

On the thermodynamics of the oceanic general circulation: entropy increase rate of an open dissipative system and its surroundings

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ABSTRACT

The rôle of thermodynamics in the oceanic general circulation is investigated. The ocean is regarded as an open dissipative system that exchanges heat and salt with the surrounding system. A new quantitative method is presented to express the rate of entropy increase for a large-scale open system and its surroundings by the transports of heat and matter. This method is based on Clausius's definition of thermodynamic entropy, and is independent of explicit expressions of small-scale dissipation processes. This method is applied to an oceanic general circulation model, and the entropy increase rate is calculated during the spin-up period of the model. It is found that, in a steady-state, the entropy increase rate of the ocean system is zero, whereas that of the surroundings shows positive values, for both heat and salt transports. The zero entropy increase rate of the ocean system represents the fact that the system is in a steady-state, while the positive entropy increase rate in the surroundings is caused by irreversible transports of heat and salt through the steady-state circulation. The calculated entropy increase rate in the surroundings is $1.9 \times 10^{11} \text{ W K}^{-1}$, and is primarily due to the heat transport. It is suggested that the existence of a steady-state dissipative system on the Earth, from a living system to the oceanic circulation, has a certain contribution to the entropy increase in its nonequilibrium surroundings.

1. Introduction

The climate system of the Earth can be seen as an open dissipative system connected with outer thermal reservoirs such as the sun and space through radiant energy interaction. It is dissipative since the solar radiation absorbed in the hot equatorial regions is transported by the atmo-

sphere and ocean to the cold polar regions where the heat is lost to space through longwave emission. As the long-term mean state of the global climate, it has been suspected that the system may represent a state of maximum entropy increase. Paltridge (1975, 1978) first suggested that the global distribution of the present climate is reproducible as a state with a maximum rate of entropy increase by the turbulent heat transport in the atmosphere and ocean. Several researchers have investigated Paltridge's work obtaining the same result (Grassl, 1981; Shutts, 1981; Mobbs, 1982; Noda and Tokioka, 1983). His suggestion was criticised by Essex (1984), however, since a pre-

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dominant contribution to the entropy increase is due to direct absorption of solar radiation at the Earth's surface, which factor was missing from Paltridge's work. In fact, Paltridge related the entropy increase rate to the radiation balance, leaving the surface temperature unspecified. This lead to ambiguity when a corresponding radiation temperature was defined (Essex, 1984). Since then, the radiation problem has been a central objection to Paltridge's work (Lesins, 1990; Stephens and O'Brien, 1993; Li and Chylek, 1994; Pujol and Llebot, 1999).

Recently, we have revised Paltridge's work in the light of a thermodynamic variational concept proposed by Sawada (1981). Sawada stated that the entropy of thermal reservoirs connected through a non-linear system will increase along a path of evolution, with the maximum rate of entropy increase among a manifold of possible paths. Ozawa and Ohmura (1997) specified the Earth's surface temperature where absorption takes place, and applied Sawada's maximum concept specifically to the entropy increase rate by the non-linear turbulent heat transport in the atmosphere, and thereby reproduced vertical distributions of air temperature and energy fluxes that resemble those of the present Earth. Thus, Paltridge's work is held to be valid if the absorption temperature is specified and the entropy increase rate by the turbulent heat transport is considered to be a maximum, regardless of the entropy increase by the absorption of solar radiation.

The ocean system, which is a major component of the climate system, can also be seen as an open dissipative system connected with the surrounding system through heat flux, salt flux and wind stress. The surrounding system consists of the atmosphere, the sun and space. Because of the curvature of the Earth's surface and the inclination of the rotation axis against the sun, the ocean receives a net input of heat from solar radiation in the equatorial regions, and excess evaporation results in an apparent salt flux at the sea's surface. In the polar regions, the ocean loses heat through long-wave emissions into space, and excess precipitation (rain and snow) results in a freshwater flux (an apparent negative salt flux) at the surface. Thus, in general, there are net inputs of heat and salt in the equatorial regions, and net outputs of heat and salt in the polar regions. (Strictly speaking,

there is a slight output of salt in the central equatorial regions, but the amount is less significant than that in the polar regions.) The net flux imbalance brings about an inhomogeneous distribution of temperature and salinity at the surface, i.e., hot, saline equatorial regions and cold, less saline polar regions. From a thermodynamic viewpoint, this inhomogeneity is a *driving force* for global-scale thermohaline circulation. The circulation thus created will reduce the inhomogeneity by direct transports of heat and salt through the movement of water. In this respect, the formation of the circulation can be seen as a path towards the final equilibrium of the whole system (the universe) including large but finite thermal reservoirs (the sun and space). The rate of approaching to the equilibrium, i.e., the rate of entropy increase by the oceanic circulation, is the central subject of this paper.

Although several studies have been carried out on the local thermodynamic properties of sea water (Fofonoff, 1962; Eckart, 1962; Gregg, 1984), we are still in need of basic understanding of the thermodynamics of the ocean system as a global-scale open system which interacts with its surroundings. The objectives of the present paper are therefore as follows:

- To provide a quantitative method to calculate the rate of entropy increase in a large-scale open system and its surroundings due to transports of heat and matter (salt) through the open system.
- To apply this method to a global-scale circulation model of the ocean, and evaluate the entropy increase rate during a spin-up period of the model.

In what follows, we shall present a set of equations to express the entropy increase rate for the open system and its surroundings from a basic definition of thermodynamic entropy so that one can apply this method to any type of open dissipative system that interacts with its surroundings (Section 2). By using this new method, we will present some original results on thermodynamic properties of the ocean system and its surroundings (Section 4). The result obtained from this study is generalised in Section 5, and a simple statement is presented to specify the thermodynamic properties of a steady-state dissipative system and its nonequilibrium surroundings.

2. Formulation of entropy

Entropy is a measure of the probability of the distribution of energy and matter in a system. The second law of thermodynamics describes the tendency of a whole isolated system to move toward a state of higher probability. For instance, in the case of sea water, heat and salt ions should be taken into consideration. Then, consider an event of local concentration of heat or salt ions in an ocean system that was once in a state with homogeneous distribution of temperature and ions (i.e., thermodynamic equilibrium). The local concentration of heat in a specific region results in an increase of temperature in that region, and this event corresponds to a decrease of entropy of the whole system. Likewise, local concentration of salt ions in a specific region in the ocean system causes an increase of salinity in that region, and it corresponds to a decrease of entropy of the whole system. The second law states that such local concentration is highly improbable, and the concentration tends to disperse toward the equilibrium state with a maximum entropy. This is a qualitative account of the second law of thermodynamics. We shall in due course present a quantitative method to evaluate the rate of entropy increase by the non-linear transports of heat and matter in an open dissipative system such as the ocean.

Let us consider a whole system, consisting of the ocean system and its surroundings. Because of the additive properties of entropy, the entropy increase rate of the whole system due to the transport processes can be expressed as the sum of each contribution

$$\dot{S}_{\text{whole}} = \dot{S}_{\text{ocn}} + \dot{S}_{\text{surr}}, \quad (1)$$

where $\dot{S}_{\text{whole}}$, $\dot{S}_{\text{ocn}}$ and $\dot{S}_{\text{surr}}$ are the entropy increase rate of the whole system, that of the ocean system, and that of the surrounding system, respectively. In the case of the ocean system, there are two main transport processes, i.e., heat and salt transports. Thus, we can express each component of the entropy increase rate in eq. (1) as a sum of contributions from heat and salt transports.

2.1. Entropy increase by heat and salt transports

In general, if a small amount of heat δQ is added quasi-statically to a small system of which

the absolute temperature is T , the entropy of the system will increase by $\delta Q/T$ (Clausius, 1865). Because of the first law of thermodynamics, this heating can be expressed as a sum of the increase of the internal energy of the system, the amount of work done by volume expansion of the system, and the decrease of number of material particles with a certain chemical potential (De Groot and Mazur, 1962, ch. 3), as

$$dS = \frac{\delta Q}{T} = \frac{dU + p dV - \sum \mu_j dN_j}{T}, \quad (2)$$

where S is the entropy, U is the internal energy, p is the pressure, V is the volume of the system, μ_j is the chemical potential of a component j , and N_j is the number of the j th component. In principle, a change of entropy for a larger system can be obtained by a volume integration of eq. (2). It follows from mathematical manipulation (see Section 7 (A7)) that the rate of entropy increase of an open fluid system (ocean) due to the heat and salt transports can be expressed by:

$$\begin{aligned} \dot{S}_{\text{ocn}} = \int \frac{1}{T} \left[\frac{\partial(\rho c T)}{\partial t} + \text{div}(\rho c T \mathbf{v}) + p \text{div} \mathbf{v} \right] dV \\ - \alpha k \int \left[\frac{\partial C}{\partial t} + \text{div}(C \mathbf{v}) \right] \ln C dV, \end{aligned} \quad (3)$$

where ρ is the density, c is the specific heat at constant volume, $\mathbf{v}$ is the velocity, $\alpha=2$ is the dissociation effect of salt into separate ions (Na^+ and Cl^-), k is the Boltzmann constant, C is the number concentration of salt per unit volume of sea water, and the integration is taken over the whole volume of the system. The first integral on the right-hand side represents the entropy increase rate by the heat transport process, and the second one represents that by the salt transport process. Strictly speaking, eq. (3) is valid for a fluid system whose state functions (e.g., T , p , ρ and C) are constant in the small volume element dV ; in other words, when the local thermodynamic equilibrium can be assumed. However, the gradient effect results only in second and higher order terms in the power series of the expansion of the entropy, and eq. (3) gives a reasonable approximation for the entropy increase rate of a system to the first order (Landau and Lifshitz, 1944, Sec. 49).

The entropy of the surrounding system will increase by the heat and salt fluxes from the ocean system through the boundary surface. The rate of

entropy increase is given by a sum of the contributions from the fluxes of heat and salt (Section 7 (A8)) as follows,

$$\dot{S}_{\text{surr}} = \int \frac{F_h}{T} dA - \alpha k \int F_s \ln C dA, \quad (4)$$

where F_h and F_s are the fluxes of heat and salt per unit surface, defined as positive outward, respectively, dA is the small surface element, and the integration is taken over the whole ocean surface.

By substituting eqs. (3) and (4) in eq. (1), we get the entropy increase rate for the whole combined system as:

$$\begin{aligned} \dot{S}_{\text{whole}} = & \int \frac{1}{T} \left[\frac{\partial(\rho c T)}{\partial t} + \text{div}(\rho c T \mathbf{v}) + p \text{div} \mathbf{v} \right] dV \\ & + \int \frac{F_h}{T} dA \\ & - \alpha k \int \left[\frac{\partial C}{\partial t} + \text{div}(C \mathbf{v}) \right] \ln C dV \\ & - \alpha k \int F_s \ln C dA. \end{aligned} \quad (5)$$

The first two terms represent the entropy increase rate by the heat transport, and the next two terms represent that by the salt transport. If we can assume that the sea water is incompressible ($\text{div} \mathbf{v} = 0$) and that the volumetric heat capacity is constant ($\rho c = \text{const.}$), then the divergence terms in eq. (5) disappear (Section 7 (A10)). In this case, we get simply,

$$\begin{aligned} \dot{S}_{\text{whole}} = & \int \frac{\rho c}{T} \frac{\partial T}{\partial t} dV + \int \frac{F_h}{T} dA \\ & - \alpha k \int \frac{\partial C}{\partial t} \ln C dV - \alpha k \int F_s \ln C dA. \end{aligned} \quad (6)$$

Eq. (6) shows the method to evaluate the entropy increase rate for the incompressible sea water, and is used in our calculations in Section 4.

The general expression [eq. (5)] can be rewritten in a different form. A mathematical transformation (Section 7 (A15)) can show that:

$$\begin{aligned} \dot{S}_{\text{whole}} = & \int \mathbf{F}_h \cdot \text{grad} \left(\frac{1}{T} \right) dV + \int \frac{\Phi}{T} dV \\ & - \alpha k \int \frac{\mathbf{F}_s \cdot \text{grad} C}{C} dV, \end{aligned} \quad (7)$$

where $\mathbf{F}_h$ and $\mathbf{F}_s$ are the flux density of heat and salt (vector in three dimensional space), respectively, and Φ is the dissipation function, representing the rate of dissipation of kinetic energy into heat by viscosity per unit volume of the fluid. The first term on the right-hand side is the entropy increase rate by thermal dissipation (heat conduction), the second term is that by viscous dissipation, and the third term is that by molecular diffusion of salt ions. It is known empirically that heat flows from hot to cold via thermal conduction, and the dissipation function is always non-negative ($\Phi \geq 0$), for kinetic energy is always dissipated into heat by viscosity. It is also known that the molecular diffusion takes place from high to low concentration (salinity). Hence, the sum should also be positive. This is a consequence of the second law of thermodynamics. The quantity of each term is determined by the turbulent nature of the system. It is quite difficult to evaluate these quantities since they depend very much on the local gradients of temperature and salinity as well as the local strain rate; they are beyond the limits of the accuracy of the current version of circulation models. In addition, each flux ($\mathbf{F}_h$ or $\mathbf{F}_s$) depends on both gradients of temperature and salinity (Landau and Lifshits, 1944, Sec. 59; Gregg, 1984). Because of these difficulties, we will use eq. (6) in this study. The advantage of using (6) is that we can evaluate the entropy increase rate by the surface fluxes of heat and salt and the distributions of temperature and salinity in the system, without knowing any flux information in the system. As we will see in Section 5, this advantage comes from the fact that eq. (6) is an integral form of eq. (7) and is free from explicit expressions of the small-scale dissipation processes.

2.2. Wind and tidal dissipation

The ocean system receives kinetic energy from the surrounding atmospheric system through the wind stress at the surface. It also receives potential energy from the moon as the tide. The energy supply to the system, if it takes place in a reversible manner, is independent of the entropy of the system concerned. The supplied energy will, however, change into heat by viscous dissipation somewhere in the ocean system, and this heating will contribute to an increase of the entropy through the dissipation function Φ in eq. (7). For the rate

of wind induced dissipation, Peixoto and Oort (1992, Sec. 14.6.2) gives an estimate of $0.007 \text{ (W m}^{-2}\text{)}$ as a global-mean. The corresponding rate of entropy increase is $2 \times 10^9 \text{ W K}^{-1}$, assuming the mean ocean temperature of 280 K and the surface area of $8 \times 10^{13} \text{ m}^2$ equivalent to our model ocean (Fig. 1a). This rate is two orders of magnitude smaller than the total rate ($1.9 \times 10^{11} \text{ W K}^{-1}$) obtained from our numerical simulation in Section 4. For tidal dissipation, Munk and Wunsch (1998) and Egbert and Ray (2000) suggest that the rate does not exceed 0.01 W m^{-2} ; it also results in negligible in comparison with the total rate. Thus, the entropy increase rate due to wind and tidal dissipation is negligible for the deep-water circulation as the first approximation.

3. Numerical model

The calculation method of the entropy increase rate (eq. (6)) is applied to an oceanic general circulation model. We use Pacanowski (1995) version of the Geophysical Fluid Dynamics Laboratory Modular Ocean Model (GFDL

MOM) originated by Bryan (1969). The configuration of our model is similar to that of Cai and Godfrey (1995). The model domain is a rectangular basin of 72° longitude by 140° latitude, representing an idealised Atlantic Ocean (Fig. 1a). The southern hemisphere includes an Antarctic Circumpolar Current passage from 48°S to 68°S , as calculated width in a staggered grid. The horizontal grid spacing is 4° longitude by 4° latitude. The depth of the ocean is 4500 m with twelve vertical levels. Sub-grid scale eddy transport coefficients are as follows: horizontal diffusivity $10^3 \text{ m}^2 \text{ s}^{-1}$, horizontal viscosity $8 \times 10^5 \text{ m}^2 \text{ s}^{-1}$, vertical diffusivity $10^{-4} \text{ m}^2 \text{ s}^{-1}$, and vertical viscosity $2 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$. This model is hydrostatic, and a convective adjustment scheme is used to represent the vertical mixing process.

The boundary conditions for wind stress, temperature and salinity are shown in Fig. 1b–d. All boundary conditions are arranged to be symmetric about the equator. The wind stress is assumed to be zonal (eastward or westward direction, Fig. 1b). A restoring boundary condition is applied: the surface temperature and salinity are relaxed to their prescribed values (Fig. 1c, d), with a relaxa-

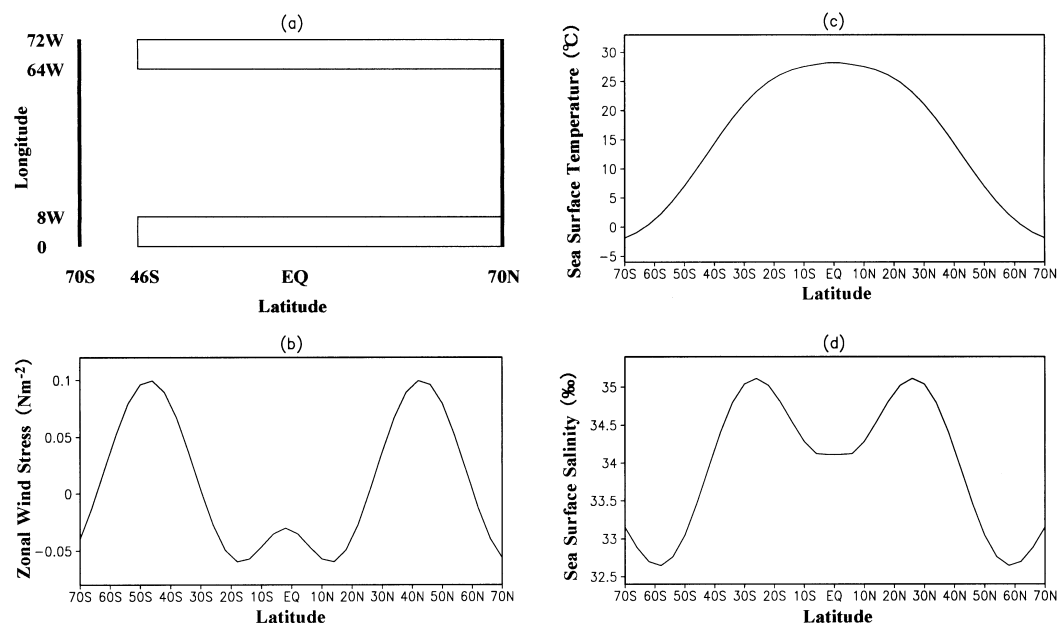


Fig. 1. (a) The model domain of an idealised Atlantic Ocean with a passage for the Antarctic Circumpolar Current, (b) zonal wind stress (N m^{-2}) defined as positive eastward, (c) prescribed sea surface temperature ($^\circ\text{C}$), and (d) prescribed sea surface salinity (‰).

tion time scale of 20 days over a mixed layer depth of 25 m. The corresponding fluxes of heat and salt are used to calculate F_h and F_s at the surface. The initial temperature distribution is described by a function of depth and latitude. The initial salinity is assumed to be constant (34.9‰). The initial velocity field is set to zero. The numerical simulation is carried out for a spin-up period of 5000 years.

4. Results

Fig. 2 shows zonally integrated meridional stream function at years 100, 1000, 2000, 3000, 4000 and 5000, after starting the calculation. At year 100, the circulation pattern is almost symmetric about the equator. The sinking cell in the southern hemisphere does not develop further because of the existence of the Antarctic Circumpolar Current. In contrast, the sinking cell in the northern hemisphere develops into deeper layers, and the circulation pattern becomes asymmetric about the equator. The oceanic circulation becomes statistically steady after the year 4000. Temperature variations are shown to be less than 0.1 K after the year 4000. In the steady-state, the northern deep-water sinking cell is accompanied by an Antarctic bottom-water sinking cell and by a northern intrusion cell from the south. The flow pattern seems to be a basic one in the idealised Atlantic Ocean.

Fig. 3 shows the entropy increase rates due to the heat and salt transports calculated with eq. (6) during the spin-up period. In this figure, (a) and (d) are those for the surrounding system, (b) and (e) are those for the ocean system, and (c) and (f) are those for the whole combined system $[(a+b)$ and $(d+e)]$, respectively. During the spin-up period prior to the year 3000, somewhat large oscillations are observed in the entropy increase rates. We confirmed by more detailed figures (not shown) that a periodicity of approximately 2 years exists in the entropy increase rates in the surroundings and a periodicity from 3 to 6 years in those in the ocean. The reason for the oscillations remains unclear, and will shortly be discussed in Section 5. These oscillations tend to disappear, however, as the system reaches the statistically steady-state.

In the steady-state after the year 4000, for both heat and salt transports, the entropy increase rates for the ocean system are zero whereas those for

the surrounding system show positive values, within the limits of the accuracy of our numerical model. The zero increase rates represent the fact that the ocean system is in a steady-state, so that the distributions of the temperature and the salinity remain unchanged ($\partial T/\partial t = \partial C/\partial t = 0$); hence the volume integrals in eq. (6) result in zero. On the contrary, heat and salt are transported from equatorial (hot and salty) to polar (cold and less salty) regions by the steady-state circulation. These irreversible transports contribute to the entropy increase in the surrounding system through the surface integrals in eq. (6). In this sense, the surrounding system is *not* in a steady-state, and its entropy is increasing slowly and steadily by the contribution of the oceanic circulation. The entropy increase rates in the surrounding system are: $1.9 \times 10^{11} \text{ W K}^{-1}$ by the heat transport and $3.6 \times 10^8 \text{ W K}^{-1}$ by the salt transport. The former is three orders of magnitude larger than the latter. Thus, the entropy increase is primarily due to the heat transport, being consistent with an earlier estimate by Gregg (1984).

For simplicity, it is occasionally assumed a geostrophic balance for the ocean currents, in which the direction of the flow is perpendicular to the horizontal pressure gradient associated with the differences in temperature and salinity. In such a geostrophic system, there would be no transport of heat or salt in the direction of the down-gradient, and consequently no entropy increase in the surrounding system. In the real ocean, however, there are down-gradient components of ocean currents (e.g., gyres and thermohaline circulation cells), which contribute to the irreversible transports of heat and salt from equatorial to polar regions. Consequently, the entropy of the surrounding system is increasing, as demonstrated in our numerical simulation. This result is consistent with our previous conjecture (Section 1) that the oceanic circulation will contribute to the entropy increase in the nonequilibrium surroundings, including the hot sun and cold space. It should be stressed here that the irreversible nature found in this study has utterly been disregarded in the conventional geostrophic systems.

5. Discussion

We have seen in the previous section that, in the steady-state, the entropy increase rate of

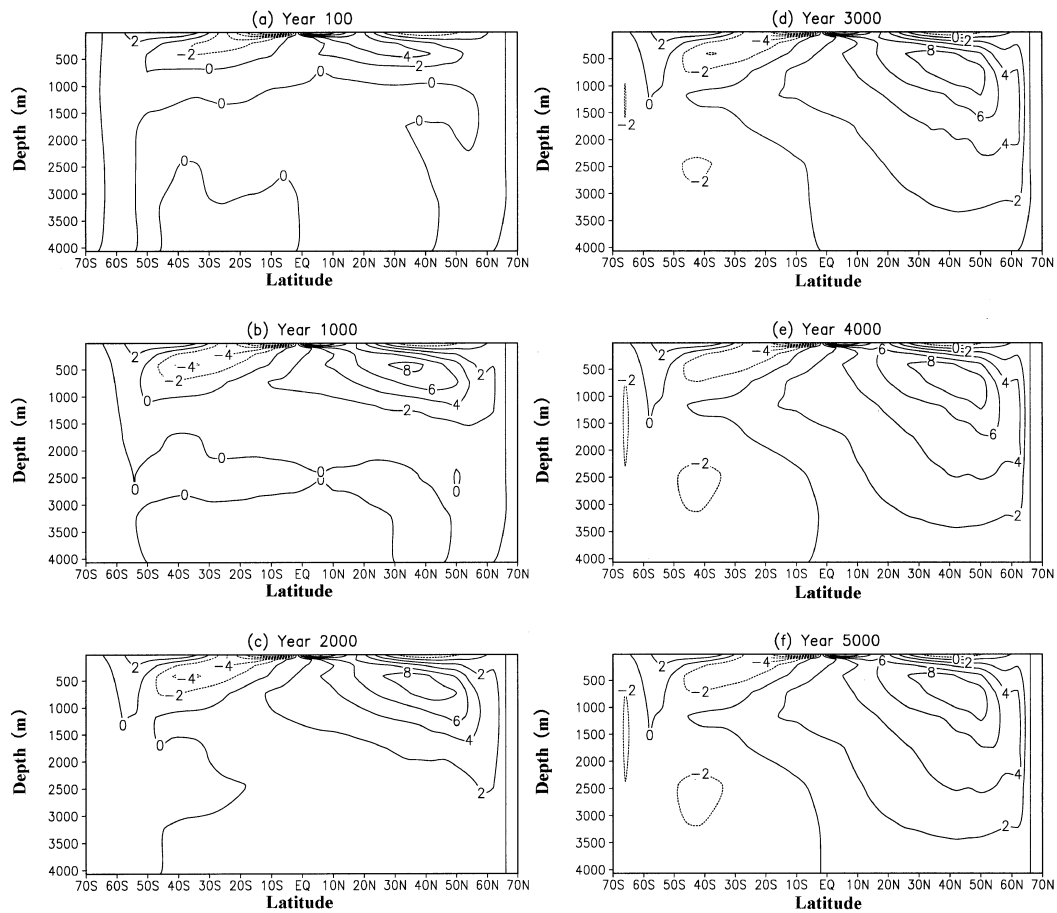


Fig. 2. Zonally integrated meridional stream function at years (a) 100, (b) 1000, (c) 2000, (d) 3000, (e) 4000, and (f) 5000 after starting the numerical calculation. The contour line interval is 2 Sv ($10^6 \text{ m}^3 \text{ s}^{-1}$). The circulation pattern arrived at a statistically steady-state after year 4000.

the ocean system is zero, whereas that of the surrounding system shows a positive value ($1.9 \times 10^{11} \text{ W K}^{-1}$). At first sight, the zero entropy increase state of the ocean system may appear to be strange, since irreversible processes are taking place in the system. Although entropy is said to be produced by the irreversible processes (Zemansky and Dittman, 1981, Sec. 8–13), it is completely discharged into the surrounding system through the boundary fluxes of heat and salt, thereby keeping the entropy of the system in a constant level. This situation is common to all steady-state dissipative systems of which state functions (T , p , ρ , C as well as S) remain unchanged

in the steady-state. This is also the case for the climate system (the atmosphere and ocean); the entropy of the climate system is constant, whereas that of the surrounding system is increasing by the irreversible processes in the climate system. And, according to previous studies, the increase rate by the turbulent heat transport is suggested to be at a maximum (Paltridge, 1975 and 1978; Ozawa and Ohmura, 1997).

Let us discuss a bit more about the entropy increase rate described by the two different expressions [(5) and (7)]. In the steady-state, the entropy of the system should be constant ($\dot{S}_{\text{ocn}} \approx 0$), so that we get

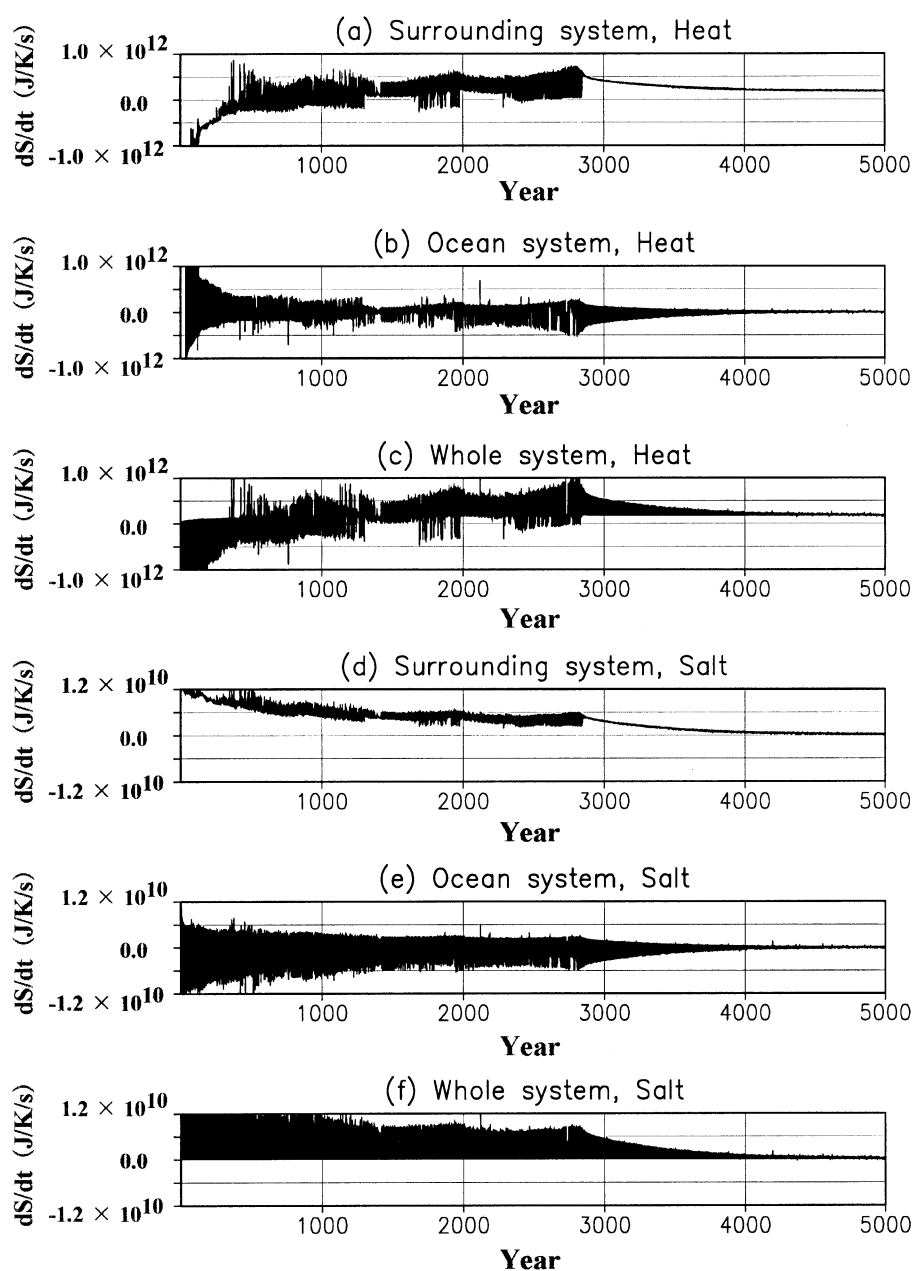


Fig. 3. Entropy increase rates calculated during the spin-up period. (a) That of the surrounding system by heat transport, (b) that of the ocean system by heat transport, (c) that of the whole system $[(a)+(b)]$ by heat transport, (d) that of the surrounding system by salt transport, (e) that of the ocean system by salt transport and (f) that of the whole system $[(d)+(e)]$.

$$\begin{aligned}
\dot{S}_{\text{whole}} &= \int \mathbf{F}_h \cdot \text{grad} \left(\frac{1}{T} \right) dV + \int \frac{\Phi}{T} dV \\
&\quad - \alpha k \int \frac{\mathbf{F}_s \cdot \text{grad} C}{C} dV \\
&\approx \int \frac{F_h}{T} dA - \alpha k \int F_s \ln C dA,
\end{aligned} \tag{7}$$

for a steady-state (5)'

Eq. (7) may be called a *local* expression since it is described by the small-scale dissipation processes in the system. On the contrary, eq. (5)' or (5) may be called a *global* expression since it is an integral form of eq. (7). The local expression has been used to study the entropy increase rate in some specific dissipation processes (Gregg, 1984; Nicolis, 1999), whereas the global expression (the first term in eq. (5)') has been used to estimate the entropy increase rates for the climate system (Paltridge, 1978; Peixoto and Oort, 1992; Ozawa and Ohmura, 1997). We have confirmed that the local expression is equivalent to the global expression. Usually, the local expression can not be applied to a large-scale circulation model of which scale of resolution is very much coarser than the dissipation scale (Nicolis, 1999). Here is the advantage of using the global expression. It can, in principle, include the effects of entropy increase by the dissipation processes, so long as phenomenological assumption on turbulence, such as eddy transport coefficients, can reproduce global-distributions of physical variables (temperature, heat flux, etc.) close to real nature.

The results obtained from this study can be summarised into a simple statement to express the thermodynamic properties of a steady-state dissipative system and its nonequilibrium surroundings:

$$\dot{S}_{\text{sys},i} = 0 \quad \text{and} \quad \sum \dot{S}_{\text{surr},i} > 0, \tag{8}$$

where i denotes the i th transport process. The first condition is for the dissipative system to be in a steady-state, and the second one represents the requirement of the second law of thermodynamics. Here the summation $\sum$ is added, since entropy can decrease along some process provided that the total sum is positive (Ozawa, 1997). The statement is of a general form, and it can also be applied to a living system. Schrödinger (1944) suggested that 'life feeds on *negative* entropy from its environment'. Our statement (8) gives an

inverse view of Schrödinger's since his negative input is just a *positive* entropy output to the surrounding environment. A living system maintains an ordered structure in it whose entropy is small but constant in a steady-state (the first condition in (8)). On the contrary, irreversible processes taking place in the system results in an entropy increase in the surroundings (the second condition in (8)). In this respect, the existence of the dissipative systems on the planet, from a living system to the oceanic circulation, has a certain contribution to the entropy increase in the surrounding system including the sun and space (i.e., the universe). In other words, the entropy of the universe is increasing slowly and steadily towards the maximum value by the contribution of all the dissipative systems on the planet.

Finally, it should be noted that the numerical simulations carried out here were slightly sensitive to the boundary conditions applied to the surface. For instance, when we used a different relaxation time (50 days) for the surface salt transport, somewhat different oscillations were observed in the entropy increase rates during the spin-up period (Shimokawa and Ozawa, 1998). In that case, a correlation was found between the entropy increase rate and the strength of the meridional circulation, but it was not evident in the present case. Thus, the oscillations seem to be sensitive to the applied boundary conditions. However, in the steady-state, both circulation patterns and the entropy increase rates are virtually identical, and the steady-state properties presented and discussed in the preceding sections are held to be valid.

6. Acknowledgements

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7. Appendix

Details of entropy formulation

The change rate of entropy of an open system is given by the following time derivative

$$\dot{S}_{\text{ocn}} = \frac{d}{dt} \left[\int \rho s \, dV \right] = \int \frac{\partial(\rho s)}{\partial t} \, dV + \int \rho s \mathbf{v} \cdot \mathbf{n} \, dA, \quad (\text{A1})$$

where ρ is the density of the fluid, s is the entropy per unit mass, $\mathbf{v}$ is the normal component of surface velocity (positive outward), V is the volume of the system, and A is the surface bounding the system. The first term on the right-hand side can be expanded and rewritten by using the equation of continuity $[\partial \rho / \partial t = -\text{div}(\rho \mathbf{v})]$ as:

$$\begin{aligned} \frac{\partial(\rho s)}{\partial t} &= \rho \frac{\partial s}{\partial t} + s \frac{\partial \rho}{\partial t} \\ &= \rho \frac{\partial s}{\partial t} - \text{div}(\rho s \mathbf{v}) + \rho \mathbf{v} \cdot \text{grad } s. \end{aligned}$$

Substituting this in the volume integral of (A1), and transforming the second term by using Gauss's theorem $[\int \text{div}(\rho s \mathbf{v}) \, dV = \int \rho s \mathbf{v} \cdot \mathbf{n} \, dA]$, we get

$$\dot{S}_{\text{ocn}} = \int \rho \left[\frac{\partial s}{\partial t} + \mathbf{v} \cdot \text{grad } s \right] \, dV. \quad (\text{A2})$$

The expression in the square brackets is the substantial time derivative of entropy per unit mass of a fluid moving about in space (ds/dt). This change rate of entropy can be expressed by using the general thermodynamic relation $[ds = \delta Q/T = \{du + p \, dV - \sum \mu_j \, dn_j\}/T]$ (De Groot and Mazur, 1962, ch. 3) as:

$$\frac{ds}{dt} = \frac{1}{T} \left(\frac{du}{dt} + p \frac{d(1/\rho)}{dt} - \sum \mu_j \frac{dn_j}{dt} \right), \quad (\text{A3})$$

where u is the internal energy per unit mass, p is the pressure, μ_j is the chemical potential of a component j , n_j is the number of the j th component per unit mass, and the summation $\sum$ is taken over all chemical components in the fluid. Substituting this in (A2), and transforming the substantial time derivatives to spatial time derivatives ($dX/dt = \partial X / \partial t + \mathbf{v} \cdot \text{grad } X$), we get

$$\begin{aligned} \dot{S}_{\text{ocn}} &= \int \left[\frac{1}{T} \left(\rho \frac{\partial u}{\partial t} + \rho \mathbf{v} \cdot \text{grad } u + p \, \text{div } \mathbf{v} \right) \right. \\ &\quad \left. - \sum \frac{\mu_j}{T} \left(\rho \frac{\partial n_j}{\partial t} + \rho \mathbf{v} \cdot \text{grad } n_j \right) \right] \, dV. \end{aligned} \quad (\text{A4})$$

Here we have used the continuity relation $[d(1/\rho)/dt = -(1/\rho^2) \, d\rho/dt = (1/\rho) \, \text{div } \mathbf{v}]$. The first and second terms in the parentheses can be rewritten using the following relation:

$$\rho \frac{\partial X}{\partial t} + \rho \mathbf{v} \cdot \text{grad } X = \frac{\partial(\rho X)}{\partial t} + \text{div}(\rho X \mathbf{v}).$$

Replacing X with u and n_j , and substituting in (A4), we get

$$\begin{aligned} \dot{S}_{\text{ocn}} &= \int \frac{1}{T} \left[\frac{\partial(\rho c T)}{\partial t} + \text{div}(\rho c T \mathbf{v}) + p \, \text{div } \mathbf{v} \right] \, dV \\ &\quad - \int \sum \frac{\mu_j}{T} \left[\frac{\partial(\rho n_j)}{\partial t} + \text{div}(\rho n_j \mathbf{v}) \right] \, dV. \end{aligned} \quad (\text{A5})$$

Here we have used the relation: $u = cT$, where c is the specific heat at constant volume.

The chemical potential of solute particles (or ions) in an ideal solution referred to that at a state of pure solute can be expressed by a function of number concentration of the particle (Zemansky and Dittman, 1981, Sec. 14.11) as

$$\mu_j = kT \ln C_j, \quad (\text{A6})$$

where k is the Boltzmann constant and C_j is the number concentration of the component j per unit volume of a fluid. In the case of sea water, all salt (mainly NaCl) is dissociated into Na^+ and Cl^- ions because of the nearly perfect dissociation in the dilute solution. Then, the summation $\sum$ in (A5) should be taken for these two components. Substituting (A6) in (A5), we get:

$$\begin{aligned} \dot{S}_{\text{ocn}} &= \int \frac{1}{T} \left[\frac{\partial(\rho c T)}{\partial t} + \text{div}(\rho c T \mathbf{v}) + p \, \text{div } \mathbf{v} \right] \, dV \\ &\quad - \alpha k \int \left[\frac{\partial C}{\partial t} + \text{div}(C \mathbf{v}) \right] \ln C \, dV, \end{aligned} \quad (\text{A7})$$

where α ($=2$) represents the effect of the dissociation, and C ($=\rho n$) is the number concentration of salt per unit volume of sea water. This equation is referred as eq. (3) in the text.

The entropy of the surrounding system will be changed by heat and material (salt) fluxes from the ocean system through the boundary surface. (In the real ocean, there is water flux instead of

the salt flux. But, it is possible to show that the entropy increase by the water flux can be replaced with that by the salt flux, if the sea water can be considered as an ideal and dilute solution, and the variation in salinity is small in comparison with the salinity itself.) Following Clausius's definition, the rate of entropy increase by the heat flux is given by the heat flux divided by the temperature. The rate of entropy increase by the salt flux is given by the salt flux times its chemical potential divided by the temperature (see eq. (2)). Therefore,

$$\dot{S}_{\text{sur}} = \int \frac{F_h}{T} dA - \alpha k \int F_s \ln C dA, \quad (\text{A8})$$

where F_h and F_s are the fluxes of heat and salt per unit surface, defined as positive outward, respectively.

The entropy increase rate for the whole system is given by the sum of (A7) and (A8) as

$$\begin{aligned} \dot{S}_{\text{whole}} = & \int \frac{1}{T} \left[\frac{\partial(\rho c T)}{\partial t} + \text{div}(\rho c T \mathbf{v}) + p \text{div} \mathbf{v} \right] dV \\ & + \int \frac{F_h}{T} dA - \alpha k \int \left[\frac{\partial C}{\partial t} + \text{div}(C \mathbf{v}) \right] \ln C dV \\ & - \alpha k \int F_s \ln C dA. \end{aligned} \quad (\text{A9})$$

This equation is referred as eq. (5) in the text. In the case of sea water, further simplification is possible. It is usual to assume the incompressibility ($\text{div} \mathbf{v} = 0$) for the sea water. The volumetric heat capacity (ρc) is practically constant (Gill, 1982, Appendix 3). Then, the divergence terms [$\text{div}(\rho c T \mathbf{v})$ and $\text{div}(C \mathbf{v})$] can be rewritten as

$$\begin{aligned} \frac{1}{T} \text{div}(\rho c T \mathbf{v}) &= \rho c \mathbf{v} \cdot \text{grad}(\ln T) + \rho c \text{div} \mathbf{v} \\ &= \text{div}(\rho c \mathbf{v} \ln T), \end{aligned}$$

and

$$\begin{aligned} \text{div}(C \mathbf{v}) \ln C &= \text{div}(C \mathbf{v} \ln C) - \mathbf{v} \cdot \text{grad} C \\ &= \text{div}[C \mathbf{v} (\ln C - 1)]. \end{aligned}$$

The volume integrals of these last terms can be transformed by Gauss's theorem to surface integrals of $(\rho c \mathbf{v} \ln T)$ and $[C \mathbf{v} (\ln C - 1)]$; they are zero since there is only negligible amount of water flux across the surface. Then, for the incompressible sea water, we get simply

$$\begin{aligned} \dot{S}_{\text{whole}} = & \int \frac{\rho c}{T} \frac{\partial T}{\partial t} dV + \int \frac{F_h}{T} dA \\ & - \alpha k \int \frac{\partial C}{\partial t} \ln C dV - \alpha k \int F_s \ln C dA. \end{aligned} \quad (\text{A10})$$

This equation is referred as eq. (6) in the text.

Eq. (A9) can be written in a different form. The surface integrals ($\int F_h/T dA$ and $\int F_s \ln C dA$) can be transformed to volume integrals by using Gauss's theorem:

$$\int \frac{F_h}{T} dA = \int \frac{\text{div} \mathbf{F}_h}{T} dV + \int \mathbf{F}_h \cdot \text{grad} \left(\frac{1}{T} \right) dV, \quad (\text{A11})$$

and

$$\begin{aligned} \int F_s \ln C dA \\ = \int \ln C \text{div} \mathbf{F}_s dV + \int \frac{\mathbf{F}_s \cdot \text{grad} C}{C} dV, \end{aligned} \quad (\text{A12})$$

where $\mathbf{F}_h$ and $\mathbf{F}_s$ is the flux density of heat and salt (vector in three dimensional space) by thermal conduction and by molecular diffusion. (In general, $\mathbf{F}_h$ should include all diabatic heat transport processes such as latent heat flux due to phase changes of water, radiative transport, etc. These processes are, however, limited to a layer of a few tens of meters from the ocean's surface, and can be disregarded in the case of oceanic general circulation (Gill, 1982, Sec. 4.4).) Because of the law of conservation of energy (the first law of thermodynamics), the terms in the first volume integral in eq. (A9) are related to the convergence of the heat flux and the rate of heating by viscous dissipation (Chandrasekhar, 1961, Sec. 7) as

$$\frac{\partial(\rho c T)}{\partial t} + \text{div}(\rho c T \mathbf{v}) + p \text{div} \mathbf{v} = -\text{div} \mathbf{F}_h + \Phi, \quad (\text{A13})$$

where Φ is the dissipation function, representing the rate of dissipation of kinetic energy into heat by viscosity per unit volume of the fluid. Similarly, due to the law of conservation of salt, the terms in the third volume integral in eq. (A9) are related to the convergence of salt flux by molecular diffusion (Landau and Lifshitz, 1944, Sec. 58) as

$$\frac{\partial C}{\partial t} + \text{div}(C \mathbf{v}) = -\text{div} \mathbf{F}_s. \quad (\text{A14})$$

By substituting eqns. (A11), (A12), (A13) and (A14) in eq. (A9), we get

$$\dot{S}_{\text{whole}} = \int \mathbf{F}_h \cdot \text{grad} \left(\frac{1}{T} \right) dV + \int \frac{\Phi}{T} dV \quad (\text{A15})$$

$$- \alpha k \int \frac{\mathbf{F}_s \cdot \text{grad } C}{C} dV.$$

The first term is the entropy increase rate by thermal dissipation (heat conduction), the second term is that by viscous dissipation, and the third term is that by molecular diffusion of salt ions. This equation is referred as eq. (7) in the text.

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