lectures by N.P. Fofonoff
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 $10^\circ$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 (Stromkabbelung) 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 \( \theta_1, \theta_2 \) and salinities \( S_1, S_2 \) respectively. Mixed together, these yield a homogeneous mass \( m \) of sea water of temperature \( \theta \) and salinity \( S \). We assume that the pressure \( p \) remains constant throughout the mixing.

Applying conservation of mass, we obtain

\[
\Delta m = m - (m_1 + m_2) = 0
\]

*The term 'coefficient of saline contraction' was introduced by R.O. Reid (1958) for the coefficient \(- \frac{1}{\alpha} \left( \frac{\partial \alpha}{\partial S} \right) \).
The change of volume $\Delta V$ is

$$\Delta V = m\alpha_1 - (m_1\alpha_1 + m_2\alpha_2)$$  \hspace{1cm} (1.3)

where $\alpha_1$, $\alpha_2$ and $\alpha$ are the specific volumes of the two initial masses and of the final mixture respectively. Conservation of energy requires that

$$m\Delta e = me - (m_1 e_1 + m_2 e_2) = -p\Delta V$$  \hspace{1cm} (1.4)

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

$$m\Delta(e + p\alpha) = m(e + p\alpha) - [m_1(e_1 + p\alpha_1) + m_2(e_2 + p\alpha_2)] = 0$$  \hspace{1cm} (1.5)

or

$$m\Delta h = mh - (m_1h_1 + m_2h_2) = 0.$$  \hspace{1cm} (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

$$\alpha = \alpha_0 + \frac{\partial \alpha}{\partial h_0}(h - h_0) + \frac{\partial \alpha}{\partial S_0}(S - S_0)$$

$$+ \frac{1}{2} \left[ \frac{\partial^2 \alpha}{\partial h^2} (h - h_0)^2 + 2 \frac{\partial^2 \alpha}{\partial h \partial S} (h - h_0)(S - S_0) + \frac{\partial^2 \alpha}{\partial S^2} (S - S_0)^2 \right] + \ldots$$  \hspace{1cm} (1.7)
Substitution of (1.7) into (1.3) yields

$$\Delta V = \frac{m_1 + m_2}{2} \left[ \frac{m_1}{m_1 + m_2} \right] \left[ \frac{m_2}{m_1 + m_2} \right] \left[ \frac{\partial^2 \alpha}{\partial h^2} (h_s - h) \right] + \frac{1}{2} \frac{\partial^2 \alpha}{\partial h \partial s} (h_s - h) (s_s - s) \right] + \frac{1}{2} \frac{\partial^2 \alpha}{\partial s^2} (s_s - s)^2 \right] + \ldots$$

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

$$\Delta V = \frac{m_1 + m_2}{2} \left[ \frac{m_1}{m_1 + m_2} \right] \left[ \frac{m_2}{m_1 + m_2} \right] \left[ \frac{\partial^2 \alpha}{\partial h^2} \Delta_{h_s}^2 \alpha \right] \right] + \frac{1}{2} \frac{\partial^2 \alpha}{\partial h \partial s} \Delta_{h_s}^2 \alpha \right]$$

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

$$\Delta V = \frac{m_1 + m_2}{2} \left[ \frac{m_1}{m_1 + m_2} \right] \left[ \frac{m_2}{m_1 + m_2} \right] \left[ \frac{\partial^2 \alpha}{\partial h^2} \Delta_{h_s}^2 \alpha \right] \right] + \frac{1}{2} \frac{\partial^2 \alpha}{\partial h \partial s} \Delta_{h_s}^2 \alpha \right]$$

where

$$\Delta_{h_s}^2 h = \frac{\partial C_p}{\partial h}(s_s - s)^2 + 2 \frac{\partial C_p}{\partial s} (s_s - s)(s_s - s) + \frac{\partial^2 h}{\partial s^2} (s_s - s)^2$$

and $C_p$ is specific volume at constant pressure.

The additional term $\chi_p \Delta_{h_s}^2 h$ 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 $\varepsilon \ m$ mixed into a large mass $m$ of sea water is given approximately by

$$\delta \alpha = \lim_{\varepsilon \to 0} \left\{ \frac{\Delta V}{\varepsilon m} \right\} = -\frac{1}{2} \left[ \Delta_{h_s}^2 \alpha \right] \approx -\frac{1}{2} \left[ \Delta_{h_s}^2 \alpha \right]$$

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
\[ y_2 - y_1 = \gamma \sin \theta \]
\[ S_2 - S_1 = \gamma \cos \theta, \]
we can convert (1.11) to
\[
\delta \alpha = \frac{\gamma^2}{2} \left( \frac{\partial \alpha}{\partial x^2} + \frac{\partial \alpha}{\partial y^2} \right) + \sqrt{\left( \frac{\partial \alpha}{\partial x} \right)^2 + \left( \frac{\partial \alpha}{\partial y} \right)^2} - \Delta \cos \left( \theta - \theta_m \right)
\]
\[ = -\gamma^{\frac{1}{2}} F(\theta', \nu', S, p) \]
where
\[ \tan \theta_m = -\frac{\partial^2 d / \partial y \partial S}{\partial^2 d / \partial x \partial S} \]
\[ D = \frac{\partial^2 \alpha}{\partial x^2} \frac{\partial^2 \alpha}{\partial y^2} - \left( \frac{\partial^2 \alpha}{\partial y \partial S} \right)^2 \]

Contraction will occur for all \( \theta \) if \( D \) is positive. Typical dependence of \( F(\theta; \nu', S, p) \) on \( \theta \) 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 \( \varphi \) can be obtained in a form similar to (1.11). The general formula for the change of the property \( \varphi \) per unit mass accompanying the mixing is

\[
\Delta \varphi = -\frac{1}{2} \left( \Delta \varphi \right)_S - \frac{1}{2} \left( \Delta \varphi \right)_S - \frac{\partial \varphi}{\partial S} \frac{\Delta \varphi}{\varphi} \]

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 \( \rho^i \), the final density \( \rho^f \) after a vertical displacement \( dz \), will be

\[
\rho^f = \rho^i + \left( \frac{\partial \rho}{\partial z} \right)_\eta dz
\]

1.16

where the subscript \( \eta \) denotes differentiation at constant entropy.

The density of the surrounding water at the final level is

\[
\rho = \rho^i + \frac{d}{dz} \rho^i dz
\]

1.17

where \( \frac{d\rho}{dz} \) is the vertical gradient of density in situ.

The buoyant force per unit mass is therefore

\[
\frac{g(\rho^f - \rho^s)}{\rho} = -g \rho \left[ \frac{d\rho}{dz} - \left( \frac{\partial \rho}{\partial z} \right)_\eta \right] dx = \rho g \left[ \frac{d\alpha}{dz} - \left( \frac{\partial \alpha}{\partial z} \right)_\eta \right] dx
\]

\[
= \rho g \left[ \frac{d\alpha}{dz} - \left( \frac{\partial \alpha}{\partial z} \right)_\eta \right] + \frac{d\alpha}{dz} \left( \frac{d\rho}{dz} \right)_\rho dx
\]

\[
= E_{\gamma\eta} dx
\]

1.18

where \( E_{\gamma\eta} \) is the stability parameter. The gradient \(- \left( \frac{\partial \rho}{\partial z} \right)_\eta\) is called the adiabatic lapse rate (approximately 0.1°C/1000 meters) and is usually denoted by \( \gamma \). 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 $\frac{1}{2} E \cdot \eta \, dz$ by the
distance $dz$, we obtain the work per unit mass $\frac{1}{2} E \cdot \eta \, dz = \frac{1}{2} E \cdot \omega \cdot \eta \, dz$
required to produce the vertical displacement. Thus, we can inter-
pret $\frac{1}{2} E \cdot \omega \cdot \eta$ 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 strati-
fication 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
$E \cdot \omega \cdot \eta$ as the work per unit mass required to interchange isentropi-
cally 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

\[ \Delta h = \frac{1}{2}(\alpha_i^f + \alpha_i^i) \Delta P_1 + \frac{1}{2}(\alpha_2^f + \alpha_2^i) \Delta P_2, \]

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

\[ \alpha_i^f = \alpha_i^i + \left( \frac{\partial \alpha}{\partial \varepsilon} \right)_\eta d\varepsilon + \ldots \]

\[ \alpha_i^i = \alpha_i^o - \frac{1}{2} \frac{d\alpha}{d\varepsilon} d\varepsilon + \ldots \]

and

\[ \alpha_2^f = \alpha_2^i - \left( \frac{\partial \alpha}{\partial \varepsilon} \right)_\eta d\varepsilon + \ldots \]

\[ \alpha_2^i = \alpha_2^o + \frac{1}{2} \frac{d\alpha}{d\varepsilon} d\varepsilon + \ldots \]

\[ \Delta P_2 = -\Delta P_1 = \int_0^g d\varepsilon \]

\[ 1.19 \]

\[ 1.20 \]

\[ 1.21 \]

\[ 1.22 \]

\[ 1.23 \]

\[ 1.24 \]
into (1.19) and neglecting all higher order terms, we obtain
\[ \Delta h = \rho g \left[ \frac{d\alpha}{dz} \left( \frac{\partial \alpha}{\partial z} \right) \right] d\varepsilon^2 \]
\[ = E_{h\eta} d\varepsilon^2 = E_{w\eta} d\varepsilon^2 \] 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 \( \delta z \) such that
\[ \delta z = \alpha^f_2 - \alpha^l_1 = -\left( \alpha^f_1 - \alpha^l_2 \right) \] 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
\[ \Delta \chi_{int} = \rho d\varepsilon \cdot g \delta z = \rho g (\alpha^f_2 - \alpha^l_1) d\varepsilon \]
\[ = \rho g \left[ \frac{d\alpha}{dz} \left( \frac{\partial \alpha}{\partial z} \right) \right] d\varepsilon^2 \]
\[ = E_{p\eta} d\varepsilon^2 \]
\[ = E_{h\eta} d\varepsilon^2 = E_{w\eta} d\varepsilon^2 \] 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

\[
\Delta \alpha = \alpha_i - \alpha_f + \alpha_2 - \alpha_1 = \left( \frac{\partial \alpha}{\partial P} \right)_T \Delta P + \left( \frac{\partial \alpha}{\partial P} \right)_T \Delta P
\]

\[
= \rho g \left\{ \frac{d}{d\zeta} \left( \frac{1}{\gamma} \frac{\partial \alpha}{\partial P} \right) - \left[ \frac{\partial \alpha}{\partial \zeta} \left( \frac{1}{\gamma} \frac{\partial \alpha}{\partial P} \right) \right] \right\} d\zeta^2
\]

\[
= \gamma \alpha \eta d\zeta^2
\]

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 \( p \Delta \alpha \) such that

\[
\Delta \alpha^{ext} = p \Delta \alpha = \rho \gamma \alpha \eta d\zeta^2
\]

\[
= \rho g \left\{ \frac{d}{d\zeta} \left( \frac{P}{\gamma} \frac{\partial \alpha}{\partial P} \right) - \left[ \frac{\partial \alpha}{\partial \zeta} \left( \frac{P}{\gamma} \frac{\partial \alpha}{\partial P} \right) \right] \right\} d\zeta^2
\]

\[
= \gamma \alpha \eta d\zeta^2
\]

and a change of internal energy \( \Delta \epsilon \) of the internal system of
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 $\varphi$ is given by

$$
\Delta \varphi = \left( \varphi_i^s - \varphi_i^e \right) + \left( \varphi_2^s - \varphi_2^e \right) = \left( \frac{\partial \varphi}{\partial \rho} \right)_\eta_1 \Delta \rho_1 + \left( \frac{\partial \varphi}{\partial \rho} \right)_\eta_2 \Delta \rho_2
$$

$$
= \rho \eta \left\{ \frac{\partial}{\partial \rho} \left( \frac{\partial \varphi}{\partial \rho} \right)_\eta - \left[ \frac{\partial}{\partial \rho} \left( \frac{\partial \varphi}{\partial \rho} \right)_\eta \right] \right\} d\varepsilon
$$

$$
= E_{\varphi \eta} d\varepsilon
$$

where $E_{\varphi \eta}$ may be interpreted as the parameter giving the change of a property $\varphi$ 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.
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.

<table>
<thead>
<tr>
<th>Work required to produce interchange</th>
<th>Energy change (internal system)</th>
<th>Energy change (external system)</th>
<th>Total energy change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy</td>
<td>$E_{\text{h}\eta} = E_{w\eta}$</td>
<td>0</td>
<td>$E_{\text{h}\eta} = E_{w\eta}$</td>
</tr>
<tr>
<td>Internal energy</td>
<td>$E_{e\eta}$</td>
<td>0</td>
<td>$E_{e\eta}$</td>
</tr>
<tr>
<td>Potential energy</td>
<td>$E_{\text{int}} = E_{\text{h}\eta}$</td>
<td>$E_{\text{ext}} = -E_{e\eta}$</td>
<td>$E_{\text{int}} = E_{\text{h}\eta} - E_{e\eta}$</td>
</tr>
</tbody>
</table>

\[
E_{w\eta} = E_{e\eta} = E_{\text{int}} = \rho g \left[ \frac{d\alpha}{d\xi} \right] - \left( \frac{\partial \alpha}{\partial \xi} \right) _{\eta} = \rho g \left[ \frac{\partial \alpha}{\partial \xi} \left( \frac{d\psi}{d\xi} + \Gamma \right) + \frac{\partial \alpha}{\partial \xi} \frac{d\xi}{d\eta} \right] , \quad \Gamma = - \left( \frac{\partial \psi}{\partial \xi} \right) _{\eta} \\
E_{\text{ext}} = -E_{e\eta} = \rho g \left[ \frac{d\alpha}{d\xi} \left( \frac{\partial \psi}{\partial \xi} \right) \left( \frac{d\psi}{d\xi} + \Gamma \right) + \frac{\partial \alpha}{\partial \xi} \frac{d\xi}{d\eta} \frac{d\xi}{d\eta} \right] \\
E_{\text{int}} = E_{e\eta} + E_{\text{ext}} = E_{\text{h\eta}}
\]
Exercises (Part 1)

1. Show that

$$\Delta \varphi = - \Delta h S \varphi = - \Delta \nu S \varphi + \frac{1}{\nu} \frac{\partial \varphi}{\partial \nu} \Delta \nu S \eta.$$  

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 $\mu$ is introduced for $(\frac{\partial \rho}{\partial S})_i, p$.

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

$$\Delta \eta = C_p \Delta \varphi + \frac{\partial C_p}{\partial \eta} \frac{d \varphi}{d \varphi} + \frac{\partial h_s}{\partial p} \frac{d \varphi}{d \varphi},$$

where $\Delta \varphi$ is the change of temperature of the system per unit distance, $C_p$ is specific heat, $h_s$ is introduced for $(\frac{\partial h_s}{\partial S})_i, p$, and $d\varphi/d\varphi$ for the potential temperature gradient $d\varphi/dz + l$. 
References


-------- 1949b. Über die Mischungsarbeit von stabil geschichteten Wassermassen. Ibid., 264-269.


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

$$dE = TdN - pdV + \sum \mu_i dm_i$$  \hspace{1cm} (2.1)

where $T$ is absolute temperature, $N$ entropy, $p$ pressure, $V$ volume, and $\mu_i$ 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

$$\epsilon = \frac{E}{M} \text{ specific internal energy},$$
$$\eta = \frac{N}{M} \text{ specific entropy},$$
$$\alpha = \frac{V}{M} \text{ specific volume},$$
$$\chi_i = m_i / M \text{ mass fraction of the } i \text{-th constituent},$$

and substituting into (2.1), we obtain the equations

$$d\epsilon = Td\eta - p\,d\alpha + \sum \mu_i \,d\chi_i$$  \hspace{1cm} (2.2)
$$\epsilon = T\eta - p\alpha + \sum \mu_i \chi_i$$  \hspace{1cm} (2.3)

and the Gibbs-Duhem equation

$$- \eta \,dT + \alpha \,dp - \sum \chi_i \,d\mu_i = 0$$  \hspace{1cm} (2.4)
Assuming that the ratios of dissolved ionic constituents is constant, we may write
\[ x_i = \lambda_i S \tag{2.5} \]
where \( S \) is salinity and \( \lambda_i \) the ratio of mass of the \( i \)-th constituent to the total mass of dissolved salts. We also introduce a combined chemical potential \( \mu_S \) for the dissolved salts such that
\[ \mu_S = \sum \lambda_i \mu_i \tag{2.6} \]
and a specific chemical potential \( \mu_w \) for water in sea water. Using these quantities, we can rewrite (2.2), (2.3) and (2.4) in the form
\[ d\epsilon = Td\eta - pdx + \mu dS \tag{2.7} \]
\[ \epsilon = T\eta - p\alpha + \mu S + \mu_w \tag{2.8} \]
\[ d\mu_w = -\eta dT + \alpha dp - S d\mu \tag{2.9} \]
where
\[ \mu = \mu_S - \mu_w \tag{2.10} \]
is the difference of chemical potentials of the dissolved salts and water.*

The Gibbs-Duhem equation (2.9) can be written in the form
\[ d\mu_w = -(\eta + S \frac{\partial \mu}{\partial T})dT + (\alpha - S \frac{\partial \mu}{\partial P})dP - S \frac{\partial \mu}{\partial S} dS \tag{2.11} \]
where \( \gamma_w \) and \( \alpha_w \) 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

\[
\frac{\partial \mu}{\partial p} = \frac{\partial \alpha}{\partial s} \quad 2.12
\]

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

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

The derivative \( \frac{\partial \mu_w}{\partial s} \), or from (2.11) \( -S \frac{\partial \mu}{\partial s} \), 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 \( \mu_w \) of the water in sea water must must equal the chemical potential of the vapour \( \mu_v \). If we compare two such equilibrium systems of slightly differing salinities, we must have for the differences of chemical potential
\[ \Delta \mu_w = \Delta \mu_v = \frac{\partial \mu_v}{\partial P} \Delta P = \alpha_v \Delta P_v \]  

2.14

where \( P_v \) is the vapour pressure and \( \alpha_v \) is the specific volume of the vapour. From (2.11) we have

\[ \Delta \mu_w = \alpha_w \Delta P - s \frac{\partial \alpha_v}{\partial s} \Delta s \]

Hence,

\[ s \frac{\partial \mu_v}{\partial s} = -(\alpha_v - \alpha_w) \Delta \frac{P}{\Delta s} \]  

2.15

Defining \( r \) to be the fractional lowering of vapour pressure \( P^0 - P/P^0 \), where \( P^0 \) is the vapour pressure of pure water at the same temperature, we have

\[ s \frac{\partial \mu_v}{\partial s} = P^0 (\alpha_v - \alpha_w) \frac{\partial r}{\partial s} \]

\[ \approx \frac{P^0 \alpha^0}{1-r} \frac{\partial r}{\partial s} \approx \frac{RT}{1-r} \frac{\partial r}{\partial s} = - \frac{\partial \mu_w}{\partial s} \]  

2.16

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

From (2.16) we obtain

\[ \mu_w = \mu_w^0 + RT \ln (1-r) \]

2.17

or

\[ \frac{\partial \mu_w}{\partial s} = - \frac{1}{s} \frac{\partial \mu_w}{\partial s} = \frac{RT}{s(1-r)} \frac{\partial r}{\partial s} > 0 \]  

2.18

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

The interpretation of the arbitrary linear function of temperature in \( \mu \) is relatively simple if we formulate the expression for entropy in terms of the thermodynamic potential \( g \), where
Differentiating with respect to temperature at constant pressure and salinity, we obtain

\[ \frac{\partial g}{\partial T} = -\eta = \mu_s + \mu_w - S \frac{\partial \mu_s}{\partial T} + (1 - S) \frac{\partial \mu_w}{\partial T} \]

where \( \eta_s \) and \( \eta_w \) are the partial specific entropies of the dissolved salts and water respectively. If \( \frac{\partial \mu}{\partial T} \) contains an arbitrary constant, then from the relation

\[ \frac{\partial \mu}{\partial T} = -\frac{\partial \eta}{\partial S} \]

the entropy \( \eta \) must contain an arbitrary linear function of salinity. Consequently, from (2.20), \( \eta_s \) and \( \eta_w \) 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
\[ \Delta T = 0, \]
\[ \Delta \mu_S = \Delta \mu_w = -d \phi, \]
\[ \Delta \mu = 0 \]

As the vertical gradient of \( \mu \) must vanish in equilibrium, we have

\[ \frac{d\mu}{d\bar{z}} = \frac{\partial \mu}{\partial p} \frac{dp}{d\bar{z}} + \frac{\partial \mu}{\partial S} \frac{dS}{d\bar{z}} = 0 \]

\[ (\frac{\partial S}{\partial \mu}) = -\frac{\partial \mu/\partial p}{\partial \mu/\partial S} = -\frac{\partial \phi/\partial S}{\partial \mu/\partial S} \]

\[ (\frac{dS}{d\bar{z}}) = -\Gamma_S = \frac{\partial \phi}{\partial S/\partial S} \sim 3-9 \% /1000 \text{ m}. \]

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 \( \mu \) to zero.

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

\[ F_Q = -k_Q \frac{d\bar{T}}{d\bar{z}} \text{(heat)} \]

2.24
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

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

\[ F^S = -k_S \left( \frac{dS}{dz} \right) \quad 2.27 \]

where \( k'_Q \) and \( k_S \) are eddy coefficients of conductivity and diffusivity respectively.

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

\[ k'_Q = k = 0.00139 \text{ (}0^\circ\text{C, }35\%) \]
\[ k'_Q = k = 0.00149 \text{ (}20^\circ\text{C, }35\%) \]

\[ k_S = 0.0000068 \text{ (}0^\circ\text{C, }35\%) \]
\[ k_S = 0.0000129 \text{ (}20^\circ\text{C, }35\%) \]

\[ \mu = 0.01826 \text{ (}0^\circ\text{C, }35\%) \]
\[ \mu = 0.01075 \text{ (}20^\circ\text{C, }35\%) \]

The Prandtl number \( \psi/K \) for sea water is 13.1 at \( 0^\circ\text{C} \) and 7.0 at \( 20^\circ\text{C} \) 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

\[ D : K : \psi = 1 : 100 : 1000 \quad 2.28 \]
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 \( \phi \), are related to the partial functions, \( \phi_s \) and \( \phi_w \), by

\[
\phi = s \phi_s + (1-s) \phi_w
\]

where

\[
\rho_s = \phi + (1-s) \frac{\partial \phi}{\partial s}
\]

\[
\rho_w = \phi - s \frac{\partial \phi}{\partial s}
\]

By subtraction

\[
\frac{\partial \phi}{\partial s} = \phi_s - \phi_w
\]

Thermodynamic Potential \( g \)

\[
g = e - T\eta + p\alpha = \rho s + \rho_w = s \rho_s + (1-s) \rho_w = s g_s + (1-s) g_w
\]

\[
dg = -\eta dT + \alpha dp + \mu ds
\]
**Internal energy** $e$

$$e = g + T\eta - p\alpha = g - T\frac{\partial g}{\partial T} - p\frac{\partial g}{\partial p}$$

$$= se + (1-s)e_\omega$$

$$de = Td\eta - p\alpha d\alpha + \mu ds$$

$$= (C_p - P\frac{\partial \alpha}{\partial T})dT - (p\frac{\partial \alpha}{\partial p} + T\frac{\partial \alpha}{\partial T})dp + (\mu - T\frac{\partial \mu}{\partial T} - p\frac{\partial \mu}{\partial p})ds$$

**Enthalpy** $h$

$$h = e + p\alpha = g + T\eta = g - T\frac{\partial g}{\partial T}$$

$$= s\tilde{h} + (1-s)h_\omega$$

$$dh = Td\eta + \alpha dp + \mu ds$$

$$= (C_p + \frac{\partial \alpha}{\partial T})dT - (p\frac{\partial \alpha}{\partial p} + T\frac{\partial \alpha}{\partial T})dp + (\mu - T\frac{\partial \mu}{\partial T} - p\frac{\partial \mu}{\partial p})ds$$

**Free energy** $f$

$$f = e - T\eta = g - p\alpha = g - p\frac{\partial g}{\partial p}$$

$$= s\tilde{f} + (1-s)f_\omega$$

$$df = -\eta dT - pd\alpha + \mu ds$$

$$= -(\eta - p\frac{\partial \eta}{\partial p})dT - p\frac{\partial \alpha}{\partial p}dp + (\mu - p\frac{\partial \mu}{\partial p})ds$$

**Entropy** $\eta$

$$\eta = -\frac{\partial g}{\partial T}$$

$$= s\eta + (1-s)\eta_\omega$$

$$d\eta = \frac{1}{\rho} de + \frac{\partial \alpha}{\partial \alpha} d\alpha - \frac{\partial \alpha}{\partial T} ds$$

$$= \frac{C_p}{T}dT - \frac{\partial \alpha}{\partial \alpha} dp - \frac{\partial \mu}{\partial T} ds$$
Specific Volume $\alpha$

\[ \alpha = \frac{\partial q}{\partial p} \]
\[ = 5\alpha_s + (1 - 5)\alpha_w \]
\[ \alpha_s = \alpha + (1 - \alpha) \frac{\partial \alpha}{\partial s} \]
\[ \alpha_w = \alpha - s \frac{\partial \alpha}{\partial s} \]

Derived relationships

\[ \frac{\partial^2 q}{\partial T \partial s} = - \frac{\partial \eta}{\partial s} = \frac{\partial \mu}{\partial T} \]

\[ \frac{\partial s}{\partial p} = \frac{\partial \alpha}{\partial T} = - \frac{\partial \eta}{\partial p} \]

\[ \frac{\partial^2 q}{\partial s \partial p} = \frac{\partial \mu}{\partial p} = \frac{\partial \alpha}{\partial s} \]

Specific Heat $C_p$

\[ C_p = T \frac{\partial \eta}{\partial T} = - T \frac{\partial^2 q}{\partial T \partial s} \]

\[ \frac{\partial C_p}{\partial p} = - T \frac{\partial \alpha}{\partial T} \]

\[ \frac{\partial C_p}{\partial s} = - T \frac{\partial \mu}{\partial T} \]

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

\[ T d\eta = C_p dT - T \frac{\partial \alpha}{\partial T} dp = C_v dT \]

\[ d\alpha = \frac{\partial \alpha}{\partial T} dT + \frac{\partial \alpha}{\partial p} dp = 0 \]

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** \( (d\eta = dS = 0) \)

\[ d\eta = \frac{C_p \Delta T}{T} - \frac{\partial \alpha}{\partial T} \Delta P = 0 \]

\[ \left( \frac{\partial \Delta T}{\partial \Delta P} \right)_{\eta} = \frac{T}{C_p} \frac{\partial \alpha}{\partial T} \]

**Adiabatic compressibility** \( (d\eta = dS = 0) \)

\[ d\alpha = \frac{\partial \alpha}{\partial T} \Delta T + \frac{\partial \alpha}{\partial P} \Delta P = \left( \frac{\partial \alpha}{\partial P} \right)_{\eta} \Delta P \]

\[ d\eta = \frac{C_p}{T} dT - \frac{\partial \alpha}{\partial T} \Delta P = 0 \]

for \( \Delta P \neq 0 \), the determinant of the coefficients of \( \Delta P \) and \( dT \) must vanish, i.e.

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

\[ \left( \frac{\partial \alpha}{\partial P} \right)_{\eta} = \frac{\partial \alpha}{\partial P} + \frac{T}{C_p} \left( \frac{\partial \alpha}{\partial T} \right)^2 \]

\[ = \frac{C_v}{C_p} \frac{\partial \alpha}{\partial P} = \frac{1}{\sigma} \frac{\partial \alpha}{\partial P} \]
References:


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

$$E = \int_{z_s}^{z_B} \rho \, dz$$

where $z_s$ and $z_B$ are the surface and bottom of the ocean respectively, $\rho$ is density, $M$ the total mass of the column (of unit cross section) and $m$ a mass coordinate defined by

$$m(z) = \int_{z}^{z_B} \rho \, dz, \quad z - z_B = \int_{0}^{m} \, dm.$$  

The total enthalpy $H$ is given by

$$H = \int_{0}^{M} h \, dm = \int_{0}^{M} (e + p\alpha) \, dm$$

$$= E + \int_{0}^{M} \frac{d\rho}{dm} \, \alpha \, dm$$

$$= E + \rho g \, z_s + \int_{0}^{M} \alpha \, dm$$

$$= E + \rho g \, z_s + \chi.$$  

where $\chi$ 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

$$H = E + \chi.$$  

Changes of total enthalpy for which the total mass of the column is constant, are given by
We have 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 \( \gamma_0 \) corresponding to a level \( \varepsilon_0 \), and extending from \( m_0 - m/2 \) to \( m_0 + m/2 \), the change of potential energy is given by

\[
\Delta \mathcal{X} = \Delta H - \Delta U = \int_{m_0}^{m_0 + m/2} \Delta (p\alpha) \, dm
\]

as no change of \( p\alpha \) occurs outside of the subsystem \( \gamma_0 \).

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

\[ E_h = E_{h\gamma} \]  
\[ E_e = E_{e\gamma} - pV_\alpha \]  
\[ E_\chi = E_{\chi\gamma} + pV_\alpha \]

where, from (1.11),

\[ V_\alpha = -\left[ \frac{\partial^2 \alpha}{\partial t^2} - \frac{\alpha}{\partial t} \frac{\partial^2 e_2}{\partial \xi^2} \right] \approx -\frac{\partial^2 \alpha}{\partial t^2} \]

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

\[
m v = (m_1 v_1 + m_2 v_2) = 0
\]

The total kinetic energy changes by an amount

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

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

\[
V_2 - V_1 = \frac{dV}{dz} \, dz
\]

so that the kinetic energy change per unit mass is

\[
\Delta K = -\left( \frac{dV}{dz} \right)^2 \, dz = -E_K \, dz
\]

The work required to produce the interchange is \( E_k \), 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

\[
R_i = E_n / E_k = \frac{E_k}{\left( \frac{dV}{dz} \right)^2}
\]

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

\begin{align}
\Delta \int_{m_0 - \frac{m_0}{2}}^{m_0 + \frac{m_0}{2}} \Delta m &= 0 \quad (3.16) \\
\Delta \int_{m_0 - \frac{m_0}{2}}^{m_0 + \frac{m_0}{2}} \Delta S \, dm &= -(F_s^2 - F_s') \Delta t \quad (3.17) \\
\Delta \int_{m_0 - \frac{m_0}{2}}^{m_0 + \frac{m_0}{2}} \Delta \frac{\rho}{\rho} \, dm &= -(F_h^2 - F_h') \Delta t \quad (3.18)
\end{align}

where $F_s$ and $F_h$ are the salt and enthalpy fluxes, and $\Delta t$ is a time interval for the deformation.

Expanding in a Taylor Series about $M_0$, we obtain

\begin{align}
-(F_s^2 - F_s') \Delta t &= \Delta S_0 m + \frac{1}{24} \Delta S_0 \frac{d^2 S_0}{dm^2} m^3 + \ldots \quad (3.19) \\
-(F_h^2 - F_h') \Delta t &= \Delta \frac{\rho}{\rho} m + \frac{1}{24} \Delta \frac{\rho}{\rho} \frac{d^2 \rho}{dm^2} m^3 + \ldots \quad (3.20)
\end{align}
Applying these basic conservation laws, we obtain the change for a general property \( \Psi \)

\[
\Delta \Psi dm = \frac{\partial \Psi}{\partial \rho} \Delta \rho m + \frac{1}{2} \frac{\partial \Psi}{\partial \frac{T}{T}} \Delta \frac{T}{T} m^2 + \frac{3}{4} \frac{\partial \Psi}{\partial \frac{p}{p}} \Delta \frac{p}{p} m^2 + \frac{5}{2} \frac{\partial \Psi}{\partial \frac{S}{S}} \Delta \frac{S}{S} m^2 + \frac{7}{8} \frac{\partial \Psi}{\partial \frac{\mu}{\mu}} \Delta \frac{\mu}{\mu} m^2.
\]

Substituting for \( \Delta \frac{S}{S} \) and \( \Delta \frac{\mu}{\mu} \) from (3.13) and (3.14), we have

\[
\Delta \Psi dm = \frac{1}{2} \frac{\partial \Psi}{\partial \frac{T}{T}} \Delta \frac{T}{T} m^2 + \frac{3}{4} \frac{\partial \Psi}{\partial \frac{p}{p}} \Delta \frac{p}{p} m^2 + \frac{5}{2} \frac{\partial \Psi}{\partial \frac{S}{S}} \Delta \frac{S}{S} m^2 + \frac{7}{8} \frac{\partial \Psi}{\partial \frac{\mu}{\mu}} \Delta \frac{\mu}{\mu} m^2.
\]

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

From the Taylor expansion, we obtain

\[
\Delta \frac{\mu}{\mu} dm = -\frac{\partial \Psi}{\partial \frac{T}{T}} \Delta \frac{T}{T} m^2 + \frac{3}{4} \frac{\partial \Psi}{\partial \frac{p}{p}} \Delta \frac{p}{p} m^2 + \frac{5}{2} \frac{\partial \Psi}{\partial \frac{S}{S}} \Delta \frac{S}{S} m^2 + \frac{7}{8} \frac{\partial \Psi}{\partial \frac{\mu}{\mu}} \Delta \frac{\mu}{\mu} m^2 = -(F^2 - F^1) \Delta t.
\]

so that

\[
\frac{1}{4} \Delta \frac{\mu}{\mu} m^2 = -(F^2 + F^1 - 2F^0) \Delta t
\]

\[
\approx -\frac{1}{4} \frac{d^2 F^0}{d m^2} m^2 \Delta t
\]

Hence

\[
\Delta F^0 \approx -\frac{d^2 F^0}{d m^2} \Delta t
\]

A similar expression is obtained for \( \Delta S_m \).
Approximating $F_{n} - F_{n}'$ by $dF_{n}/dm$ and $F_{s} - F_{s}'$ by $dF_{s}/dm$, we obtain

$$
\Delta \varphi dm = - \left( \frac{\partial \varphi}{\partial h} \frac{dF_{n}}{dm} + \frac{\partial \varphi}{\partial s} \frac{dF_{s}}{dm} \right) m \Delta t + o(\Delta t m^{3})
$$

Hence the rate of change of $\varphi$ per unit mass per unit time is

$$
\frac{\partial \varphi}{\partial t} = - \frac{\partial \varphi}{\partial h} \frac{dF_{n}}{dm} - \frac{\partial \varphi}{\partial s} \frac{dF_{s}}{dm}
$$

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

In the case of an isolated system,

$$
\Delta h_{m} = + \varphi F_{n}^{0} \Delta t / m^{2}
$$

$$
\Delta s_{m} = + \varphi F_{s}^{0} \Delta t / m^{2}
$$

and

$$
\Delta \varphi dm = + \frac{2}{3} \left( \frac{d}{dm} \left( \frac{\partial \varphi}{\partial h} \right) F_{n}^{0} + \frac{d}{dm} \left( \frac{\partial \varphi}{\partial s} \right) F_{s}^{0} \right) m \Delta t.
$$

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

$$
\frac{\partial \varphi}{\partial t} = \left[ \frac{d}{dm} \left( \frac{\partial \varphi}{\partial h} \right) F_{n} + \frac{d}{dm} \left( \frac{\partial \varphi}{\partial s} \right) F_{s} \right] = \varphi
$$

As we are considering an isolated system, we can consider $\varphi$ as the internal source of $\varphi$ due to diffusion. The open system (3.26) can be written

$$
\frac{\partial \varphi}{\partial t} = - \frac{d}{dm} \left( \frac{\partial \varphi}{\partial h} F_{n} + \frac{\partial \varphi}{\partial s} F_{s} \right) + \left[ \frac{d}{dm} \left( \frac{\partial \varphi}{\partial h} \right) F_{n} + \frac{d}{dm} \left( \frac{\partial \varphi}{\partial s} \right) F_{s} \right]
$$

$$
= - \frac{dF_{p}}{dm} + \varphi
$$
Hence, we can consider the change of a general property $\varphi$ due to diffusion as being equivalent to a diffusive flux $F_\varphi$ and an internal source $q_\varphi$. 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 $F_\eta$

$$F_\eta = \frac{\partial \eta}{\partial s} F_h + \frac{\partial \eta}{\partial \theta} F_s = \frac{F_h}{T} + \frac{\partial \eta}{\partial s} F_s$$  \hspace{1cm} (3.32)

Substituting

$$\left(\frac{\partial \eta}{\partial s}\right)_h = \left(\frac{\partial \eta}{\partial T}\right)_s \left(\frac{\partial \eta}{\partial s}\right)_h = \left(\frac{\partial \eta}{\partial s}\right)_T - \frac{h_s}{T}$$

we obtain

$$F_\eta = \frac{F_h}{T} - \frac{\nu}{T} F_s = \frac{\nu}{T} F_s$$  \hspace{1cm} (3.33)

where $\frac{\nu}{T} \equiv F_h - h_s F_s$ is interpreted as a "heat" flux.

2. Entropy source $q_\eta$

$$q_\eta = \frac{d}{dm} \left(\frac{\partial \eta}{\partial s}\right) F_h + \frac{d}{dm} \left(\frac{\partial \eta}{\partial \theta}\right) F_s$$

$$= -\frac{1}{T} \frac{\partial T}{\partial m} F_\theta - \frac{1}{T} \frac{\partial \mu}{\partial s} \left[\frac{d \eta}{d m} + \Gamma s\right] F_s$$  \hspace{1cm} (3.35)

where

$$\Gamma_s = - q \frac{\partial \mu}{\partial \eta} \frac{\partial \eta}{\partial s} = q \frac{\partial \mu}{\partial \eta} \frac{\partial \eta}{\partial s} = -\frac{\partial \mu}{\partial m} \mu$$
3. Internal energy flux $F_e$

$$F_e = (1 - P \frac{\partial x}{\partial n}) F_h - P \frac{\partial x}{\partial s} F_s$$

$$= F_h - \frac{p}{\rho_p} P \frac{\partial x}{\partial t} F_q - P \frac{\partial x}{\partial s} F_s$$  \hspace{1cm} 3.36

4. Internal energy source $q_e$

$$q_e = \frac{d}{d m} (\frac{d e}{d m}) F_h + \frac{d}{d m} (\frac{\partial e}{\partial s}) F_s$$

$$= - \left[ \frac{d}{d m} (P \frac{\partial x}{\partial n}) \right] F_q + \left[ \frac{d}{d m} (P \frac{\partial x}{\partial s}) \right] F_s$$

$$= - \left\{ \left[ \frac{d}{d m} (P \frac{\partial x}{\partial n}) \right] \frac{F_q}{\rho_p} + \left[ \frac{d}{d m} (P \frac{\partial x}{\partial s}) \right] F_s \right\}$$

$$+ \frac{\rho}{\rho_p} \frac{\partial x}{\partial t} \left[ \frac{d C_p}{d m} \frac{F_q}{\rho_p} + \frac{d \delta_s}{d m} F_s \right]$$  \hspace{1cm} 3.37
Exercises

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

$$E_{\chi} = E_{\chi}^\eta - E_{\eta}^\eta - \rho V_\alpha$$

$$= -\left\{ \frac{d}{dz}\left[ \rho \frac{\partial \alpha}{\partial \eta} \right] \left[ \frac{d h}{dz} - \frac{\partial h}{\partial \eta} \right] + \frac{d}{dz}\left[ \rho \frac{\partial \alpha}{\partial s} \right] \frac{ds}{dz} \right\} + \rho \frac{\partial \alpha}{\partial \eta} E_\eta.$$

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
\[
\frac{\partial}{\partial t} \int_S p u_i dV = -\int_S p u_i u_j n_j dA - \int_V 2 \Omega_{ji} \Omega_j \rho u_k dV
\]
Rate of change of momentum
Convection of momentum by current \(u_i\)
Momentum change due to Coriolis force

\[-\int_S p \delta_i^j n_j dA - \int_V \rho \frac{\partial \phi}{\partial \xi_i} dV\]
Momentum change due to net pressure force
Momentum change due to gravity

\[+\int_S \tau_{ij} n_j dA\] 4.1
Momentum change due to net viscous force.

The unit vector \(\eta_i\) is directed outward and perpendicular to the surface of integration.

Applying the divergence theorem

\[
\int_S \phi_j n_j dA = \int_V \frac{\partial \phi_i}{\partial x_i} dV
\] 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

\[
\frac{\partial p u_i}{\partial t} + \frac{\partial p u_i u_j}{\partial x_j} - 2 \Omega_{ji} \Omega_j \rho u_k = -\frac{\partial \rho}{\partial x_i} - \rho \frac{\partial \phi}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j}\] 4.3
that must be satisfied at every point of the fluid.

For the kinetic and internal energies, we have
\[
\frac{\partial}{\partial t} \int_{V} \rho (e + k) \, dV = - \int_{S} \rho (e + k) u_j n_j \, dA - \int_{S} \rho u_j \frac{\partial \phi}{\partial x_j} \, dV
\]

convection by current
rate of work against gravity

\[
- \int_{S} \rho u_j n_j \, dA + \int_{S} u_i T_{ij} n_j \, dA
\]
rate of work against pressure
rate of work against viscous forces

\[
- \int_{S} F_j n_j \, dA
\]
net diffusion of internal energy

Transforming to volume integrals, we obtain

\[
\frac{\partial \rho (e + k)}{\partial t} + \frac{\partial \rho (e + k) u_j}{\partial x_j} = - \frac{\partial \rho u_j}{\partial x_j} - \rho u_j \frac{\partial \phi}{\partial x_j} - \frac{\partial F_i}{\partial x_j} + \frac{\partial u_i T_{ij}}{\partial x_j}
\]

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

\[
\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_i}{\partial x_j} = 0
\]

4.6

or

\[
\rho \frac{\partial x}{\partial t} = \frac{\partial u_i}{\partial x_j}
\]

4.7

where

\[
\frac{\partial}{\partial t} = \frac{\partial}{\partial x_j} + u_j \frac{\partial}{\partial x_j}
\]

4.8

for the conservation of mass and
for the conservation of salt, the flux of salt relative to
the motion of the fluid is denoted by \( F_i^S \).

Using (4.6), we obtain the transformation

\[
\frac{\partial \rho \phi}{\partial t} + \frac{\partial \rho \phi u_i}{\partial x_j} = \rho \frac{\partial \phi}{\partial t}
\]

for a general property \( \phi \).

From the momentum equation, we obtain by contraction

with \( u_i \):

\[
\rho \frac{D(k+\phi)}{Dt} = -u_j \frac{\partial P}{\partial x_j} + u_i \frac{\partial T_{ij}}{\partial x_j}
\]

for the rate of change of "mechanical" energy.

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

\[
\rho \frac{De}{Dt} = -\rho \frac{\partial u_i}{\partial x_j} - \frac{\partial F_i}{\partial x_j} + T_{ij} \frac{\partial u_i}{\partial x_j}
\]

The term \( T_{ij} \frac{\partial u_i}{\partial x_j} \) 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

\[
\rho \frac{Db}{Dt} = \rho \frac{D(e+p\phi)}{Dt} = \frac{DP}{Dt} - \frac{\partial F_i}{\partial x_j} + q_k
\]
where \( q_k \) is introduced for the dissipation function \( \tau_{ij} \frac{\partial u_i}{\partial u_j} \).

For an isentropic flow

\[
\frac{Dh}{Dt} = \alpha \frac{DP}{Dt},
\]

hence, we may write (4.13) in the form

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

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

\[
\frac{Dh}{Dt} = \Upsilon \frac{DP}{Dt} + \alpha \frac{DP}{Dt} + \mu \frac{DS}{Dt}
\]

we can derive the relationship

\[
P \left[ \frac{Dh}{Dt} - \left( \frac{Dh}{Dt} \right)_\eta \right] = P C_P \left[ \frac{Dy}{Dt} - \Upsilon \frac{DP}{Dt} \right] + P h_s \frac{DS}{Dt}
\]

\[
= -\frac{\partial F_i}{\partial x_j} + q_k
\]

Substituting for \( P \frac{Dy}{Dt} \) from (4.9) and rearranging terms, we obtain

\[
P C_P \left[ \frac{Dy}{Dt} - \left( \frac{Dy}{Dt} \right)_\eta \right] = -\frac{\partial (F_j - h_s F_j)}{\partial x_j} - \frac{\partial h_s}{\partial x_j} F_j + q_k
\]

\[
= -\frac{\partial F_i}{\partial x_j} - \frac{\partial h_s}{\partial x_j} F_j + q_k
\]

where
The flux $F_i^s$ can be interpreted as a heat flux. The term $\frac{\partial h_i}{\partial x_j} F_j^s$ 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 $\frac{\partial h}{\partial s} \frac{\partial s}{\partial x_j} F_j^s$).

**Entropy Equation**

The entropy equation can be formulated from the equation

$$\frac{D\eta}{Dt} = \frac{1}{T} \frac{Dh}{Dt} - \frac{\alpha_s}{T} \frac{DP}{Dt} - \frac{\mu}{T} \frac{DS}{Dt}.$$  \hspace{1cm} 4.21

Multiplying through by the density $\rho$ and substituting the fluxes for enthalpy and salt, we have

$$\rho \frac{D\eta}{Dt} = -\frac{1}{T} \frac{\partial F_i}{\partial x_j} \frac{\partial h}{\partial s} + \frac{\mu}{T} F_j^s + \frac{\mu}{T} \frac{\partial F_i}{\partial x_j} F_j^s.$$  \hspace{1cm} 4.22

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

$$\rho \frac{D\eta}{Dt} = -\frac{3}{T} \left[ \frac{\partial F_i}{\partial x_j} + \frac{\mu}{T} F_j^s \right]^{\text{Flux} \, F_i} - \frac{1}{T^2} \frac{\partial T}{\partial x_j} F_j^b - \frac{\partial \mu}{\partial x_j} F_j^s + \frac{\mu}{T} F_j^s^{\text{Source} \, \eta}.$$  \hspace{1cm} 4.22(a)

The source or rate of entropy production $q_{\eta}$ can be further transformed to

$$q_{\eta} = \frac{\mu}{T} \left[ \frac{1}{T^2} \frac{\partial T}{\partial x_j} F_j^b + \frac{1}{T} \frac{\partial \mu}{\partial s} \left( \frac{\partial s}{\partial x_j} - \frac{K}{\partial x_j} \frac{\partial P}{\partial x_j} \right) F_j^s \right].$$  \hspace{1cm} 4.23
where
\[ \mathcal{S} \frac{\partial \rho}{\partial x_j} = \left( \frac{\partial s}{\partial x_j} \right) \mu \]

is the equilibrium salinity gradient in the presence of a pressure gradient \( \frac{\partial \rho}{\partial x_i} \).

The entropy production is positive definite if we assume phenomenological laws for heat and salt flux of the form
\[ F_i^q = -k \frac{\partial T}{\partial x_i} \]
\[ F_i^s = -D \left( \frac{\partial s}{\partial x_i} - \mathcal{S} \frac{\partial \rho}{\partial x_i} \right) \]

More generally, we can assume
\[ F_i^q = -k \frac{\partial T}{\partial x_i} - \ell \frac{\partial s}{\partial x_i} \left( \frac{\partial s}{\partial x_i} - \mathcal{S} \frac{\partial \rho}{\partial x_i} \right) \]
\[ F_i^s = -\ell \frac{\partial s}{\partial x_i} \left( \frac{\partial s}{\partial x_i} - \mathcal{S} \frac{\partial \rho}{\partial x_i} \right) \]

In this case, the requirement for \( q \eta \) to be positive definite implies
\[ \left( \ell \frac{\partial s}{\partial s} + T \frac{\partial \mu}{\partial s} \right) \ell_{sq}^2 < 4T \frac{\partial \mu}{\partial s} kD \]

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 \( \overline{\rho u S} \) associated with the mean flow of mass \( \overline{\rho u_i} \), and a "diffusive" flux \( (\rho u_i)'S' + F_{i\text{nd}}^s \), representing the flow relative to the mean flow of mass, where \( (\rho u_i)'S' \) are deviations having zero average with respect to the particular averaging process chosen.

The macroscopic flux of heat and salt may be written

\[
F_i^Q = (\rho u_i)'C_p(T' - \Gamma p') \approx \overline{\rho C_p(u'T')} \tag{4.30}
\]

\[
F_i^S = (\rho u_i)'S' \approx \overline{\rho (u'S')}. \tag{4.31}
\]

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

\[
K_i^Q = -\frac{F_i^Q}{\overline{\rho C_p}} \frac{\partial T'}{\partial x_i} = -\frac{(u_i'T')}{\partial x_i} \tag{4.32}
\]

\[
K_i^S = -\frac{F_i^S}{\rho} \frac{\partial S'}{\partial x_i} = -\frac{(u_i'S')}{\partial x_i} \tag{4.33}
\]

For molecular processes, the flow of heat is more rapid than the flow of salt, i.e., \( K_i^Q \gg K_i^S \). In many parts of the ocean, particularly in deep water, the spatial variation of temperature and salinity appears to be closely correlated so that the ratio \( \frac{\partial T'}{\partial S} \) is constant.

If the ratio is constant for the fluctuations also, we must have \( K_i^Q = K_i^S \). 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 $K_s > K_l$.

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

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

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

$$
\rho \frac{\partial u_i}{\partial x_j} = \rho \frac{D\alpha}{Dt} = \rho \left[ \frac{\partial \alpha}{\partial h} \frac{Dh}{Dt} + \frac{\partial \alpha}{\partial P} \frac{DP}{Dt} + \frac{\partial \alpha}{\partial S} \frac{DS}{Dt} \right]
$$

$$
= \rho \left\{ \frac{\partial \alpha}{\partial h} \left[ \frac{Dh}{Dt} - \left( \frac{Dh}{Dt} \right)_p \right] + \frac{\partial \alpha}{\partial S} \frac{DS}{Dt} + \left[ \frac{\partial ^2 \alpha}{\partial P \partial \theta} \right] \frac{DP}{Dt} \right\} \quad 4.35
$$

Substituting the enthalpy and salt flux, we obtain

$$
\rho \frac{\partial u_i}{\partial x_j} = \rho \left\{ \frac{\partial \alpha}{\partial h} \left[ \frac{Dh}{Dt} - \left( \frac{Dh}{Dt} \right)_p \right] + \frac{\partial \alpha}{\partial S} \frac{DS}{Dt} + \left[ \frac{\partial ^2 \alpha}{\partial P \partial \theta} \right] \frac{DP}{Dt} \right\} - \frac{\partial \alpha}{\partial \theta} \frac{D\theta}{Dt} + \frac{\partial \alpha}{\partial \phi} \frac{D\phi}{Dt} + \frac{\partial \alpha}{\partial \theta} \frac{D\theta}{Dt} \quad 4.36
$$

Converting further to temperature, we have

$$
\rho \frac{\partial u_i}{\partial x_j} = \frac{\partial \alpha}{\partial \theta} \left[ \frac{Dh}{Dt} - \left( \frac{Dh}{Dt} \right)_p \right] + \frac{\partial \alpha}{\partial S} \frac{DS}{Dt} + \left[ \frac{\partial ^2 \alpha}{\partial P \partial \theta} \right] \frac{DP}{Dt} - \frac{\partial \alpha}{\partial \theta} \frac{D\theta}{Dt} + \frac{\partial \alpha}{\partial \phi} \frac{D\phi}{Dt} + \frac{\partial \alpha}{\partial \theta} \frac{D\theta}{Dt}
$$

$$
+ \frac{\partial \alpha}{\partial \phi} \frac{D\phi}{Dt} + \frac{\partial \alpha}{\partial \theta} \frac{D\theta}{Dt} \quad 4.37
$$
The final form of the mechanical energy equation can be obtained by substituting (4.37) for $p \frac{\partial u_j}{\partial x_j}$ in (4.34).
Part V.

Interpretation of the energy parameters

The energy parameters $E_i$, $E_x$, $E_{\phi}$ for isentropic and $E_i$, $E_x$, $E_{\phi}$ 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

$$\int K_\alpha E_{hi}^* = -\frac{\partial}{\partial h} \left[ \frac{\partial X_i}{\partial h} F_i + \frac{\partial X_i}{\partial S} F_i^S \right]$$

$$\int K_\alpha E_{h}^* = +\left[ \frac{\partial}{\partial h} \left( \frac{\partial X_i}{\partial h} \right) F_i + \frac{\partial X_i}{\partial S} \left( \frac{\partial X_i}{\partial S} \right) F_i^S \right]$$

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

$$F_1 = F_2 = 0, \quad F_3 = -K_\alpha \left( \frac{dX_i}{dz} + \pi \right) - \pi_{\phi} \frac{dS}{dz}$$

$$F_i^S = F_2 = 0, \quad \mu_{\phi} = -\pi_{\phi} \frac{dS}{dz}$$

and $K_\alpha = K_{\phi}$.

Using the generalized parameters, we may write the equation for mechanical energy in the form
By adding \( \frac{\partial P}{\partial t} \) to both sides of (5.5), we can transform the equation to

\[
\rho \frac{D(k + \xi)}{Dt} = -\frac{\partial}{\partial x_j} \left( \mu \frac{\partial k}{\partial x_j} \right) - (1 - \mu \frac{\partial \xi}{\partial t}) \frac{\partial k}{\partial t} - \rho \frac{\partial (P \xi)}{\partial t} + \frac{\partial}{\partial x_j} \left[ \rho \kappa_0 \left( \frac{P}{x_j} \right) E_{h_j}^* \right] + \rho \kappa_0 E_{h_j}^* \tag{5.5}
\]

where

\[
\left( \frac{D(k + \xi)}{Dt} \right) = -\nabla \cdot \left( \frac{\xi}{\rho} \right) \frac{\partial P}{\partial t} \tag{5.6}
\]

\[
\xi = \nabla / \rho \tag{5.7}
\]

**Hydrostatic approximation**

If we introduce the hydrostatic approximation

\[
\alpha d\phi = -\alpha dP = \mathbf{g} \mathbf{d} \mathbf{z} \tag{5.8}
\]

we can write

\[
\phi = f_0 - \int_{\mathbf{r}}^{\mathbf{r}} \alpha dP = \mathbf{f}_0 \mathbf{z} \tag{5.9}
\]

where \( \mathbf{f}_0 = \mathbf{f}_0 + \mathbf{g} \mathbf{z}_0 \) is the geopotential at the free surface

\[
\mathbf{z}_0 = \mathbf{z}_0 \tag{5.9}
\]

and \( \mathbf{P}_0 \), \( \mathbf{\alpha}_0 \) the pressure (atmospheric) and specific volume at the surface. For convenience, we shall neglect atmospheric pressure, and neglect the term \( \mathbf{P}_0 \mathbf{\alpha}_0 \) in (5.9).

We may write
Substitution of (5.9) and (5.10) into (5.6) yields

\[
\rho \frac{D}{Dt} (k + \frac{d}{dz} \int_0^z \hat{E}_h (\zeta, z) d\zeta) = \frac{\partial p}{\partial t} + \frac{\partial u_j}{\partial x_j} \hat{\zeta} - \hat{q}_R + \frac{\partial}{\partial x_j} (\rho k \hat{E}_h) + \rho k \hat{E}_h \hat{E}_h 
\]

where

\[
\frac{D}{Dt} \int_0^z \rho \frac{\partial \zeta}{\partial \zeta} d\zeta = \frac{\partial p}{\partial t} \frac{\partial \zeta}{\partial \zeta} \frac{Dp}{Dt} \frac{D}{Dt} \int_0^z \rho \frac{\partial \zeta}{\partial \zeta} d\zeta = \frac{\partial p}{\partial t} \frac{\partial \zeta}{\partial \zeta} \frac{Dp}{Dt} 
\]

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

If we assume that the motion at some depth \( z_0 \) in the ocean is small so that horizontal pressure gradients can be neglected, we can evaluate \( \int_0^{z_0} \hat{E}_h d\zeta \).

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

\[
\phi_s = \int_{z_0}^{z_R} \hat{E}_h d\zeta 
\]
provided, of course, that strong fluxes of heat and salt do not occur at \( \mathcal{Z}_y \). Hence, at every other layer in which the diffusive terms are negligible, steady flow must satisfy a Bernoulli equation of the form

\[
K + \int_{\mathcal{Z}} e \chi \, d\mathcal{Z} = \text{constant} \quad 5.14
\]

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

For the hypothetical two-layer ocean,

\[
(E_i = \frac{\Delta \rho}{\rho} \delta (\mathcal{Z} - \mathcal{Z}_i), \delta = \text{delta function})
\]

(5.14) becomes zero for \( \mathcal{Z} < \mathcal{Z}_i \) (lower layer) and

\[
K + \frac{\Delta \rho}{\rho} \delta \mathcal{Z}_i = K + \frac{\Delta \rho}{\rho} \delta \mathcal{Z}_i = \text{constant} \quad 5.15
\]

for the upper layer, where \( \mathcal{Z}_i = \mathcal{h} \) is the thickness of the upper layer.

Because the compressibility of sea water is slight, \( \mathcal{Z} \) can be interpreted as the geometric distance to the free surface \( (\mathcal{Z}_3 - \mathcal{Z}) \).

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

\[
\tau_{ij} = \tau_{ij} \tau = \tau \chi \frac{\mathcal{U}_i}{\mathcal{Z}} \quad 5.16
\]
we obtain the energy equation

\[
\frac{\sigma}{\partial t} (\zeta + \zeta') = -\frac{\alpha}{c^2} + K_m \frac{\partial^2 \zeta}{\partial z^2} - \sigma_c
\]

\[
+ K_c \frac{\partial^2 \zeta'}{\partial z^2} + \frac{\partial \zeta}{\partial x}
\]

5.17

where

\[
\Phi = \int_{\sigma_0}^{\sigma} \frac{E}{\sigma} \, d\sigma
\]

5.18

\[
\frac{\partial}{\partial x} \left( K \frac{\partial z}{\partial x} \right) = \frac{\partial}{\partial z} \left( K \frac{\partial z}{\partial z} \right)
\]

5.19

Equation (5.17) contains two terms in the form of sources - the dissipation function \( K \) representing loss of kinetic energy and \( K_c \bar{E}_x \) representing production of potential energy due to heat and salt diffusion. The divergence terms \( K_m \frac{\partial^2 \zeta}{\partial z^2} \) and \( K_c \frac{\partial^2 \zeta'}{\partial z^2} \) 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 \( \zeta + \zeta' \) 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

\[
\frac{\partial^2}{\partial z^2} \ln \left( \frac{\zeta + \zeta'}{\zeta} \right) = \frac{\partial}{\partial z} \left( K_c \bar{E}_x \right) - \frac{\zeta}{\sigma}
\]

5.20

where the bar indicates a vertical average. The contribution to the energy production comes entirely from the thermocline and is positive if \( K_c \bar{E}_x \) is greater than \( \frac{\zeta}{\sigma} \). It is
It would be interesting to know more explicitly how the energy is distributed between $K$ and $\Phi'$. 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

$$\chi = \chi_c + \chi_T \left( \gamma - \gamma_c \right) + \frac{1}{2} \chi_{TT} \left( \gamma - \gamma_c \right)^2$$

5.21

where $\chi_c$, $\chi_T$, $\chi_{TT}$ are constants, we obtain

$$\hat{\mathbf{\nabla}} \mathbf{E}_T \approx \hat{\mathbf{\nabla}} \mathbf{E}_{cT} - \frac{p_c}{\rho_c} \frac{\Delta \gamma}{\Delta \gamma_c} \left[ \chi_T \gamma_c - Z_c \chi_{TT} \gamma_c^2 \right] \mathbf{Z}^'$$

$$- \rho_c \gamma \chi_{TT} \gamma_c^2 \mathbf{Z}^{'2}$$

$$\mathbf{E}_h \mathbf{Z}^' - \frac{p_c}{\rho_c} \frac{\Delta \gamma}{\Delta \gamma_c} \left[ \chi_T \gamma_c - Z_c \chi_{TT} \gamma_c^2 \right] \mathbf{Z}^{'2}$$

5.22
where \( z' \) is measured from \( \widehat{z}_{\infty} \). Integrating (5.22), we obtain

\[
\int_{z}^{\infty} \theta' \; dz = \int_{z}^{\infty} \frac{1}{2} \bar{E}_{\infty} \left( z' + \ell \right) + \bar{E}_{x} \left( \frac{z^2 - z'^2}{2} \right) - \rho \bar{q} \frac{\partial}{\partial \bar{q}} \theta \left( z' + \ell \right) \bar{\chi} \left( \frac{z^2 + \ell^2}{2} \right) \]

\[= \frac{\Delta \rho}{\rho} \theta \widehat{z}_{\infty} - \frac{1}{2} \rho \bar{q} \bar{q} \bar{\chi} \widehat{z}_{\infty} \ell^3 \]  

5.23

in the thermocline \( \theta' \lesssim \ell \). Above the thermocline (5.23) reduces to

\[
\int_{-\ell}^{z} \theta' \; dz = 2 \frac{\bar{z}_{\infty}}{\bar{E}_{\infty}} \left( \frac{z^2 - \ell^2}{2} \right) \]

\[= \frac{\Delta \rho}{\rho} \theta \widehat{z}_{\infty} - \frac{1}{2} \rho \bar{q} \bar{q} \bar{\chi} \widehat{z}_{\infty} \ell^3 \]  

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 \( \frac{\Delta \rho}{\rho} \bar{q} \bar{\chi} \ell \) and increases linearly with \( \ell \) for a fixed temperature difference (\( \bar{q} \bar{\chi} \ell \) constant).

Although small, the non-linear term must be compensated by changes in \( \widehat{z}_{\infty} \) if the thickness of the thermocline \( \ell \) changes.

For a change in \( \ell \) of 10 meters

\[
\Delta \frac{1}{2} \rho \bar{q} \bar{q} \bar{\chi} \widehat{z}_{\infty} \ell^2 \]

\[= \frac{1}{2} \rho \bar{q} \bar{q} \bar{\chi} \left( z_{\infty} - z_{\infty}' \right) \ell^2 \Delta \ell = \frac{\Delta \rho}{\rho} \bar{q} \Delta \widehat{z}_{\infty} \]

\[\leq 200 \text{ cm}^2 \text{ sec}^{-2} \text{ (deg yr}^{-1}) \]  

5.25

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

In the thermocline, the change of \( \frac{\bar{q}}{z} \) cannot be com-
pensated if \( C \) changes. At \( z' = 0 \), we can write (5.23) in the form
\[
\Phi' = \nu_e \frac{\Delta \rho}{\rho} g \frac{2}{z_c} + \nu_t \frac{\Delta \rho}{\rho} g \frac{2}{z_c} - \nu_e \rho_0 \frac{2}{z_c} g \frac{2}{T_T} (\bar{v}_x - \bar{v}_y)^2 
\]

Therefore, using (5.25)
\[
\Delta \Phi' = \nu_t \frac{\Delta \rho}{\rho} g \Delta \bar{v}_x \approx \frac{25 c \text{ m/s}}{g m^{-1}} 5.27
\]
the increase in \( \Phi' \) 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 \( \bar{v}_x \) is zero. Hence, if the temperature distribution can adjust downstream to reduce \( E_x \) to zero, the flow in the thermocline would not be decelerated. If \( E_x \) is zero, (5.20) implies that the total flux of mechanical energy \( K + \phi' \) is approximately non-divergent, except for the dissipation of kinetic energy. The vertical gradient of temperature required to reduce \( E_x \) to zero is
\[
\bar{v}_x = \frac{\Delta T}{2z_c} \approx \frac{2 \times 10^{-4} \text{ cm^{-1}}} {2 \text{ C/1000 meters}} 5.28
\]
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 $\vec{F}_x \approx C$ 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 $\vec{F}_x$ 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

\[
\frac{\partial \rho u}{\partial x} + \frac{\partial \rho vw}{\partial z} = -\frac{\partial p}{\partial x} + \frac{\partial}{\partial z} \left( \rho \kappa_m \frac{\partial v}{\partial z} \right)
\]  

6.1

where frictional stress due to vertical shear only is included.

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

\[
\frac{\partial}{\partial x} \int_{z}^{z_s} \rho u^2 dz = -\frac{\partial}{\partial x} \int_{z}^{z_s} p dz + p_s \frac{\partial z_s}{\partial x}
\]  

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 \( \bar{z} \). Integrating by parts and using the hydrostatic equation, we obtain

\[
\int_{\bar{z}}^{z_s} \rho dz = p_s z_s - p_{\bar{z}} + \int_{\bar{z}}^{z_s} \rho g z' dz'
\]

\[
= p_s z_s + \int_{\bar{z}}^{z_s} \rho g (z' - \bar{z}) dz'
\]

\[
= p_s z_s + \chi \simeq \chi
\]  

6.3

assuming \( p_s \bar{z}_s \) and its variations to be small.

Integrating with respect to \( \chi \), the difference of momentum flux across two sections becomes
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.

\[ \Delta \int_{y_{a}}^{y_{b}} \Delta \rho \alpha dm = - \Delta \mathcal{X}. \]

Thus, \( \Delta \int_{y_{a}}^{y_{b}} \rho \mathbf{u} \cdot \mathbf{d}z = - \Delta \mathcal{X} \).
(6.5), we obtain

$$
\Delta x = \int [\alpha \Delta p + p \Delta \alpha] \, dm \\
= \int p \alpha T \Delta v \, dm
$$

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

$$u \frac{\partial^2 u}{\partial z^2} + w \frac{\partial u}{\partial x} = \frac{1}{\rho} \frac{\partial}{\partial z} \left( \rho K_q \frac{\partial T}{\partial z} \right)
$$

6.7

and taking

$$
\Delta v = \left( u \frac{\partial^2 u}{\partial z^2} + w \frac{\partial u}{\partial x} \right) \Delta t = \frac{2}{\rho m} \left( \rho K_q \frac{\partial T}{\partial z} \right) \Delta t
$$

6.8

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

$$
\Delta x = \int p \alpha T \frac{2}{\rho m} \left( \rho K_q \frac{\partial T}{\partial z} \right) \Delta t \, dm \\
= \Delta t \int \rho K_q \frac{\partial T}{\partial z} \frac{\partial^2 u}{\partial z^2} \, dz \\
= \Delta t \int \rho K_q \bar{E}_x \, dz
$$

6.9

For the momentum flux in the thermocline to be constant we must have \( \Delta x \) zero, or

$$
\int \rho K_q \bar{E}_x \, dz = 0
$$

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**

The potential energy parameter $E_x$ has the form

$$E_x = E_{\bar{x}} + p V\alpha - p \delta_{n_5}^2 \alpha$$  \hspace{1cm} (6.11)

where

$$V\alpha = g \left\{ \frac{2}{\delta_x} \left( \frac{\partial x}{\partial p} \right) \frac{dx}{dz} + \left[ \frac{2}{\delta_5} \left( \frac{\partial \delta}{\partial p} \right) \right] \frac{ds}{dz} \right\}$$  \hspace{1cm} (6.12)

$$\delta_{n_5}^2 \alpha \approx \delta_{s_5}^2 \alpha = \frac{\partial \delta}{\partial x} \left( \frac{dx}{dz} \right)^2 + 2 \frac{\partial \delta}{\partial s_5} \frac{ds}{dz} \frac{ds}{dz} + \frac{\partial \delta}{\partial s_5} \frac{(ds)^2}{dz}$$  \hspace{1cm} (6.13)

and

$$\frac{d\Theta}{dz} = \frac{dy}{dz} + \Gamma$$  \hspace{1cm} (6.14)

The deformation used to derive $E_x$ does not alter the ratio

$$\beta = \frac{ds/\bar{z}}{d\Theta/\bar{z}}$$  \hspace{1cm} (6.15)

so that (6.11) may be expressed as
\[ E_\chi = \rho g \left\{ \left( \frac{\partial \alpha}{\partial x} \right)^* \frac{d \theta}{d z} + \left[ \frac{\partial}{\partial \theta} \left( \frac{P}{\rho} \frac{\partial \alpha}{\partial P} \right) \right]^* \frac{d \theta}{d z} \right\} - p \left( \frac{\partial^2 \alpha}{\partial x^2} \right)^* \left( \frac{d \theta}{d z} \right)^2 \] 6.16

where

\[ \left( \frac{\partial \alpha}{\partial x} \right)^* = \frac{\partial \alpha}{\partial x} + \frac{\partial \alpha}{\partial y} \beta \] 6.17

\[ \left( \frac{\partial^2 \alpha}{\partial x^2} \right)^* = \frac{\partial^2 \alpha}{\partial x^2} + 2 \frac{\partial^2 \alpha}{\partial y \partial z} \beta + \frac{\partial \alpha}{\partial z} \beta^2 \] 6.18

eetc.

The critical potential temperature gradient \( \xi_1 \) is

chosen so that the internal energy change is zero, i.e.

\[ \xi_1 = \left( \frac{d \theta}{d z} \right)_1 = \rho g \left[ \frac{\partial}{\partial \theta} \left( \frac{1}{\gamma} \frac{\partial \alpha}{\partial P} \right) \right]^*/\left( \frac{\partial \alpha}{\partial z} \right)^* \] 6.19

The gradient \( \xi_2 \) is chosen so that the total potential energy change is zero, i.e.,

\[ \xi_2 = \left( \frac{d \theta}{d z} \right)_2 = \rho g \left[ \frac{\partial}{\partial \theta} \left( \alpha + \frac{P}{\gamma} \frac{\partial \alpha}{\partial P} \right) \right]^*/p \left( \frac{\partial \alpha}{\partial z} \right)^* \] 6.20

The potential and internal energy parameters, expressed in terms of \( \xi_1 \), \( \xi_2 \), \( E_\eta \) and the actual potential temperature gradient \( \xi \), are

\[ E_{\chi \eta} = \frac{\xi_2}{\xi_2 - \xi_1} E_\chi \quad E_{e \eta} = - \frac{\xi_1}{\xi_2 - \xi_1} E_\eta \] 6.21

\[ E_\chi = \frac{\xi_2 - \xi}{\xi_2 - \xi_1} E_\eta \quad E_e = - \frac{(\xi - \xi_1)}{\xi_2 - \xi_1} E_\eta \] 6.22
where $E_h$ is the ordinary stability parameter $\rho g \left( \frac{\partial^2}{\partial z^2} \right) \frac{1}{\mu} \frac{d \theta}{d \mu}$.

For $\xi < \xi_1$, 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 $E_x$ 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 $\xi > \xi_2$. 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, $E_x$, is negative.

The gradient $\xi_1$ does not depend strongly on pressure, whereas, $\xi_2$ is approximately inversely proportional to pressure. Both gradients become infinitely large if the perfect gas law is assumed. The dependence of $\xi_1$, $\xi_2$ on the slope, $\beta$, 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 $\nu - S$ characteristic curves for the stations are shown in
Fig. 2. Variation of the critical gradients $\xi_1, \xi_2$ with $\beta$.
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 $E_x \eta$. 
Fig. 5. Variation with depth of stability $E$, potential energy $E_\chi$, and $E_\chi \eta$. The parameter $E_\chi \eta$ is also shown at the critical gradient $\xi_2$. 

R.R.S. Discovery II
Station *2153
Figure 3. The slopes of these curves define $\beta$ 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 $\xi_2$ 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 $\vartheta-S$ 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 $E_R$ 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

$$-K_Q p \frac{\partial V_x}{\partial x} = K_Q \rho \alpha_T \frac{V_x^2}{e} = \beta_0 \frac{K_m}{m} V_x^2$$

6.23

Using the thermal wind equation

$$V_x = -\frac{\alpha}{f} \frac{\partial p}{\partial x} = \frac{\rho g \alpha_T}{f} V_x$$

6.24

we obtain

$$K_Q \rho \alpha_T \frac{V_x^2}{e} = \beta_0 \frac{K_m}{m} \frac{\rho g \alpha_T}{f^2} V_x^2$$

6.25

Solving for $\left(\frac{\partial x/\partial z}{y}\right)_x$

$$\left(\frac{\partial x/\partial z}{y}\right)_x = \left(\frac{K_m}{K_Q}\right)^2 \frac{\rho g \alpha_T}{f (\rho \alpha_T)^2} V_x^2$$

$$= 70 \left(\frac{K_m}{K_Q}\right)^2$$

6.26
for \( P = 10^8 \text{ dynes cm}^{-2} \), \( f = 10^{-4} \text{ sec}^{-1} \), \( \alpha_T = 2 \times 10^{-4} \text{ cm}^3 \text{ gm}^{-1} \text{ oC}^{-1} \), \( \alpha_T = 10^{-5} \text{ cm}^3 \text{ gm}^{-1} \text{ oC}^{-2} \). For \( k_m/k_a \sim 10 \), 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 estimated from oceanographic data, an estimate for the ratio \( k_m/k_a \) can be obtained by "forcing" a balance of the type assumed in (6.23), at least for the mean values, i.e.

\[
K_a \int \rho \alpha_T \delta z^2 \, dz \sim k_m \int \rho v_z^2 \, dz
\]

Or

\[
\frac{k_m}{K_a} \sim \frac{\int \rho \alpha_T \delta z^2 \, dz}{\int \rho v_z^2 \, dz}
\]

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 \( K_a \).

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.

<table>
<thead>
<tr>
<th>Stations</th>
<th>Geostrophic Surface Velocity $v'_s/1500$ cm sec$^{-1}$</th>
<th>$\int \rho V_{x}^2 d\zeta$ ergs cm$^{-4}$</th>
<th>$\int \rho V_{z}^2 d\zeta$ ergs cm$^{-4}$</th>
<th>$K_m/K_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5295-96</td>
<td>15</td>
<td>1.12</td>
<td>.011</td>
<td>$\sim 100$</td>
</tr>
<tr>
<td>5296-97</td>
<td>100</td>
<td>.90</td>
<td>.49</td>
<td>$\sim 2$</td>
</tr>
<tr>
<td>5297-98</td>
<td>90</td>
<td>1.16</td>
<td>.23</td>
<td>5</td>
</tr>
<tr>
<td>5298-99</td>
<td>200</td>
<td>1.88</td>
<td>.44</td>
<td>4</td>
</tr>
<tr>
<td>5299-01</td>
<td>50</td>
<td>2.17</td>
<td>.08</td>
<td>$\sim 30$</td>
</tr>
</tbody>
</table>

(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 $\rho V_{x}$ 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°45'N 138°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, $E_x - E_x$, (solid curve) and viscous dissipation $10 \nu^2$ (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 $E_{x\eta}$ and $E_x$ 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 $k_m/k_Q$ 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 $E_{x_\eta}$ 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 $p\sqrt{\alpha}$ 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

$$\bar{\Phi}' = \int \bar{E}_h d z.$$  \hspace{1cm} 6.28

The value of $\bar{E}_h$ at the critical gradient $\xi$ (defined by $E_{x_\eta} = 0$, eq. (6.20)) is given by

$$\begin{align*}
(\bar{E}_h)' &= \frac{\rho g (\frac{\partial \alpha}{\partial x})}{\left( \frac{\partial^2 \alpha}{\partial x^2} \right)} \sim 3 \text{ cm sec}^{-2} \hspace{1cm} 6.29
\end{align*}$$

to the approximation used in deriving (6.28).

Pressure does not appear explicitly in (6.29) so that the variation of $\bar{E}_h$ 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 $(\bar{E}_h)'$ is, therefore, not very large.

The values of $\bar{E}_h$, 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 $E_{\alpha}$ varies over several orders of magnitude, the product $\hat{\alpha} E_{\alpha}$ appears to be limited in its range of magnitude. A possible interpretation of the limitation on $\hat{\alpha} E_{\alpha}$ is that the potential energy parameter $E_{\chi}$ 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 $E_{\chi}$ is negative. Whether or not the result of possible acceleration of flow for negative values of $E_{\chi}$ would be a tendency to weaken vertical gradients and limit stratification to positive values of $E_{\chi}$ 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 \( \frac{\partial E_k}{\partial \rho} \) and the thermal expansion \( \frac{\partial \rho}{\partial \rho} \) with depth for a station near the Gulf Stream.
Figure 10: Variation of $\tilde{z}$, $E_n$, and $\partial n \partial z$ with depth for a station in the centre of an eddy in the Gulf of Alaska.
Figure 11. Variation of $\mathcal{E}_H^2$ with depth for a station near the centre of the Gulf of Alaska. The changes become small below the halocline at 150 metres.
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:

\[
\begin{align*}
    m_1^f &= m_1^i = m_1 \\
    m_2^f &= m_2^i = m_2 \\
    m_1^fs_1^f + m_2^fs_2^f &= m_1^is_1^i + m_2^is_2^i \\
    m_1^fh_1^f + m_2^fh_2^f &= m_1^ih_1^i + m_2^ih_2^i \\
    p_1^f &= p_1^i = p_1^f = p_2^i = p_2^f = p_2
\end{align*}
\]

where the superscripts refer to the final and initial states.
The total change of entropy \( \Delta N \) is given by

\[
\Delta N = m_1 \eta_1^f + m_2 \eta_2^f - (m_1 \eta_1^i + m_2 \eta_2^i)
\]

\[
= m_1 (\eta_1^f - \eta_1^i) + m_2 (\eta_2^f - \eta_2^i)
\]  

(2)

We expand \( \eta \) 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

\[
\eta = \eta_0 + \eta_h (h - h_0) + \eta_s (s - s_0) + \eta_p (p - p_0)
\]

\[
+ \frac{1}{2} \left[ \eta_{hh}(h - h_0)^2 + \eta_{ss}(s - s_0)^2 + \eta_{pp}(p - p_0)^2 \right] + \ldots
\]

(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

\[
\Delta N = \frac{1}{2} \left\{ \eta_{hh} [(m_1 h_1^i + m_2 h_2^i)^2 - (m_1 h_1^i + m_2 h_2^i)^2] + \ldots 
\]

\[
+ 2 \eta_{ss} [(m_1 s_1^i + m_2 s_2^i)^2 - (m_1 s_1^i + m_2 s_2^i)^2] + \ldots 
\]

\[
\right. + \text{terms of same general form}
\]  

(4)

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

Using identities of the form

\[
m_1 h_1^i + m_2 h_2^i = \frac{(m_1 h_1^i + m_2 h_2^i)^2}{m_1 + m_2} (h_1^i - h_2^i)^2
\]

\[
m_1 s_1^i + m_2 s_2^i = \frac{(m_1 s_1^i + m_2 s_2^i)^2}{m_1 + m_2} (s_1^i - s_2^i)^2
\]

(5)

we can write (4) in the form
\[ \Delta N = -\frac{1}{2} \frac{m m_1 m_2}{m + m_1} \left\{ \eta_h \left[ \Delta h_i^2 - \Delta h_i^\dagger - \Delta h_i^\dagger \Delta h_i^\dagger \right] + \cdots + 2 \eta_s \left[ \Delta h_i^\dagger \Delta s_i^\dagger - \Delta h_i^\dagger \Delta s_i^\dagger \right] + \cdots + 2 \eta_p \Delta p \left[ \Delta h_i^\dagger - \Delta h_i^\dagger \right] + \cdots \right\} \]  

where

\[ \Delta h_i = h_i^i - h_i^0, \quad \Delta h^\dagger = h_i^+ - h_i^0, \]
\[ \Delta s = s_i^i - s_i^0, \quad \Delta s^\dagger = s_i^+ - s_i^0, \]
\[ \Delta p = p_i^2 - p_i. \]  

As \( \Delta h_i, \Delta s_i, \Delta p \) are fixed by initial conditions, the entropy change can be varied only by changing \( \Delta h_i^\dagger \) and \( \Delta s_i^\dagger \). We find the extreme value of \( \Delta N \) with respect to \( \Delta h_i^\dagger \) and \( \Delta s_i^\dagger \). For stationary values of \( \Delta N \), we have

\[ \frac{\partial \Delta N}{\partial \Delta h_i^\dagger} = \frac{m m_1 m_2}{m + m_1} \left[ \eta_h \Delta h_i^\dagger + \eta_s \Delta s_i^\dagger + \eta_p \Delta p \right] = 0 \]
\[ \frac{\partial \Delta N}{\partial \Delta s_i^\dagger} = \frac{m m_1 m_2}{m + m_1} \left[ \eta_h \Delta h_i^\dagger + \eta_s \Delta s_i^\dagger + \eta_p \Delta p \right] = 0 \]  

Solving for \( \Delta h_i^\dagger \) and \( \Delta s_i^\dagger \), we obtain

\[ \frac{\Delta h_i^\dagger}{\Delta p} = \frac{\eta s \eta_s^2 - \eta h \eta_p}{\eta h \eta_s - \eta_s} \]  
\[ \frac{\Delta s_i^\dagger}{\Delta p} = \frac{\eta h \eta_s - \eta s \eta_p}{\eta h \eta_s - \eta_s} \]  

Using the transformations

\[ \eta h = -\frac{1}{Cp T^2} \]
\[ \eta p = +\frac{\alpha - T \alpha T}{Cp T^2} \]
\[ \eta s = \frac{\eta s}{Cp T^2} \]
\[ \eta s = -\frac{\alpha s}{T} - \frac{\alpha - T \alpha T}{Cp T^2} \]
\[ \eta s = \mu - T \mu T \]  

We obtain
\[
\frac{\Delta h}{\Delta p} = +\left(\alpha - T \alpha_T\right) - \frac{\alpha s h_s}{\mu_s} \tag{12}
\]
\[
\frac{\Delta s}{\Delta p} = -\frac{\alpha s}{\mu_s} = -\frac{\mu p}{\mu_s} = \left(\frac{d s}{dp}\right) \tag{13}
\]

But, from the relationship

\[
\Delta h = C_p \Delta T + \left(\alpha - T \alpha_T\right) \Delta p + \mu_s \Delta s \tag{14}
\]

we see on substituting (13) that

\[
\Delta T = 0 \tag{15}
\]

Hence, the maximum entropy is attained when

\[
T_1 = T_2 \quad \mu_1 = \mu_2 \tag{16}
\]

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

\[
\frac{C_p}{T_2} \Delta Q_e^2 + \frac{\mu_s}{T} \left(\Delta s_e^f\right)^2 - \frac{C_p}{T_1} \left(\Delta Q_e - \Delta Q_e^e\right)^2 - \frac{\mu_s}{T} \left(\Delta S - \Delta s_e^f\right)^2 \tag{17}
\]

where

\[
\Delta Q = \Delta h - k_s \Delta S \tag{18}
\]

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