$$

$$\rho g \bar{K} = \rho K_m \frac{\partial \bar{K}}{\partial z} \quad 5.19$$

Equation (5.17) contains two terms in the form of sources - the dissipation function $\rho g \bar{K}$ representing loss of kinetic energy and $K_G E_y$ representing production of potential energy due to heat and salt diffusion. The divergence terms $K_m \frac{\partial^2 \bar{K}}{\partial z^2}$ and $K_G \frac{\partial^2 \bar{\phi}'}{\partial z^2}$ redistribute the energy but do not create or destroy it. The time-derivative of pressure is present because no local horizontal accelerations can occur from a vertical shift of the mass field.

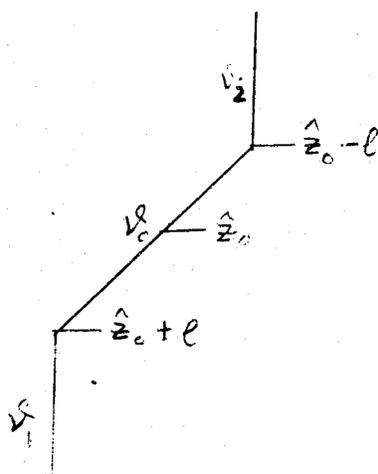
In a homogeneous layer, the flux terms vanish and $K + \phi'$ is constant along a streamline for steady flow. For steady flow in a two-layer ocean with a thermocline separating the layers, the energy balance equations become

$$\frac{\partial}{\partial t} \overline{\rho g (K + \phi')} = \overline{\rho K_G E_y} - \overline{\rho g K} \quad 5.20$$

where the bar indicates a vertical average. The contribution to the energy production comes entirely from the thermocline and is positive if $\overline{\rho K_G E_y}$ is greater than $\overline{\rho g K}$. It is

interesting to note that $\overline{E_x}$ is approximately zero over the Atlantic thermocline; the average is generally greater than zero ($E_x > 0$) in most other regions of the ocean.

It would be interesting to know more explicitly how the energy is distributed between K and ϕ' . We can gain some insight into the energy balance by considering a simple example. Suppose two homogeneous layers are separated by a



thermocline with a linear temperature gradient as shown in the adjacent diagram. The flow is assumed to be one dimensional in the x-direction diminishing to zero in the lower layer. Assuming

a simple equation of state of the form

$$\alpha = \alpha_c + \alpha_T (\nu - \nu_c) + \frac{1}{2} \alpha_{TT} (\nu - \nu_c)^2 \quad 5.21$$

where $\alpha_c, \alpha_T, \alpha_{TT}$ are constants, we obtain

$$\begin{aligned} \hat{z} E_x &\approx \hat{z}_c \rho_c g \alpha_T \nu_c^2 - \rho_c g \left[\alpha_T \nu_c^2 - z_0 \alpha_{TT} \nu_c^2 \right] z' \\ &\quad - \rho_c g \alpha_{TT} \frac{\nu_c^2}{2} z'^2 \\ &= \hat{z}_c E_{hc} - E_x z' - \frac{\rho_c g \alpha_{TT} \nu_c^2}{2} z'^2 \end{aligned} \quad 5.22$$

where z' is measured from \hat{z}_0 . Integrating (5.22), we obtain

$$\int_{-\ell}^z E_h dz = \hat{z}_0 E_{h0} (z' + \ell) + E_x \left(\frac{\ell^2 - z'^2}{2} \right) - \rho_0 g \alpha_{TT} \left(\frac{z'^3 + \ell^3}{3} \right) \quad 5.23$$

in the thermocline $z' < \ell$. Above the thermocline (5.23) reduces to

$$\begin{aligned} \Phi_2' &= \int_{-\ell}^z E_h dz = 2\hat{z}_0 E_{h0} \ell - \frac{2}{3} \rho_0 g \alpha_{TT} \ell^3 \\ &\approx \frac{\Delta \rho}{\rho} g \hat{z}_0 \ell - \frac{2}{3} \rho_0 g \alpha_{TT} \ell^3 \end{aligned} \quad 5.24$$

where $\frac{\Delta \rho}{\rho}$ is the total difference of density across the thermocline. For the Atlantic thermocline, the non-linear term is about 2% of $\frac{\Delta \rho}{\rho} g \hat{z}_0 \ell$ and increases linearly with ℓ for a fixed temperature difference ($\alpha_{TT} \ell$ constant). Although small, the non-linear term must be compensated by changes in \hat{z}_0 if the thickness of the thermocline ℓ changes. For a change in ℓ of 10 meters

$$\begin{aligned} \Delta \left(\frac{2}{3} \rho_0 g \alpha_{TT} \ell^3 \right) &= \frac{1}{6} \rho_0 g \alpha_{TT} (\ell_2^3 - \ell_1^3) \Delta \ell = \frac{\Delta \rho}{\rho} g \Delta \hat{z}_0 \\ &\approx 200 \text{ cm}^2 \text{ sec}^{-2} (\text{erg gr}^{-1}) \end{aligned} \quad 5.25$$

This change can be compensated by increasing \hat{z}_0 by two metres. Provided changes in thickness are not large, the compensation can be made by an adjustment of the depth \hat{z}_0 without appreciable effects on the velocity in the upper layer.

In the thermocline, the change of Φ' cannot be com-

pensated if ℓ changes. At $z' = 0$, we can write (5.23) in the form

$$\Phi' = \frac{1}{2} \frac{\Delta \rho}{\rho} g \hat{z}_0 + \frac{1}{4} \frac{\Delta \rho}{\rho} g \ell - \frac{1}{8} \rho_0 g \hat{z}_0 \alpha_{TT} (\nu_2^x - \nu_1^x)^2 - \frac{1}{2} \rho_0 g \alpha_{TT} (\nu_2^x - \nu_1^x)^2 \ell \quad 5.26$$

Therefore, using (5.25)

$$\Delta \Phi' = \frac{1}{4} \frac{\Delta \rho}{\rho} g \Delta \ell \approx 250 \text{ ergs gm}^{-1} \quad 5.27$$

the increase in Φ' produced by an increase in thickness of the thermocline represents a strong deceleration of the flow in the thermocline.

In order to remove the decelerations, the thermocline thickness must either be held constant by convective flow of heat into the thermocline to offset diffusion, or by lowering the thermocline downstream sufficiently to reduce the decelerations to zero. From (5.23), it can be seen that the decelerative term would vanish if \bar{E}_x is zero. Hence, if the temperature distribution can adjust downstream to reduce \bar{E}_x to zero, the flow in the thermocline would not be decelerated. If \bar{E}_x is zero, (5.20) implies that the total flux of mechanical energy $K + \dot{Q}'$ is approximately non-divergent, except for the dissipation of kinetic energy. The vertical gradient of temperature required to reduce \bar{E}_x to zero is

$$\nu_2^x = \frac{\alpha_{TT}}{\hat{z}_0} \approx 2 \times 10^{-4} \text{ } ^\circ\text{C cm}^{-1} \approx 2^\circ\text{C}/100 \text{ metres} \quad 5.28$$

which is the correct order of magnitude for the Atlantic thermocline.

For the two-layer ocean with the flow constrained to one direction in both the upper layer and thermocline, the condition $\bar{E}_\chi = 0$ in the thermocline appears to be necessary to maintain uniform flow. It should be noted that this conclusion is suggested, but not explicitly shown, in the simple example considered. In order to show more explicitly the dependence of flow on \bar{E}_χ it is necessary to examine the momentum flux equations. This is done in the next section.

Part VI.

Momentum flux

If steady flow in a two-layer ocean with a thermocline of finite thickness is constrained to a single horizontal direction, say the east-west x -direction, so that Coriolis forces act only in the y -direction, a simplified momentum flux equation can be written as

$$\frac{\partial \rho v^2}{\partial x} + \frac{\partial \rho v w}{\partial z} = -\frac{\partial p}{\partial x} + \frac{\partial}{\partial z} \left(\rho k_m \frac{\partial u}{\partial z} \right) \quad 6.1$$

where frictional stress due to vertical shear only is included.

Integrating (6.1) from a depth z to the surface yields

$$\frac{\partial}{\partial x} \int_z^{z_s} \rho v^2 dz = -\frac{\partial}{\partial x} \int_z^{z_s} p dz + p_s \frac{\partial z_s}{\partial x} \quad 6.2$$

if it is assumed that no stresses are applied at the surface and no motion exists in the bottom layer.

The integral of pressure with respect to z is the total potential energy per unit area relative to z . Integrating by parts and using the hydrostatic equation, we obtain

$$\begin{aligned} \int_z^{z_s} p dz &= p_s z_s - p z + \int_z^{z_s} \rho g z' dz' \\ &= p_s z_s + \int_z^{z_s} \rho g (z' - z) dz' \\ &= p_s z_s + \chi \approx \chi \end{aligned} \quad 6.3$$

assuming $p_s z_s$ and its variations to be small.

Integrating with respect to x , the difference of momentum flux across two sections becomes

$$\Delta \int_{z_1}^{z_2} \rho U^2 dz = -\Delta \chi. \quad 6.4$$

Thus, changes of total momentum flux are expressed in terms of the potential energy. Any process, such as thermal diffusion, that changes the potential energy of the system will also affect the momentum flux.

From the simple example considered in Part V, we concluded that the free surface must remain approximately level to prevent large downstream changes of velocity in the upper homogeneous layer. Therefore, the thermocline deepens slightly to compensate for changes of volume in the thermocline brought about by diffusion of heat. If the thermocline is lowered downstream its potential energy is decreased. Hence, if the increase in potential energy within the thermocline due to diffusion is equal and opposite to the change produced by lowering the entire thermocline, the total potential energy remains constant and no change of momentum flux occurs. We can calculate the conditions necessary for the momentum flux to remain constant by considering small changes of the temperature distribution within the thermocline. The changes of potential energy within the thermocline can be evaluated using the relationship given in Part III, (3.6), i.e.

$$\Delta \chi = \int_{m_0 - m/2}^{m_0 + m/2} \Delta p \alpha dm \quad 6.5$$

where $m_0 \pm m/2$ are the limits of the thermocline. It is assumed that no changes occur beyond these limits. Expanding

(6.5), we obtain

$$\begin{aligned}\Delta \chi &= \int [\alpha \Delta p + p \Delta \alpha] dm \\ &= \int \rho \alpha_T \Delta \nu^2 dm\end{aligned}\quad 6.6$$

as $\Delta p = 0$ from the hydrostatic equation (p is a function of m only). Using a simplified heat flux equation of the form

$$u \frac{\partial \nu}{\partial x} + w \frac{\partial \nu}{\partial z} = \frac{1}{\rho} \frac{\partial}{\partial z} \left(\rho K_Q \frac{\partial \nu}{\partial z} \right) \quad 6.7$$

and taking

$$\Delta \nu \approx \left(u \frac{\partial \nu}{\partial x} + w \frac{\partial \nu}{\partial z} \right) \Delta t = \frac{\partial}{\partial m} \left(\rho K_Q \frac{\partial \nu}{\partial z} \right) \Delta t \quad 6.8$$

where $\Delta t > 0$ is the mean time interval required for the flow to traverse the section, we obtain

$$\begin{aligned}\Delta \chi &\approx \int \rho \alpha_T \frac{\partial}{\partial m} \left(\rho K_Q \frac{\partial \nu}{\partial z} \right) \Delta t dm \\ &\approx \Delta t \int \rho K_Q \frac{\partial \rho \alpha_T}{\partial z} \frac{\partial \nu}{\partial z} dz \\ &\approx \Delta t \int \rho K_Q \bar{E}_x dz\end{aligned}\quad 6.9$$

For the momentum flux in the thermocline to be constant we must have $\Delta \chi$ zero, or

$$\int \rho K_Q \bar{E}_x dz = 0 \quad 6.10$$

If the mean value of potential energy parameter \bar{E}_x is zero in the thermocline, the mean horizontal pressure gradient vanishes and no deceleration of the flow occurs. If

the mean of E_x is negative, the flow is accelerated and, if positive, the flow is decelerated. The flow is always decelerated if a linear equation of state is assumed ($\alpha_{TT} = 0$).

If the flow is not constrained to one direction, the horizontal pressure gradients arising from diffusion of heat can be balanced by Coriolis forces. In this case, the velocity vector would change direction through the thermocline if the mean value of E_x is not zero.

Critical vertical gradients of potential temperature \int_1^2

The potential energy parameter E_x has the form

$$E_x = E_h + pV\alpha_\eta - p\delta_{hs}^2\alpha \quad 6.11$$

where

$$V\alpha_\eta = \rho g \left\{ \left[\frac{\partial}{\partial z} \left(\frac{1}{\gamma} \frac{\partial \alpha}{\partial p} \right) \right] \frac{d\theta}{dz} + \left[\frac{\partial}{\partial s} \left(\frac{1}{\gamma} \frac{\partial \alpha}{\partial p} \right) \right] \frac{ds}{dz} \right\} \quad 6.12$$

$$\delta_{hs}^2\alpha \approx \delta_{ps}^2\alpha = \frac{\partial^2 \alpha}{\partial s^2} \left(\frac{ds}{dz} \right)^2 + 2 \frac{\partial^2 \alpha}{\partial s \partial z} \frac{d\theta}{dz} \frac{ds}{dz} + \frac{\partial^2 \alpha}{\partial z^2} \left(\frac{dz}{dz} \right)^2 \quad 6.13$$

and

$$\frac{d\theta}{dz} = \frac{d\eta}{dz} + \Gamma \quad 6.14$$

The deformation used to derive E_x does not alter the ratio

$$\beta = \frac{ds/dz}{d\theta/dz} \quad 6.15$$

so that (6.11) may be expressed as

$$E_x = \rho g \left\{ \left(\frac{\partial \alpha}{\partial y} \right)^* \frac{d\theta}{dz} + \left[\frac{\partial}{\partial y} \left(\frac{p}{\gamma} \frac{\partial \alpha}{\partial p} \right) \right]^* \frac{d\theta}{dz} - p \left(\frac{\partial^2 \alpha}{\partial y^2} \right)^* \left(\frac{d\theta}{dz} \right)^2 \right\} \quad 6.16$$

where

$$\left(\frac{\partial \alpha}{\partial y} \right)^* = \frac{\partial \alpha}{\partial y} + \frac{\partial \alpha}{\partial s} \beta \quad 6.17$$

$$\left(\frac{\partial^2 \alpha}{\partial y^2} \right)^* = \frac{\partial^2 \alpha}{\partial y^2} + 2 \frac{\partial^2 \alpha}{\partial y \partial s} \beta + \frac{\partial^2 \alpha}{\partial s^2} \beta^2 \quad 6.18$$

etc.

The critical potential temperature gradient ξ_1 is chosen so that the internal energy change is zero, i.e.

$$\xi_1 = \left(\frac{d\theta}{dz} \right)_1 = \rho g \left[\frac{\partial}{\partial y} \left(\frac{1}{\gamma} \frac{\partial \alpha}{\partial p} \right) \right]^* / \left(\frac{\partial^2 \alpha}{\partial y^2} \right)^* \quad 6.19$$

The gradient ξ_2 is chosen so that the total potential energy change is zero, i.e.,

$$\xi_2 = \left(\frac{d\theta}{dz} \right)_2 = \frac{\rho g \left[\frac{\partial}{\partial y} \left(\alpha + \frac{p}{\gamma} \frac{\partial \alpha}{\partial p} \right) \right]^*}{p \left(\frac{\partial^2 \alpha}{\partial y^2} \right)^*} \quad 6.20$$

The potential and internal energy parameters, expressed in terms of ξ_1 , ξ_2 , E_h and the actual potential temperature gradient ξ , are

$$E_{x\eta} = \frac{\xi_2}{\xi_2 - \xi_1} E_h, \quad E_{e\eta} = - \frac{\xi_1}{\xi_2 - \xi_1} E_h \quad 6.21$$

$$E_x = \frac{\xi_2 - \xi}{\xi_2 - \xi_1} E_h, \quad E_e = - \frac{(\xi_1 - \xi)}{\xi_2 - \xi_1} E_h \quad 6.22$$

where E_h is the ordinary stability parameter $\rho g \left(\frac{\partial \alpha}{\partial T} \right)^* \frac{d\theta}{dz}$.

For $\xi_0 < \xi_1$, the internal energy change is negative (net expansion). The potential temperature and salinity gradients in the deep water are usually in this range.

For $\xi_1 < \xi < \xi_2$, the contraction on mixing has a larger effect on the internal energy than the variation of adiabatic compressibility with temperature and salinity. Hence, a net contraction of volume occurs in the deformation. The total potential energy change E_χ is positive. Most vertical gradients in the ocean above 1000 metres depth fall in this range. The notable exception is the Atlantic thermocline for which $\xi_0 > \xi_2$. For $\xi > \xi_2$, the net contraction is large enough to offset the increase of potential energy within the deformed volume and the total potential energy change, E_χ , is negative.

The gradient ξ_1 does not depend strongly on pressure, whereas, ξ_2 is approximately inversely proportional to pressure. Both gradients become infinitely large if the perfect gas law is assumed. The dependence of ξ_1, ξ_2 on the slope, β , is shown in Figure 2. The broken line in the Figure separates the gradient plane into stable and unstable regions according to the ordinary gravitational stability criterion ($E_h \geq 0$).

A section of stations extending from Australia to Antarctica along the longitude 115°E have been analyzed and are given as an example of the magnitudes of the energy parameters. The ν -S characteristic curves for the stations are shown in

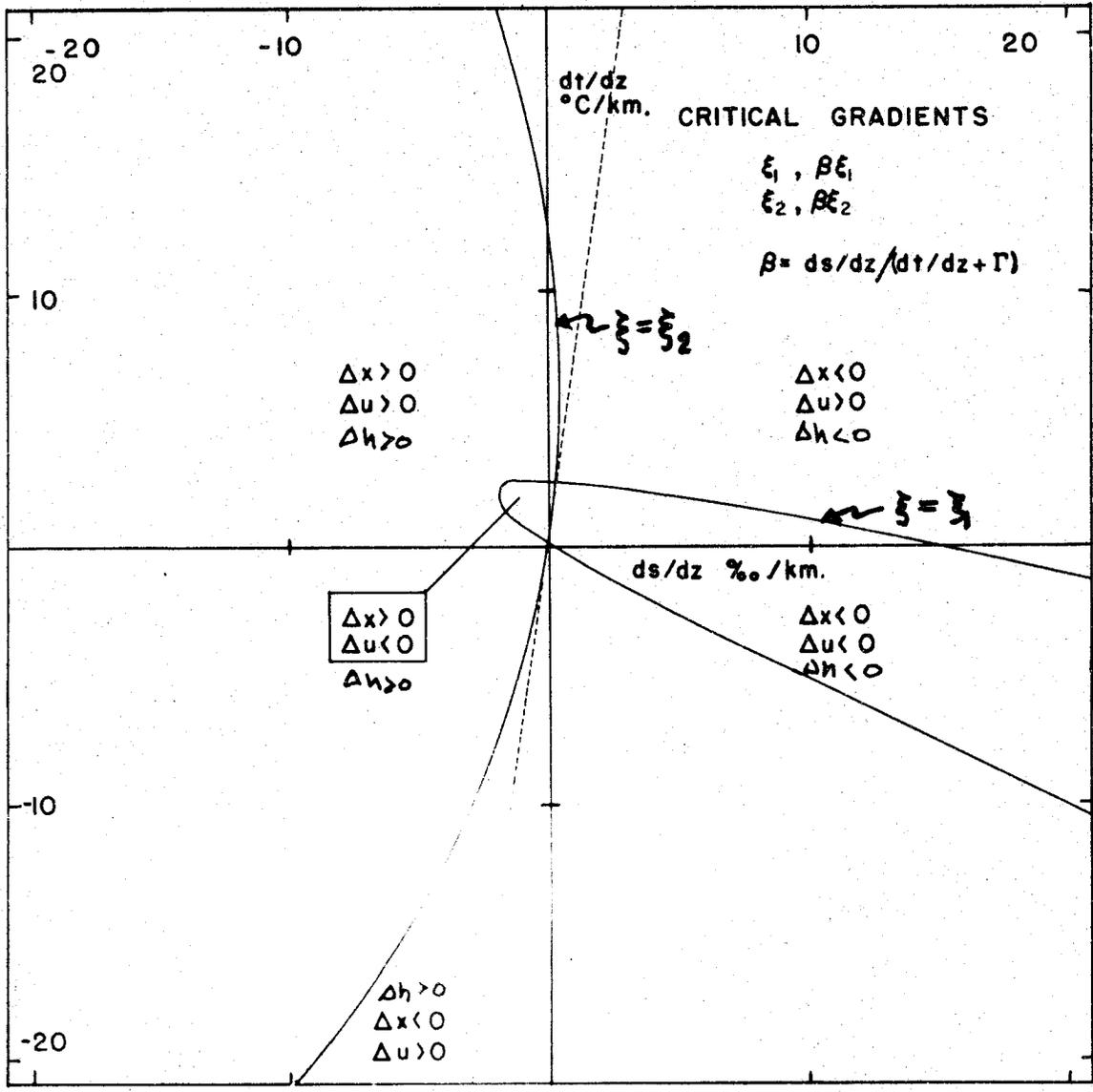


Fig. 2. Variation of the critical gradients ξ_1, ξ_2 with β .

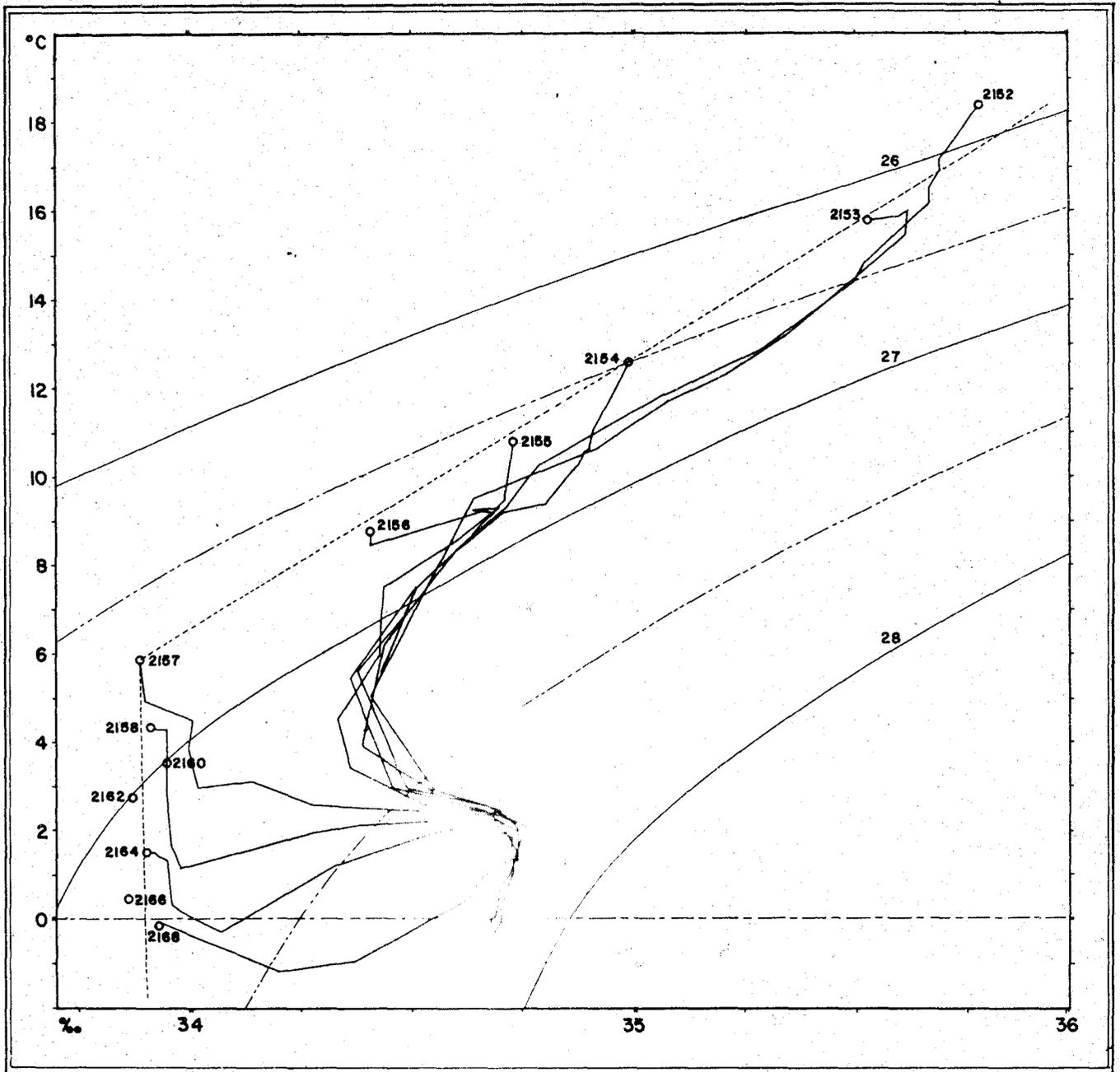


Fig. 3. T-S curves for stations along the meridian 115°E.

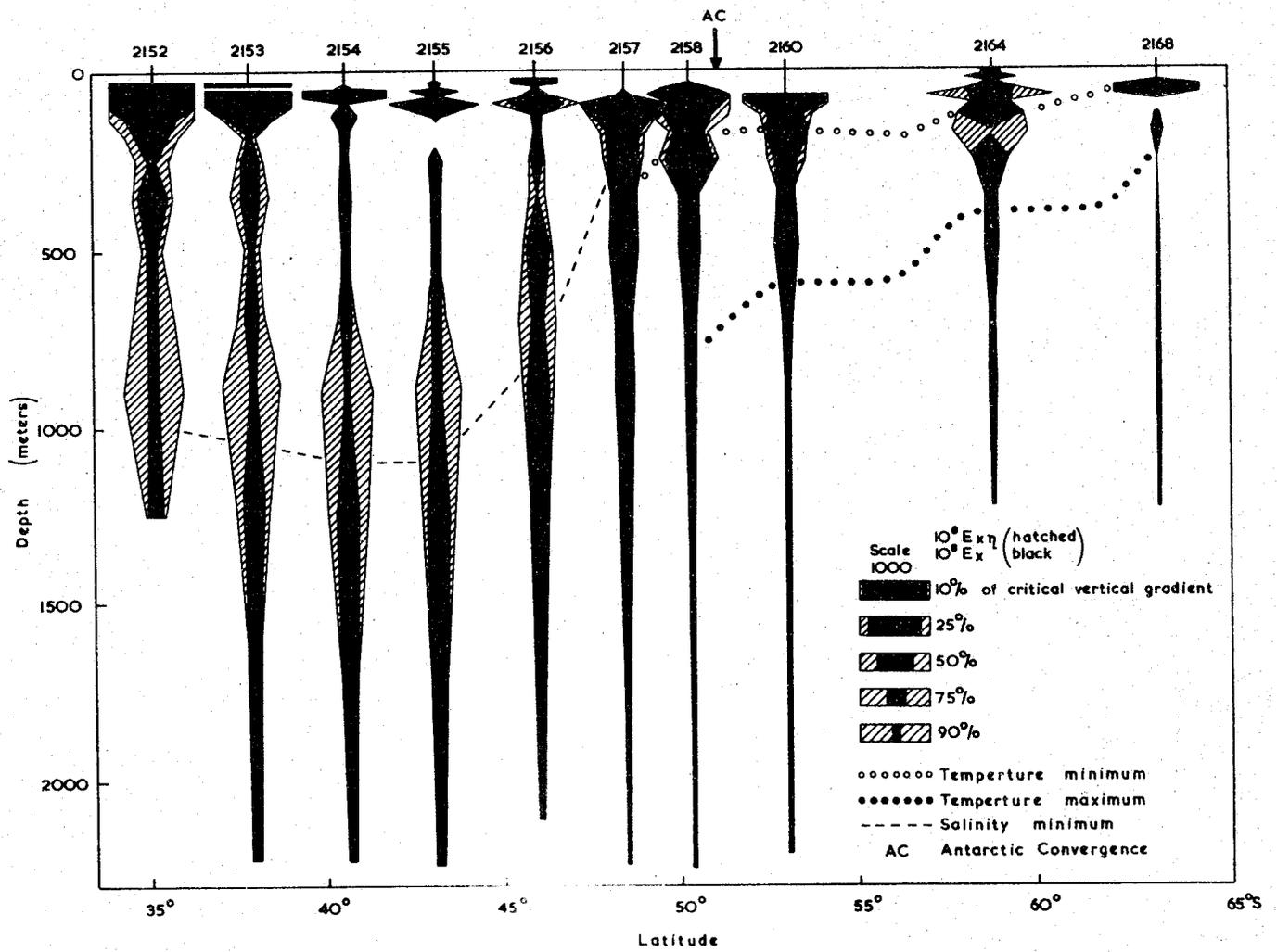


Fig. 4. A section along 115°E long. showing relative magnitudes of the potential energy parameters E_x and $E_{x\eta}$.

Figure 3. The slopes of these curves define β approximately as the adiabatic gradient is small compared to the actual gradients of temperature. Stations north of the antarctic convergence (2152-2156) have characteristic $\vartheta - S$ curves that differ sharply from those south of the convergence (2157-2168). The salinity minimum north of the convergence lies at depths of about 1000 metres. The potential energy parameters E_x and $E_{x\eta}$ for these stations are compared in Figure 4. As may be seen from the Figure, the vertical gradients of potential temperature approach ξ_2 throughout the salinity minimum north of the convergence, and in the temperature minimum south of the convergence. Regions of ordinary gravitational instability also occur (station 2155, 200 metres). The existence of gravitational instability is supported also by the structure of $\vartheta - S$ curves for stations 2155 and 2156. (Figure 4).

The potential energy parameters are shown in more detail in Figure 5 for station 2153. For comparison, the value of $E_{x\eta}$ at $\xi = \xi_2$ is given for each depth. As $E_{x\eta}(\xi_2)$ does not involve the actual vertical gradients, but only physical properties of sea water and the $\theta - S$ slope, it is interesting to note the similarity of the curve to those obtained from the observed gradients in the upper 1000 metres. In the deep water the non-linear effects are small and $E_{x\eta}(\xi_2)$ becomes large compared with E_x and $E_{x\eta}$.

Other possible interpretations of E_x

The parameter E_x contains the local change of potential energy equal to E_p and an external change due to net volume changes. The volume change can be interpreted as an energy-producing mechanism. If the change of volume produces a lowering of the surface or of streamlines of the flow, the kinetic energy is increased. In a more complex density field it may be possible to replace kinetic energy lost by dissipation by lowering streamlines through volume contraction. Suppose that at each level the volume contraction releases as much energy as is lost by dissipation. The kinetic energy would appear in the layers above that in which contraction takes place. A simple form of the balance is

$$-K_Q \rho V \alpha = K_Q \rho \alpha_{TT} v_z^2 = g_K = K_m v_x^2 \quad 6.23$$

Using the thermal wind equation

$$v_z \approx -\frac{\alpha g}{f} \frac{\partial \rho}{\partial x} = \frac{\rho g \alpha_T}{f} v_x \quad 6.24$$

we obtain

$$K_Q \rho \alpha_{TT} v_z^2 = K_m \frac{\rho^2 g^2 \alpha_T^2}{f^2} v_x^2 \quad 6.25$$

Solving for $(\partial x / \partial z)_v$

$$\begin{aligned} \left(\frac{\partial x}{\partial z}\right)_v &= \left(\frac{K_m}{K_Q}\right)^{1/2} \frac{\rho g \alpha_T}{f (\rho \alpha_{TT})^{1/2}} \\ &\approx 70 \left(\frac{K_m}{K_Q}\right)^{1/2} \end{aligned} \quad 6.26$$

for $P = 10^8$ dynes cm^{-2} , $f = 10^{-4} \text{sec}^{-1}$, $\alpha_T = 2 \times 10^{-4} \text{cm}^3 \text{gm}^{-1} \text{ } ^\circ\text{C}^{-1}$,
 $\alpha_{TT} = 10^{-5} \text{cm}^3 \text{gm}^{-1} \text{ } ^\circ\text{C}^{-2}$. For $K_m/K_Q \sim 10$, the horizontal
 slope of the isotherm is about 1 kilometre in 200 kilometers -
 about the slope found in the Gulf Stream.

As both the contraction and vertical shear can be esti-
 mated from oceanographic data, an estimate for the ratio K_m/K_Q can
 be obtained by "forcing" a balance of the type assumed in (6.23),
 at least for the mean values, i.e.

$$K_Q \int \rho \alpha_{TT} v_z^2 dz \sim K_m \int \rho v_z^2 dz$$

Or

$$\frac{K_m}{K_Q} \sim \frac{\int \rho \alpha_{TT} v_z^2 dz}{\int \rho v_z^2 dz} \quad 6.27$$

The ratio has been evaluated for several stations taken across
 the Gulf Stream and is given in Table II.

From Table II, it can be seen that the non-linear
 effect of volume contraction can be a significant factor in the
 energy balance of the Gulf Stream if K_m is assumed to be of
 the same order of magnitude as K_Q .

Approximating the rate of dissipation of kinetic energy
 in the Gulf Stream by $K_m \int \rho v_z^2 dz$ and assuming a total kinetic
 energy per unit area of 10^9 ergs, we obtain a time constant for
 the Stream of one year for $K_m \sim 100 \text{cm}^2 \text{sec}^{-1}$.

If larger values of K_m are assumed, the dissipation
 rate could be sufficient to destroy the kinetic energy in a few
 weeks. If the kinetic energy dissipation is large, it is also

Table II

A comparison of the potential energy change due to contraction on mixing and kinetic energy dissipation, for oceanographic stations across the Gulf Stream.

<u>Stations</u>	Geostrophic Surface Velocity $v'_0/1500 \text{ cm sec}^{-1}$	$\int \rho \rho' v'_\alpha dz$ ergs cm^{-4}	$\int \rho v_z^2 dz$ ergs cm^{-4}	K_m/K_Q
5295-96	15	1.12	.011	~ 100
5296-97	100	.90	.49	~ 2
5297-98	90	1.16	.23	5
5298-99	200	1.88	.44	4
5299-01	50	2.17	.08	~ 30

(Stations 5295-5301 were taken in 1955 in an east-west section at 36°N .)

possible that the energy release is large and may tend to offset the dissipation. Whether or not the non-linear effects of volume contraction do contribute significantly to the energy balance is a matter of speculation at present and cannot be decided in terms of present understanding of the effects.

Another study of the magnitude of the energy-releasing and dissipative terms has been made for an intense anticyclonic "eddy" observed in the Gulf of Alaska during the summer of 1960. The temperature distribution within the eddy is shown in Figure (6). The values of $\rho v'_\alpha$ and v_z^2 are compared at several locations within the eddy in Figure (7), assuming $K_m/K_Q = 10$. For this value of the "Prandtl number", the terms are of comparable magnitude and exhibit some similarities of form as a function of depth.

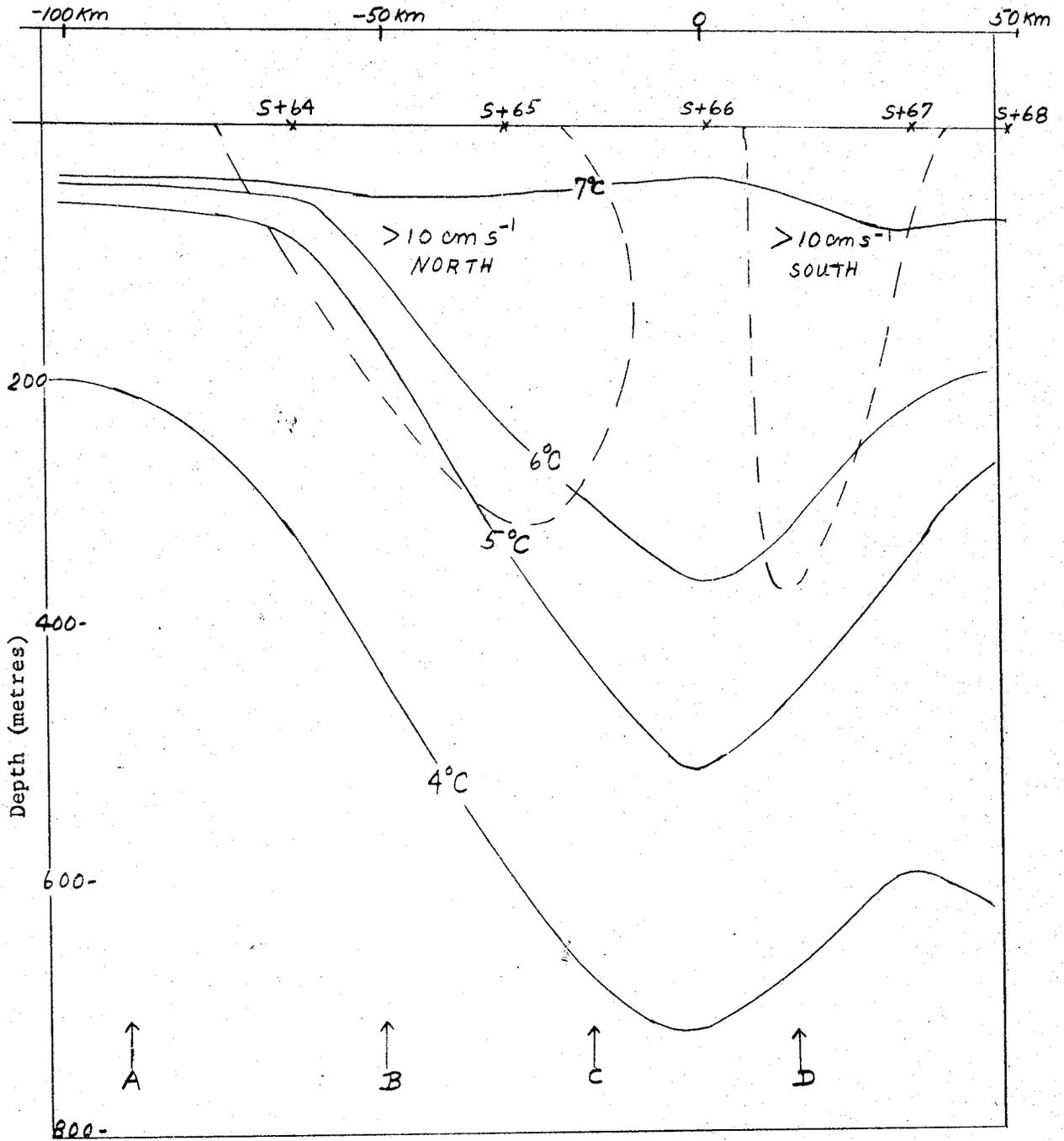


Figure 6: Anticyclonic eddy in Gulf of Alaska (August, 1960) centred at $56^{\circ}45'N$ $138^{\circ}00'W$ (Station 66). Mean energy parameters are compared at Sections A, B, C and D in following Figures.

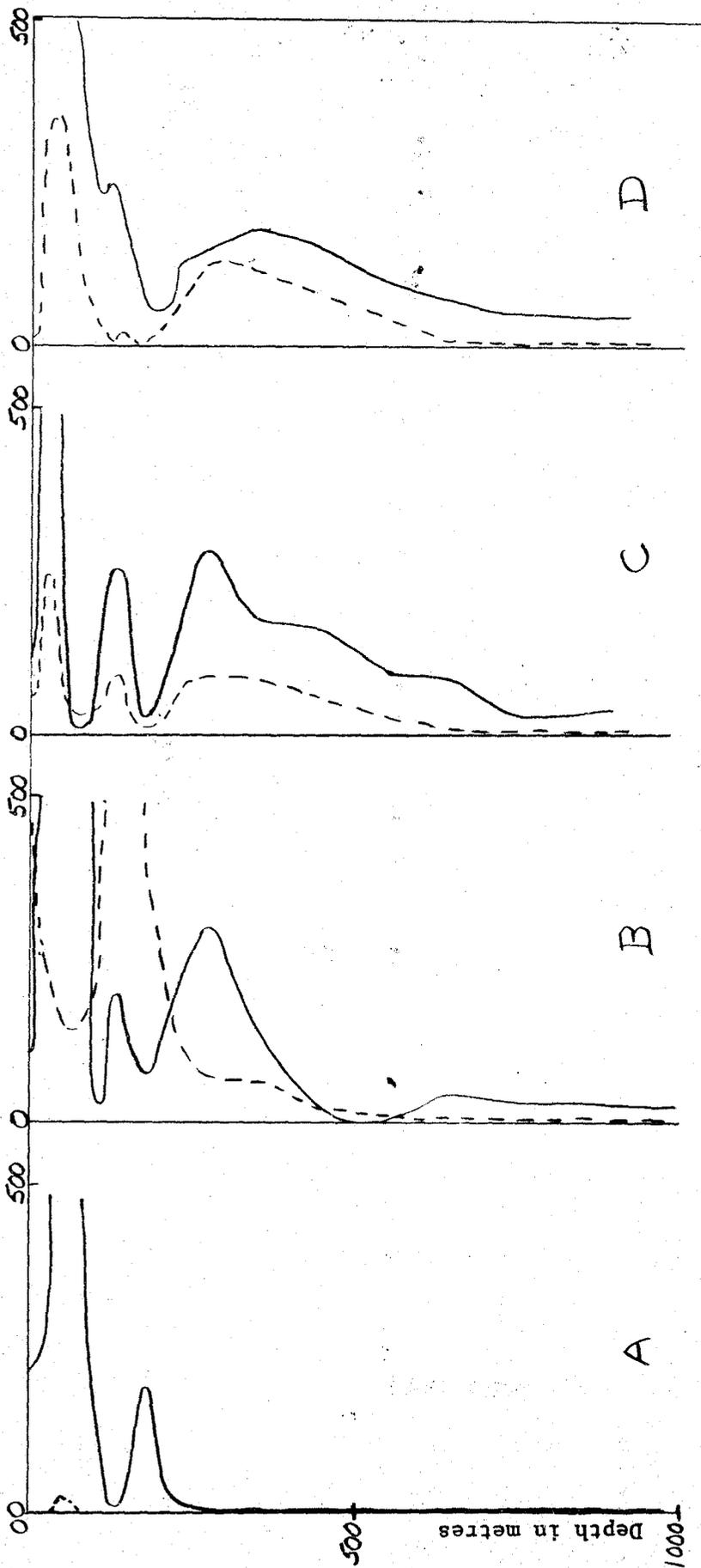


Figure 7: Comparison of potential energy release by contraction, $E_{\eta} - E_{\chi}$, (solid curve) and viscous dissipation $/ 0 V_{\xi}^2$ (broken curve). The magnitudes are comparable if the Prandtl number is 10. The energy changes are given in units of 10^{-8} ergs per gram per square centimetre.

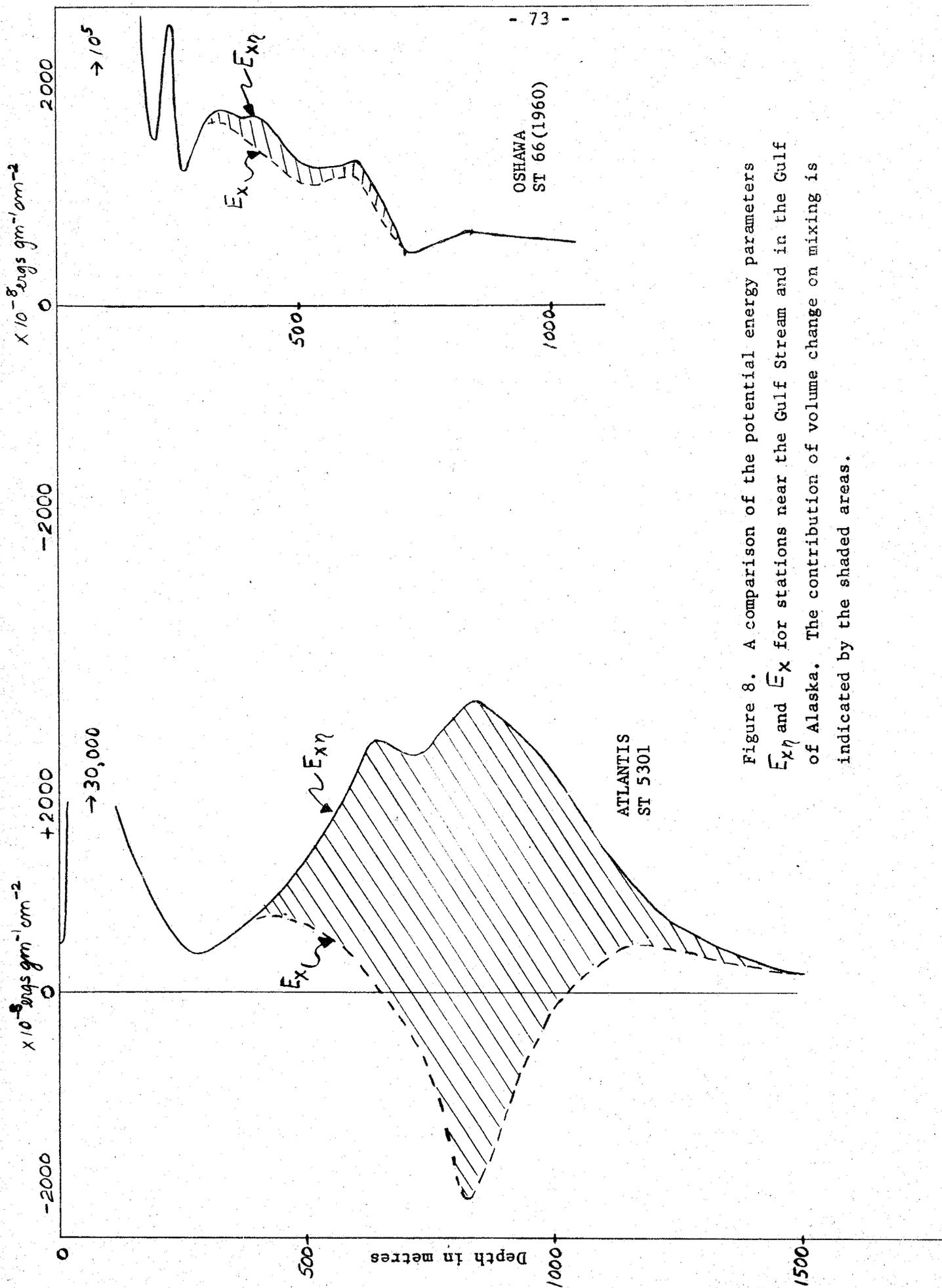


Figure 8. A comparison of the potential energy parameters E_x and $E_{x\eta}$ for stations near the Gulf Stream and in the Gulf of Alaska. The contribution of volume change on mixing is indicated by the shaded areas.

It is interesting to note that the ratio K_m/K_ρ is of the same order of magnitude for the Gulf of Alaska eddy and for the Gulf Stream even though the velocity structures, temperature and salinity distributions differ greatly. For comparison, the parameters $E_{x\eta}$ and E_x at the seaward edge of the Gulf Stream (Station 5301) and in the centre of the eddy (Station 66) are shown in Figure 8. The energy-releasing term $\rho V\alpha$ is proportional to the shaded areas in the Figure.

Bernoulli: Equation

In Part V, it was shown that the effective geopotential for flow in a stratified ocean could be expressed as

$$\Phi' = \int_{z_r}^z \hat{z} E_h dz. \quad 6.28$$

The value of $\hat{z} E_h$ at the critical gradient ξ_2 (defined by $E_x = 0$, eq. (6.20)) is given by

$$\left(\hat{z} E_h\right)_{\xi_2} = \frac{\rho g \left(\frac{\partial \alpha}{\partial x}\right)^{*2}}{\left(\frac{\partial^2 \alpha}{\partial y^2}\right)^*} \sim 3 \text{ cm sec}^{-2} \quad 6.29$$

to the approximation used in deriving (6.28).

Pressure does not appear explicitly in (6.29) so that the variation of $\left(\hat{z} E_h\right)_{\xi_2}$ with depth depends only on the changes of thermal and saline expansion coefficients and on the slope of the $\Theta - S$ characteristic curve. The range of magnitudes of

$\left(\hat{z} E_h\right)_{\xi_2}$ is, therefore, not very large.

The values of $\hat{z} E_h$, calculated from observed distributions of temperature and salinity, show surprisingly little varia-

tion with depth and reach maximum values comparable to the critical value given by (6.29). Examples are given in Figures (9) (10) and (11). Thus, although E_R varies over several orders of magnitude, the product $\hat{z} E_R$ appears to be limited in its range of magnitude. A possible interpretation of the limitation on $\hat{z} E_R$ is that the potential energy parameter E_χ determines the stability of flow in the ocean in some sense. From considerations of momentum flux, it is evident that flow in a stratified layer could be accelerated through vertical diffusion or mixing if E_χ is negative. Whether or not the result of possible acceleration of flow for negative values of E_χ would be a tendency to weaken vertical gradients and limit stratification to positive values of E_χ has not been determined explicitly. It is hoped that some experimental means of evaluating the non-linear effects of volume changes in mixing processes can be devised.

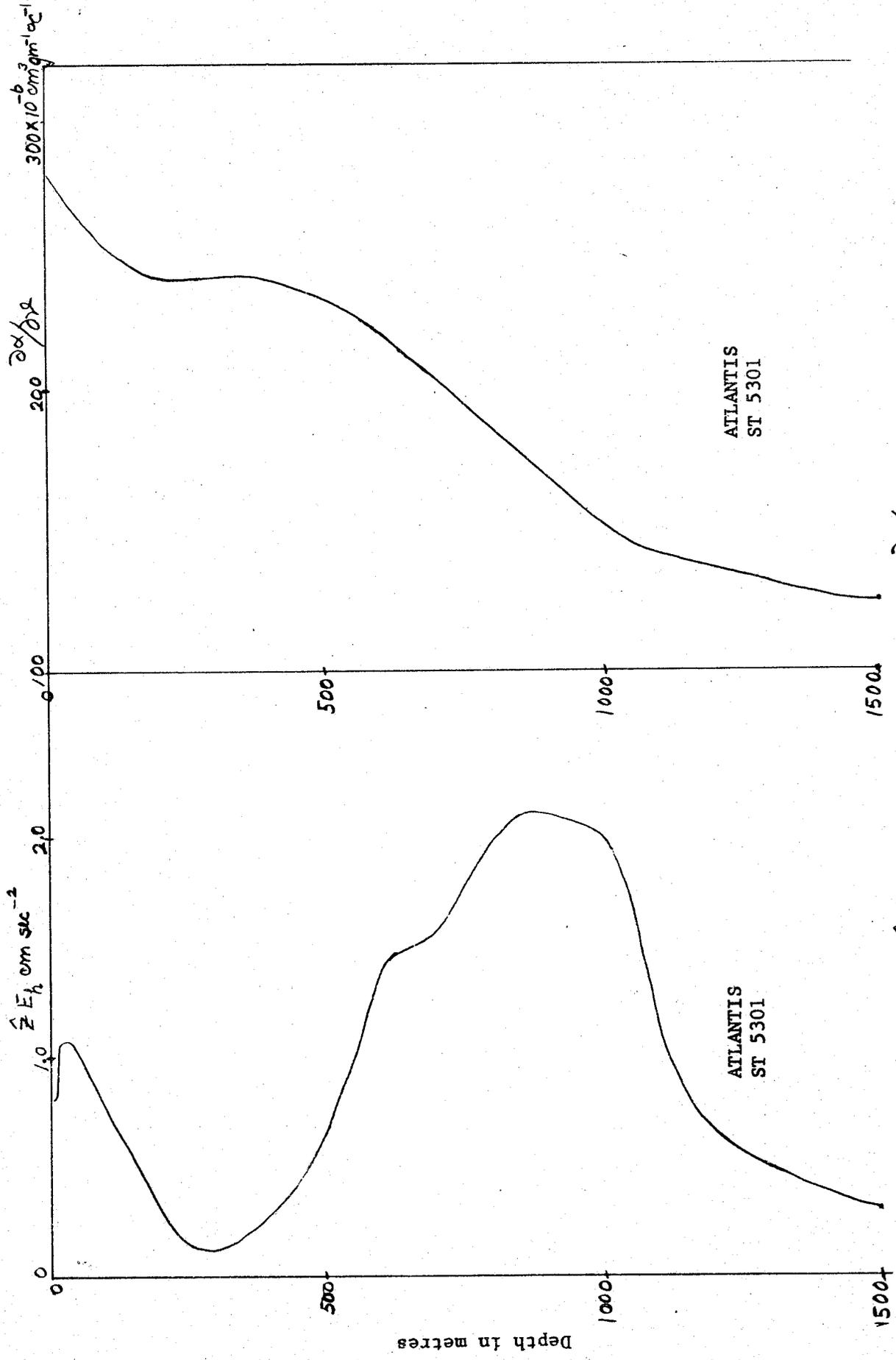


Figure 9. Variation of \hat{E}_k and the thermal expansion σ_t with depth for a station near the Gulf Stream.

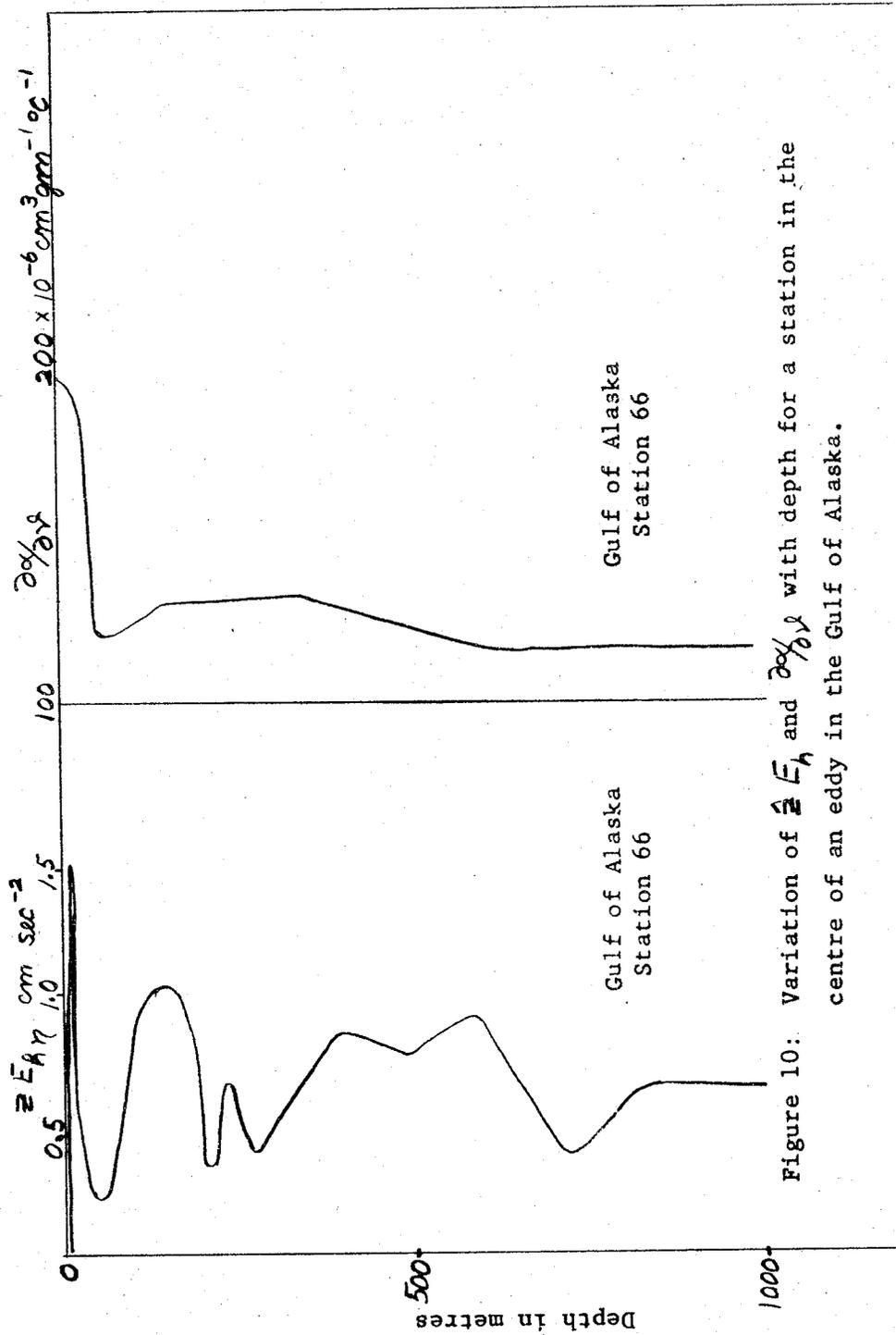
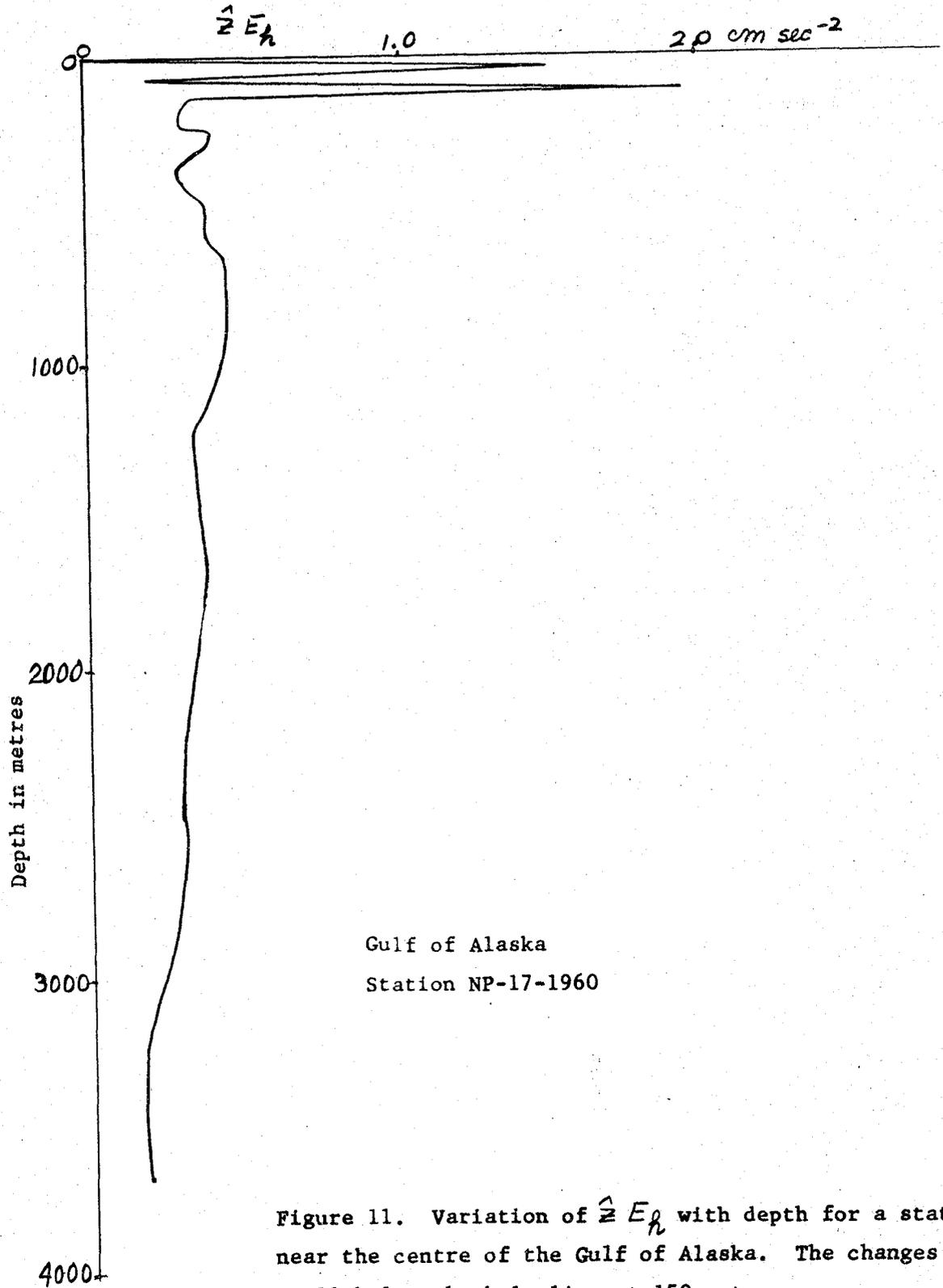


Figure 10: Variation of E_h and $\frac{d\rho}{dz}$ with depth for a station in the centre of an eddy in the Gulf of Alaska.



Appendix

Maximum entropy principle

Consider a system of sea water consisting initially of a mass m_1 at pressure p_1 , salinity s_1 , enthalpy h_1 , and a mass m_2 at pressure p_2 , salinity s_2 , and enthalpy h_2 . The two masses are assumed to be free to exchange heat and salt between each other but not with the surroundings. The pressures are assumed to be constant but different ($p_1 \neq p_2$). The problem is to find the final equilibrium state (or states) towards which the system will proceed. In order to find the final equilibrium system, we shall assume the maximum entropy principle, i.e., in such an isolated system in which total enthalpy, mass and pressure are constant with time, that the final equilibrium state will have the highest entropy consistent with the constraints on enthalpy, mass and pressure.

We shall assume that in the final equilibrium state the enthalpy and salinity are not equalized. Hence, the conservation equations have the form

$$m_1^f = m_1^i = m_1$$

$$m_2^f = m_2^i = m_2$$

$$m_1^f s_1^f + m_2^f s_2^f = m_1^i s_1^i + m_2^i s_2^i$$

$$m_1^f h_1^f + m_2^f h_2^f = m_1^i h_1^i + m_2^i h_2^i$$

$$p_1^f = p_1^i = p_1, \quad p_2^f = p_2^i = p_2$$

where the superscripts refer to the final and initial states.

The total change of entropy ΔN is given by

$$\begin{aligned} \Delta N &= m_1 \eta_1^f + m_2 \eta_2^f - (m_1 \eta_1^i + m_2 \eta_2^i) \\ &= m_1 (\eta_1^f - \eta_1^i) + m_2 (\eta_2^f - \eta_2^i) \end{aligned} \quad (2)$$

We expand η in a Taylor series with respect to h , s , and p , keeping terms to second order. The expansion about an arbitrary reference point h_0, s_0, p_0 is of the form

$$\begin{aligned} \eta &= \eta_0 + \eta_h (h - h_0) + \eta_s (s - s_0) + \eta_p (p - p_0) \\ &\quad + \frac{1}{2} [\eta_{hh} (h - h_0)^2 + \eta_{ss} (s - s_0)^2 + \eta_{pp} (p - p_0)^2 \\ &\quad + 2\eta_{hs} (h - h_0)(s - s_0) + 2\eta_{hp} (h - h_0)(p - p_0) + 2\eta_{sp} (s - s_0)(p - p_0)] \\ &\quad + \dots \end{aligned} \quad (3)$$

By expressing $\eta_1^f, \eta_1^i, \eta_2^f, \eta_2^i$ in terms of the Taylor series and substituting into (2), we obtain

$$\begin{aligned} \Delta N &= \frac{1}{2} \left\{ \eta_{hh} [(m_1 h_1^f + m_2 h_2^f)^2 - (m_1 h_1^i + m_2 h_2^i)^2] + \dots \right. \\ &\quad \left. + 2\eta_{sh} [(m_1 h_1^f s_1^f + m_2 h_2^f s_2^f) - (m_1 h_1^i s_1^i + m_2 h_2^i s_2^i)] + \dots \right. \\ &\quad \left. + \text{terms of same general form} \right\} \end{aligned} \quad (4)$$

All linear terms in (3) drop out on application of the conservation equations in (1).

Using identities of the form

$$\begin{aligned} m_1 h_1^i + m_2 h_2^i &= \frac{(m_1 h_1^i + m_2 h_2^i)^2}{m_1 + m_2} - \frac{m_1 m_2}{m_1 + m_2} (h_2^i - h_1^i)^2 \\ m_1 h_1^i s_1^i + m_2 h_2^i s_2^i &= \frac{(m_1 h_1^i + m_2 h_2^i)(m_1 s_1^i + m_2 s_2^i)}{m_1 + m_2} - \frac{m_1 m_2}{m_1 + m_2} (h_2^i - h_1^i)(s_2^i - s_1^i) \end{aligned} \quad (5)$$

we can write (4) in the form

$$\Delta N = -\frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} \left\{ \eta_{hh} [\Delta h^i]^2 + \dots + 2\eta_{hs} [\Delta h^i \Delta s^i - \Delta h^f \Delta s^f] + \dots + 2\eta_{hp} \Delta p [\Delta h^i - \Delta h^f] + \dots \right\} \quad (6)$$

where

$$\begin{aligned} \Delta h^i &= h_2^i - h_1^i, & \Delta h^f &= h_2^f - h_1^f \\ \Delta s^i &= s_2^i - s_1^i, & \Delta s^f &= s_2^f - s_1^f \\ \Delta p &= p_2 - p_1 \end{aligned} \quad (7)$$

As $\Delta h^i, \Delta s^i, \Delta p$ are fixed by initial conditions, the entropy change can be varied only by changing Δh^f and Δs^f . We find the extreme value of ΔN with respect to Δh^f and Δs^f . For stationary values of ΔN , we have

$$\begin{aligned} \frac{\partial \Delta N}{\partial \Delta h^f} &= \frac{m_1 m_2}{m_1 + m_2} [\eta_{hh} \Delta h^f + \eta_{hs} \Delta s^f + \eta_{hp} \Delta p] = 0 \\ \frac{\partial \Delta N}{\partial \Delta s^f} &= \frac{m_1 m_2}{m_1 + m_2} [\eta_{hs} \Delta h^f + \eta_{ss} \Delta s^f + \eta_{sp} \Delta p] = 0 \end{aligned} \quad (8)$$

Solving for Δh^f and Δs^f , we obtain

$$\frac{\Delta h^f}{\Delta p} = \frac{\eta_{sp} \eta_{hs} - \eta_{hp} \eta_{ss}}{\eta_{hh} \eta_{ss} - \eta_{hs}^2} \quad (9)$$

$$\frac{\Delta s^f}{\Delta p} = \frac{\eta_{hs} \eta_{hp} - \eta_{sp} \eta_{hh}}{\eta_{hh} \eta_{ss} - \eta_{hs}^2} \quad (10)$$

Using the transformations

$$\begin{aligned} \eta_{hh} &= -\frac{1}{c_p T^2} & \eta_{hp} &= +\frac{\alpha - T\alpha_T}{c_p T^2} \\ \eta_{hs} &= h_s / c_p T^2 & \eta_{sp} &= -\frac{\alpha_s}{T} - \frac{\alpha - T\alpha_T}{c_p T^2} h_s \\ \eta_{ss} &= -\frac{\mu_s}{T} - \frac{h_s^2}{c_p T^2} & h_s &= \mu - T\mu_T \end{aligned} \quad (11)$$

We obtain

$$\frac{\Delta h^f}{\Delta p} = +(\alpha - T\alpha_T) - \frac{\alpha_s h_s}{\nu_s} \quad (12)$$

$$\frac{\Delta S^f}{\Delta p} = -\frac{\alpha_s}{\nu_s} = -\frac{\nu_p}{\nu_s} = \left(\frac{\partial S}{\partial p}\right)_\nu \quad (13)$$

But, from the relationship

$$\Delta h = C_p \Delta T + (\alpha - T\alpha_T) \Delta p + h_s \Delta S \quad (14)$$

we see on substituting (13) that

$$\Delta T = 0 \quad (15)$$

Hence, the maximum entropy is attained when

$$T_1 = T_2 \quad (16)$$

$$\nu_1 = \nu_2$$

To show that the stationary value of entropy is a maximum, the terms in (6) depending on the final values can be written as

$$\begin{aligned} & \frac{C_p}{T_2} \Delta Q_e^f + \frac{\nu_s}{T} (\Delta S_e^f)^2 \\ & - \frac{C_p}{T_1} (\Delta Q^f - \Delta Q_e^f)^2 - \frac{\nu_s}{T} (\Delta S - \Delta S_e^f)^2 \end{aligned} \quad (17)$$

where

$$\Delta Q = \Delta h - h_s \Delta S \quad (18)$$

Thus, any departure from the equilibrium gradients, denoted by a subscript "e" in (17), would yield a lower total entropy.