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Gross thermodynamics of two-component core convection

David Gubbins,[1]* Dario Alfè,[2,4] Guy Masters,[3] G. David Price[2] and Michael Gillan[4]

[1]*School of Earth Sciences, University of Leeds, Leeds* LS2 9JT, *UK. E-mail: d.gubbins@earth.leeds.ac.uk*
[2]*Research School of Earth Sciences, Birkbeck College & University College London, Gower Street, London* WC1E 6BT, *UK*
[3]*IGPP, Scripps Institution of Oceanography, University of California, San Diego, La Jolla* 92093-0225, *CA, USA*
[4]*Physics and Astronomy Department, University College London, Gower Street, London* WC1E 6BT, *UK*

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SUMMARY

We model the inner core by an alloy of iron and 8 per cent sulphur or silicon and the outer core by the same mix with an additional 8 per cent oxygen. This composition matches the densities of seismic model, Preliminary Reference Earth Model (PREM). When the liquid core freezes S and Si remain with the Fe to form the solid and excess O is ejected into the liquid. Properties of Fe, diffusion constants for S, Si, O and chemical potentials are calculated by first-principles methods under the assumption that S, O, and Si react with the Fe and themselves, however, not with each other. This gives the parameters required to calculate the power supply to the geodynamo as the Earth's core cools. Compositional convection, driven by light O released at the inner-core boundary on freezing, accounts for half the entropy balance and 15 per cent of the heat balance. This means the same magnetic field can be generated with approximately half the heat throughput needed if the geodynamo were driven by heat alone. Chemical effects are significant: heat absorbed by disassociation of Fe and O almost nullify the effect of latent heat of freezing in driving the dynamo. Cooling rates below 69 K Gyr^{-1} are too low to maintain thermal convection everywhere; when the cooling rate lies between 35 and 69 K Gyr^{-1} convection at the top of the core is maintained compositionally against a stabilizing temperature gradient; below 35 K Gyr^{-1} the dynamo fails completely. All cooling rates freeze the inner core in less than 1.2 Gyr, in agreement with other recent calculations. The presence of radioactive heating will extend the life of the inner core, however, it requires a high heat flux across the core–mantle boundary. Heating is dominated by radioactivity when the inner core age is 3.5 Gyr. We, also, give calculations for larger concentrations of O in the outer core suggested by a recent estimation of the density jump at the inner-core boundary, which is larger than that of PREM. Compositional convection is enhanced for the higher density jumps and overall heat flux is reduced for the same dynamo dissipation, however, not by enough to alter the qualitative conclusions based on PREM. Our preferred model has the core convecting near the limit of thermal stability, an inner-core age of 3.5 Gyr and a core heat flux of 9 TW or 20 per cent of the Earth's surface heat flux, 80 per cent of which originates from radioactive heating.

Key words: Earth's core, geodynamo, inner core, thermal history.

1 INTRODUCTION

The Earth has possessed a magnetic field for most of its history, which means a geodynamo has operated in the liquid core throughout that time (McElhinny 1973). The magnetic field is generated by convection driven by a source of buoyancy. In Gubbins *et al.* (2003), hereafter referred to as Paper I, we explored purely thermal convection. In this paper we consider compositional convection. The model has been worked on many times before (Braginsky 1963; Gubbins 1977; Loper 1978b; Gubbins *et al.* 1979; Häge & Müller 1979; Mollett 1984; Glatzmaier & Roberts 1995; Lister & Buffett 1995; Buffett *et al.* 1996; Labrosse *et al.* 1997) and reviewed recently by Buffett (2000). Here, we use a two-component model of the liquid core based on first-principles calculations of an iron-oxygen alloy (Alfè *et al.* 1999a,b, 2002a,b). Previous studies (e.g. Gubbins *et al.* 1979) used ideal-solution theory to predict changes in density and chemical potential and laboratory measurements on liquid iron at standard pressure for diffusion constants. The calculations in this paper give the first opportunity to account for real chemistry in core convection.

Seismologically-determined densities for the solid inner and liquid outer cores have long been thought to be lighter than those for pure iron at the same temperature and pressure. The inner core is too light for solid iron (Poirier 2000) and the liquid outer core is lighter

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*Corresponding author.

still, the density jump at the inner core boundary (ICB) being too great to be explained by melting alone. Alfè *et al.* (2000) matched the inner-core density with the density of alloys of Fe and 8 per cent S. However, the chemical potential of the lighter element was found to be the same in both liquid and solid phases: on freezing the S or Si in the liquid would, therefore, go into the solid at roughly the same composition. The S and Si atoms are comparable in size to Fe atoms and, therefore, fit into the solid lattice relatively easily.

Oxygen does not have the same chemical potential between solid and liquid phases (Alfè *et al.* 1999a,b, 2002a,b) because O atoms are a different size at this temperature and pressure. An Fe-O alloy on freezing would therefore leave the oxygen in the liquid phase. 8 per cent of O in the liquid outer core explains the density jump across the ICB. This light element is available to drive convection in the outer core.

So far, calculations have only been performed on mixtures of two elements at a time: Fe and S, Fe and Si, Fe and O. In this paper, we adopt an Fe-S(or Si)-O alloy; we assume there is no chemical reaction between S (or Si) and O, and apply the properties determined from the Fe-O calculation to the Fe-S(Si)-O mix.

We consider two heat sources: radioactivity and secular cooling of the whole core (and, by implication, the whole Earth). Radioactive heating was treated in Paper I; cooling introduces some new chemical effects. Freezing at the ICB releases latent heat, however, it also releases excess O, which is buoyant. This lighter fluid rises, driving convection and becoming mixed uniformly throughout the outer core.

Growth of the solid inner core, and the gradual dilution of the liquid outer core, results in a change in the Earth's gravitational energy, which is the ultimate source of power for compositional convection. The kinetic energy of motion is eventually dissipated by the main frictional force in the core, magnetic resistance. Gravitational energy is, therefore, ultimately turned into heat via the magnetic field, the heat itself being available to drive a little more convection and, perhaps, help a little more with generating the magnetic field by dynamo action.

All the gravitational energy released by compositional convection becomes magnetic energy, making it a highly efficient way to power the geodynamo, whereas most of the heat driving thermal convection is convected away without generating any magnetic field. This is why compositional convection is more efficient than thermal convection at generating magnetic field.

Chemical effects arise in a two-component system. The heat of solution is similar to latent heat, being released at the ICB on dissociation and absorbed as the O recombines in the outer core. Unlike latent heat, it can be of either sign, depending on whether the reaction is endothermic or exothermic.

We assume that convection is sufficiently vigorous to mix the constituents and the entropy throughout the core. This is likely to be an excellent approximation outside thin boundary layers because conduction of heat and solute (O) is very much slower than the time it takes core fluid to move around the core. Molecular diffusion acts against this mixing process. In the absence of convection it would produce a state of constant chemical potential, just as diffusion of heat would produce a state of constant temperature. Molecular diffusion produces an entropy gain and reduces the efficiency of convection.

2 THEORY

The theoretical development follows that of Paper I. The entropy balance is used first to determine the cooling rate and heat sources required to balance a given dissipative gain, then conservation of energy gives the total heat flux across the core–mantle boundary (CMB). This paper focusses on additional entropy and energy contributions arising from compositional convection: heat of solution, redistribution of solute in a gradient of chemical potential and, most importantly, gravitational energy loss that, unlike the contribution from thermal contraction (Paper I), is available to drive the dynamo.

Table 1. Density reductions from pure iron at ICB pressure and temperature conditions. PREM densities are 12.76 and 12.17 on either side of the ICB.

	ρ	Per cent ρ	$\Delta\rho$
Solid iron	13.16		
8 per cent S/Si	12.76	3.0	0.40
Melting	12.52	1.8	0.24
8 per cent O	12.17	2.8	0.37

2.1 The core model

We adopt a slightly simplified form of the core model found by Alfè *et al.* (2002a,b) to fit the seismological densities of the inner and outer cores. The solid inner core contains 8 per cent molar volume of sulphur or silicon and the liquid outer core an additional 8 per cent oxygen. Densities are shown in Table 1. The density of pure solid iron at ICB pressure and temperature was found to be 13.16 Mgm^{-3}. This value is reduced by mixing with S or Si to the Preliminary Reference Earth Model (PREM) value, melting provides a further 1.8 per cent reduction, and oxygen reduces the density by 2.8 per cent to meet the PREM value.

The outer-core mixture contains a heavy component, the Fe/S/Si mix that comprises the inner core, and a light element, O. Oxygen is assumed to react with the heavy component, however, not with its individual elements, which do not react with each other. This is undoubtedly an oversimplification, however, it is an essential first step towards a more complex core chemistry.

The thermodynamic properties of a two-component mixture require three state variables rather than the usual two for a single component: we shall use pressure P, temperature T and concentration or mass fraction c, the mass of the minor constituent (solute) per unit mass of alloy. Chemical quantities are often given in terms of the mole fraction $\bar{c}$, the number of atoms or molecules of solute divided by the total number of atoms. They are related through the molecular weights

$$\bar{c} = \frac{\bar{A}}{A_L} c, \tag{1}$$

where $\bar{A}$ and A_L are the mean molecular weights of the mixture and solute, respectively.

The chemical potential μ is conjugate to the concentration: their product has dimensions of energy per unit mass. The exact differential of the internal energy becomes

$$de = T\,ds + \frac{P}{\rho^2} d\rho + \mu\,dc, \tag{2}$$

μ obeys a set of Maxwell relations, the relevant two being derived from the exact differential for the Gibbs free energy:

$$\left(\frac{\partial \mu}{\partial T}\right)_{P,c} = -\left(\frac{\partial s}{\partial c}\right)_{P,T}, \tag{3}$$

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,c} = -\frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial c}\right)_{P,T} = \frac{\alpha_c}{\rho}, \tag{4}$$

where we have introduced the compositional expansion coefficient

$$\alpha_c = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial c}\right)_{P,T}. \tag{5}$$

We assume, as in Paper I, a well-mixed basic state in which the pressure is close to hydrostatic:

$$\frac{dP}{dr} = -\rho g. \tag{6}$$

In this case, composition as well as entropy are well mixed: c is uniform and T is adiabatic outside thin boundary layers. The mixing is accomplished by vigorous core convection, which overturns in a time much shorter than that taken by heat or solute to diffuse. The convection, therefore, prevents the outer core from reaching a state of chemical equilibrium in which μ is constant: μ depends on radius because of the vertical variation of P and T.

2.2 Diffusion and the constitutive relations

The mass of solute passing per unit area per second is described by the solute flux vector $\boldsymbol{i}$. Conservation of mass of solute gives

$$\rho\frac{\partial c}{\partial t} + \rho\boldsymbol{v}\cdot\nabla c + \nabla\cdot\boldsymbol{i} = 0, \tag{7}$$

which applies in addition to the full conservation of mass eq. (2) of Paper I (hereafter equations from Paper I will be referred to in the form eq. I2).

Solute is released on freezing at the ICB and redistributed uniformly throughout the outer core by convection, which leads to a gradual dilution of the outer-core liquid. The rate of release of light material into the outer core is related to the rate of growth of the inner core,

$$\frac{Dc}{Dt} = C_c\frac{dr_\mathrm{i}}{dt}, \tag{8}$$

where

$$C_c = \frac{4\pi r_\mathrm{i}^2\rho(r_\mathrm{i})c}{M_\mathrm{oc}}, \tag{9}$$

where M_oc is the mass of the outer core. Ultimately, the cooling rate at the core surface through (eq. I39) is

$$\frac{dr_\mathrm{i}}{dt} = C_r\frac{dT_\mathrm{c}}{dt}, \tag{10}$$

where

$$C_r = \frac{T_\mathrm{i}}{\tau T_\mathrm{c}}, \tag{11}$$

where τ is the difference in melting and adiabatic temperature gradients at the ICB:

$$\tau = \rho(r_\mathrm{i})g(r_\mathrm{i})[dT_\mathrm{m}/dP - (\partial T/\partial P)_{S,c}]. \tag{12}$$

In the inner core c does not change.

In Paper I we used Fourier's law of heat conduction, however, in a two-component system the heat flow also depends on composition. Both $\boldsymbol{q}$ and $\boldsymbol{i}$, the heat and solute flux vectors, depend on gradients of all three state variables P, T, c. The Onsager reciprocal relations (Landau & Lifshitz 1959) take account of thermodynamic interrelationships between the coefficients:

$$\boldsymbol{q} - \mu\boldsymbol{i} = -k\nabla T + \frac{\beta T}{\alpha_D}\boldsymbol{i}, \tag{13}$$

$$\boldsymbol{i} = -\alpha_D\nabla\mu - \beta\nabla T, \tag{14}$$

where α_D and β are material constants and k is the usual thermal conductivity. Eq. (14) has the alternative form, a generalization of Fick's law, given by:

$$\boldsymbol{i} = -\rho D\left(\nabla c + \frac{K_T}{T}\nabla T + \frac{K_P}{P}\nabla P\right), \tag{15}$$

where D is the molecular diffusivity and K_T, K_P are dimensionless thermodiffusion and baro-diffusion coefficients (note K_T is not the bulk modulus). K_T is usually neglected: it would be very difficult to calculate from first principles and is taken to be zero from now on.

Expressing μ in terms of gradients of P, T, c, substituting into eq. (14), and comparing terms with eq. (15), gives relationships between the various coefficients:

$$\alpha_D = \frac{\rho D}{(\partial\mu/\partial c)_{P,T}}, \tag{16}$$

$$K_P = P\frac{(\partial\mu/\partial P)_{T,c}}{(\partial\mu/\partial c)_{P,T}} = P\frac{\alpha_c\alpha_D}{\rho^2 D}. \tag{17}$$

These equations, together with the Maxwell eq. (4), give the parameters required for the constitutive relations.

2.3 Energy equation

Paper I gave the energy equation for a pure iron core (eq. I8). Oxygen, the second component, enters the energy equation through the gravitational energy, the internal energy (eq. 2), and the heat-flux vector (eq. 13). The most important contribution is the gravitational energy change arising when solute is removed from the ICB and redistributed throughout the outer core. Material has to be physically moved by the convection, which results in friction. This energy is available to drive convection and the dynamo. In Paper I, we showed that gravitational energy change associated with pressure changes, contraction and the volume change accompanying freezing are not available to drive convection, except for a small amount of pressure heating. The change in gravitational energy can be estimated from eq. (I11) using only the density change caused by separation of light material:

$$Q_g = -\int\psi\left(\frac{\partial\rho}{\partial t}\right)_{P,T}dV = \int\rho\psi\alpha_c\frac{Dc}{Dt}dV. \tag{18}$$

The heat flux $\boldsymbol{q}$ depends on $\boldsymbol{i}$ according to eq. (13), however, it yields a surface integral that remains unchanged provided solute does not cross the boundary ($\boldsymbol{i}\cdot d\,\boldsymbol{S} = 0$):

$$\begin{aligned} Q &= \oint\boldsymbol{q}\cdot d\boldsymbol{S} \\ &= \oint\left[-k\nabla T + \left(\mu + \frac{\beta T}{\alpha_D}\right)\boldsymbol{i}\right]\cdot d\boldsymbol{S} \\ &= \oint -k\nabla T\cdot d\boldsymbol{S}. \end{aligned} \tag{19}$$

The internal energy depends on the chemical potential and composition as well as temperature and pressure. Eq. (2) gives

$$\int\rho\frac{De}{Dt}dV = \int\rho T\frac{Ds}{Dt}dV + \int\frac{P}{\rho}dV + \int\rho\mu\frac{Dc}{Dt}dV. \tag{20}$$

Two additional terms arise that were not present in the single-component core studied in paper I: the last integral on the right hand side of eq. (20) and the dependence of s on concentration c. These combine to give

$$Q_H = \int \rho\mu \frac{Dc}{Dt}\,dV + \int \rho T \left(\frac{\partial S}{\partial c}\right)_{P,T} \frac{Dc}{Dt}\,dV$$
$$= \int \rho \left[\mu - T\left(\frac{\partial \mu}{\partial T}\right)_{P,c}\right]\frac{Dc}{Dt}\,dV, \tag{21}$$

where the Maxwell relation (eq. 3) has been used to transform the entropy derivative. The quantity in brackets is the heat of reaction, R_H:

$$R_H = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{P,c}. \tag{22}$$

This term represents heat absorbed or released by chemical reaction of Fe and O; the reaction is exothermic and heat is absorbed in the dissociation at the ICB and released throughout the liquid core as the concentration of O increases. Note that the definition of the heat of reaction given by Gubbins *et al.* (1979) is incorrect and as a result their chemical change in internal energy should really be part of the heat of reaction.

Adding new terms to the global energy eq. (I72) gives

$$Q = Q_R + Q_S + Q_L + Q_P + Q_g + Q_H \tag{23}$$

(Q_{PL} has been absorbed into the latent heat). The heat flux out through the CMB is the sum of energy sources within the core, which now includes the gravitational energy of rearrangement of oxygen in the outer core and change in internal energy from the gradual dilution of core liquid.

2.4 Entropy equation

The entropy equation at a point (*cf.* eq. I24) now includes heat generated by diffusion of light material Landau & Lifshitz (1959)

$$\rho\frac{Ds}{Dt} = -\frac{\nabla\cdot\boldsymbol{q}}{T} + \frac{\rho h}{T} + \frac{\Phi}{T} + \frac{\mu\nabla\cdot\boldsymbol{i}}{T}. \tag{24}$$

Integrating over the core gives the same thermal terms as Paper I plus two additional terms arising from the last term on the right hand side, the dependence of $\boldsymbol{q}$ on $\boldsymbol{i}$ in eq. (13) and the dependence of s on chemical composition. These are the dissipation entropy associated with molecular diffusion and the entropy of the heat of reaction. Q also contains the gravitational energy of rearrangement. The divergence theorem may be used to show that

$$\int\left[-\frac{\nabla\cdot\boldsymbol{q}}{T} + \frac{\mu\nabla\cdot\boldsymbol{i}}{T}\right]dV = -\frac{Q}{T_c} + \int k\left(\frac{\nabla T}{T}\right)^2 dV$$
$$+ \int \frac{\boldsymbol{i}^2}{\alpha_D T}\,dV. \tag{25}$$

The second term on the right hand side is the entropy of thermal diffusion, defined as E_k in eq. (I70); the last term is the entropy of molecular conduction, which we define as E_α:

$$E_\alpha = \int \frac{\boldsymbol{i}^2}{\alpha_D T}\,dV. \tag{26}$$

The heat of reaction gives the entropy

$$E_H = -\int \frac{\rho R_H}{T}\frac{Dc}{Dt}\,dV. \tag{27}$$

The gross entropy balance of Paper I (*cf.* eq. I73), after omitting pressure effects, becomes

$$E_k + E_\Phi + E_\alpha = E_R + E_S + E_L + E_P + E_H + \frac{Q_g}{T_c}. \tag{28}$$

Compositional convection enters the calculation primarily through Q_g, the gravitational energy release. Its efficiency in driving the dynamo is reflected in eq. (28): it is multiplied by $1/T_c$ rather than the small difference $1/T_c - 1/T$ as is the case with other heat terms.

3 CORE CHEMISTRY

3.1 First-principles calculations

The properties of Fe alloyed with O, S and Si have been studied using first-principles (FP) simulations, the details of which have already been described in Paper I. The techniques used to calculate the chemical potentials of various impurities in liquid Fe have also been reported previously (Alfè *et al.* 2000, 2002a,b): we summarize them here.

The chemical potential $\bar{\mu}_X$ of a component X can be defined as the change of Helmholtz free energy F when an atom of X is introduced at constant volume and temperature. As the concentration of the impurity goes to zero the chemical potential has a logarithmic singularity as a result of the divergent number of different possible arrangements of the atoms in the system. It is, therefore, convenient to write it as $\bar{\mu}_X = k_B T \ln \bar{c}_X + \tilde{\mu}_X$. The term $\tilde{\mu}_X$ can be calculated using thermodynamic integration. It is computationally convenient to work with a fixed number of atoms, so we calculate the free energy difference $\Delta F = F(N_{Fe} - 1, N_X + 1) - F(N_{Fe}, N_X)$. This gives the difference of chemical potentials $\tilde{\mu}_X - \tilde{\mu}_{Fe}$, which we add to our previously computed chemical potential of pure Fe (Alfè *et al.* 1999a,b). To compute ΔF we calculate the integral

$$\int_0^1 d\lambda \langle U_1 - U_0\rangle_\lambda, \tag{29}$$

where U_0 is the potential energy of the system with N_{Fe} iron atoms and N_X impurity atoms, and U_1 the potential energy of the system with one Fe transmuted into X. The thermal average $\langle\cdot\rangle_\lambda$ is evaluated as a time average using molecular dynamics for several values of λ and the integral is calculated numerically. This demands an unusual kind of simulation: for the atom positions $\mathbf{r}_1, \ldots \mathbf{r}_N$ at each instant of time, we have to perform two independent FP calculations, one for each chemical composition. As well as U_0 and U_1 for the given positions, we calculate two sets of FP forces, $\mathbf{F}_{0i} \equiv -\nabla_i U_0$ and $\mathbf{F}_{1i} \equiv -\nabla_i U_1$, and the linear combinations $\mathbf{F}_{\lambda i} \equiv (1-\lambda)\mathbf{F}_{0i} + \lambda\mathbf{F}_{1i}$ are used to generate the time evolution. In practice, the statistical accuracy is rather poor if one transmutes only a single Fe atom into X and it is preferable to transmute several at the same time. Instead of $\tilde{\mu}_X - \tilde{\mu}_{Fe}$ for a given mole fraction $\bar{c}_X$, this then yields an integral of $\tilde{\mu}_X - \tilde{\mu}_{Fe}$ over a range of $\bar{c}_X$ values. The results obtained by transmuting different numbers of atoms can then be processed to obtain $\tilde{\mu}_X - \tilde{\mu}_{Fe}$ as a function of $\bar{c}_X$. For small concentrations, $\bar{c}_X \leq 0.2$, we find that the chemical potential can be accurately represented in the following way:

$$\bar{\mu}_X = k_B T \log \bar{c}_X + \bar{\mu}_{0X} + \lambda_X \bar{c}_X. \tag{30}$$

Properties for pure iron that are used in this paper were taken from the first-principles calculations of Alfè & Gillan (1998) and Alfè *et al.* (2000) (see also Paper 1). They are given in Table 2. Thermal conductivity is not given by these calculations; we use a value in common use in the literature.

Properties that depend on the Fe-O alloy were calculated with 64 atoms of Fe and O at different concentrations and two (P, T) conditions: 370 GPa, 7000 K representing the ICB and 135 GPa, 4400 K

Table 2. Properties of iron used for the calculations in this paper. More details are given in Paper I. The range of α represents its variation in pressure as calculated from the Grüneisen parameter. ICB gradient is the difference between melting and adiabatic gradients at the ICB, which controls the rate of growth of the inner core.

		Units	
Thermal expansion	α	K^{-1}	$1.02\text{–}1.95 \times 10^{-5}$
Specific heat	C_p	$\mathrm{J\,kg^{-1}\,K^{-1}}$	715
Grüneissen parameter	γ	–	1.5
Latent heat	L	$\mathrm{J\,kg^{-1}}$	0.75×10^6
Thermal conductivity	k	$\mathrm{W\,m^{-1}\,K^{-1}}$	60
ICB temperature	T_{i}	K	5500
CMB temperature	T_{c}	K	4123
Melting gradient	dT_{m}/dP	$\mathrm{KG\,Pa^{-1}}$	9.0
ICB gradient	τ	$\mathrm{K\,km^{-1}}$	0.14

Table 3. Properties of the alloys of Fe with O, S and Si needed to estimate core energies.

			O	S	Si
α_c	–	–	−1.10	−0.64	−0.87
D	10^{-9}	$\mathrm{m^2\,s^{-1}}$	10	5	5
R_H	10^6	$\mathrm{J\,kg^{-1}}$	−27.7	–	–
λ	–	$\mathrm{ev\ atom^{-1}}$	3.25	6.2	3.5
α_D	10^{-12}	$\mathrm{kg\,m^{-3}\,s}$	0.70	1.06	1.04
K_P	–	–	0.17	0.34	0.45
ι	10^{-12}	$\mathrm{kg\,m^{-2}\,s^{-1}}$	3.4	3.0	4.0
E_α	MW/K		0.51	0.26	0.47

for the CMB (Alfè *et al.* 2002a,b). Separate calculations were performed for S and Si at inner-core conditions only. No calculations have been performed with more than two components. The compositional expansion coefficient is estimated from the density gradient simply by fitting splines to the densities and differentiating. Results are shown in Table 3. The diffusion coefficient D was calculated for each species. The heat of reaction is very difficult to estimate accurately. The value for O is given in Table 3; values for S and Si are not required because they do not separate on freezing.

The chemical potential is computed from its definition as the partial derivative of the Gibbs free energy. The chemical potential per atom is expanded as

$$\bar{\mu} = \bar{\mu}_0 + kT \log \bar{c} + \lambda \bar{c} + \mathcal{O}(\bar{c}^2). \tag{31}$$

The values of λ are given in Table 3. The convection equations need the derivative of the chemical potential with respect to mass concentration c:

$$\frac{\partial \mu}{\partial c} = \frac{\partial \bar{\mu}}{\partial \bar{c}} \frac{\bar{A}}{A_L} E_V N_A \frac{1000}{A_L} \ \mathrm{J\,kg^{-1}}, \tag{32}$$

where A_L is the atomic weight of solute O, S, or Si; E_V is the electron volt; and N_A is Avogradro's number.

The diffusion coefficients α_D and K_P are estimated from eqs (16) and (17), and the flux of light material in a hydrostatic pressure gradient is approximated using only the pressure term in eq. (15):

$$\iota = -\frac{K_P}{P} \rho^2 D g = -\alpha_c \alpha_D g. \tag{33}$$

3.2 Comparison with ideal-solution theory

Ideal-solution theory (see e.g. Nordstrom & Munoz 1986) was used by Gubbins *et al.* (1979) to estimate outer-core chemical properties and densities. It only requires knowledge of the mean atomic weight; everything else is then determined in terms of fundamental constants and the densities of solid and liquid at the ICB. Nothing depends on the chemistry of the constituents of the outer core. The first-principles calculations give an opportunity, for the first time, to assess the importance of chemistry in core convection. The chemistry is still severely restricted because we have ignored chemical reactions between the different solutes, however, it is still worth examining the relevant departures from ideal-solution theory.

An ideal solution suffers no change in volume on mixing. The approximation should be accurate for small concentrations and the first-principles calculations confirm this. Results for the densities at molar concentrations up to 10 per cent agree with ideal-solution theory to less than 0.2 per cent in the density. An ideal solution of two liquids with densities given by ρ_1, ρ_2, $\rho_1 < \rho_2$ has density given by

$$\rho = \frac{\rho_1 \rho_2}{\rho_1(1-c) + \rho_2 c}. \tag{34}$$

The densities ρ_1, ρ_2 may be found from this formula and the seismologically-determined densities on both sides of the inner-core boundary and the calculated change in density of iron on freezing. This gives $\rho_1 = 5.56$ and $\rho_2 = 12.52\ \mathrm{Mg\,m^{-3}}$. Eq. (34) may then be used to compute the density and its gradients, including α_c.

The chemical potential expressed per mole of solute is

$$\bar{\mu} = \bar{\mu}_0 + RT \ln \bar{c} \tag{35}$$

(Nordstrom & Munoz 1986). The derivative is required to estimate the diffusion of solute in a pressure gradient:

$$\frac{\partial \bar{\mu}}{\partial \bar{c}} = \frac{kT}{\bar{c}} = 5.9. \tag{36}$$

Departures from ideal-solution theory are, therefore, found by comparing λ in Table 3 with 5.9 ev atom^{-1}. The differences are quite large.

3.3 Changing the density jump at the inner-core boundary

A recent study of normal-mode eigenfrequencies gives a best estimate of the inner-core density jump of $\Delta\rho = 0.82 \pm 0.18$ gm cc^{-1} (Masters & Gubbins 2003) significantly higher than the PREM value of 0.59. This density jump determines the relative importance of compositional and thermal convection in the core and we have, therefore, studied models with $\Delta\rho = 0.82$ and 1.00 in addition to the PREM value, which is very close to 0.82 minus one standard deviation. The largest value we have taken, 1.00, is probably an upper limit because higher density jumps would lead to more body wave reflections *PKiKP* than are actually observed.

The composition of the outer core is determined by the observed density jump minus the part resulting from melting, which we have taken to be 0.24 gm cc^{-1}. Performing the subtraction leaves 0.35, 0.58 and 0.76 gm cc^{-1} for that part resulting from additional oxygen in the outer core. The highest value, therefore, represents more than a doubling of the importance of compositional convection over that in the PREM model. A new first-principles study into the implications of this higher density jump is underway; here we use ideal-solution theory to incorporate the new density jumps into our calculations. This is likely to be a very good approximation for present purposes.

The densities were calculated using eq. (34) with $\rho_1 = 5.56$, $\rho_2 = 12.52$. This gives mass concentrations $c = 0.0252$, 0.0426 and 0.0567 for the three density jumps, respectively. The compositional expansion coefficient α_c remains unchanged and we ignore any small changes in the properties of the outer-core mix associated with the small changes in composition. Concentration only enters the equations through the parameter C_c [defined in eq. (9)], and this affects only the gravitational energy and heat of reaction. Changing the density jump with these approximations is, therefore, very simple.

4 ESTIMATING INDIVIDUAL TERMS

All quantities except radioactive heat and entropy are proportional to the cooling rate at the CMB. C_r in eq. (10) controls the growth rate of the inner core and C_c in eq. (8) controls the rate of increase of composition of oxygen throughout the outer core. $C_r = -9.56$ m K^{-1} for all models. C_c depends on c and, therefore, the density jump at the inner-core boundary: $C_c = -3.12, -5.28, -7.22 \times 10^{-9}$ for $\Delta\rho = 0.59, 0.82, 1.00$, respectively.

Each energy integral that depends on the rate of change of concentration contains two parts: one over the outer core involving the gradual dilution of the liquid and a singular contribution at the ICB from the removal of oxygen in the solid. For example, the heat of solution is, from eqs (21), (22) and (9), (11)

$$\begin{aligned}
&\int \rho R_H(r)\frac{Dc}{Dt}\,dV \\
&\quad= \left(\int_{\mathrm{oc}} R_H\rho\,dV\,C_c - R_H(r_\mathrm{i})\rho(r_\mathrm{i})4\pi r_\mathrm{i}^2 c\right)\frac{dr_\mathrm{i}}{dt} \\
&\quad= \left(\int_{\mathrm{oc}} R_H(r_\mathrm{i})\rho\,dV - R_H(r)M_{\mathrm{oc}}\right)C_c C_r \tfrac{dT_\mathrm{c}}{dt}.
\end{aligned} \tag{37}$$

4.1 Gravitational energy

Eq. (18) gives the change in gravitational energy associated with the separation of the light component. The integral has contributions from the outer core ($Dc/Dt = 0$ in the inner core) and the shell of freezing material at the inner core surface. The latter contribution is, from the first form of the integral in eq. (18) and the definition of C_c in eq. (9),

$$-\psi(r_\mathrm{i})4\pi r_\mathrm{i}^2\rho(r_\mathrm{i})\alpha_c c\frac{dr_\mathrm{i}}{dt} = -\psi(r_\mathrm{i})\alpha_c C_c M_{\mathrm{oc}}\frac{dr_\mathrm{i}}{dt}. \tag{38}$$

The outer-core integral, using eq. (8), is

$$\int \rho\psi\,dV\,\alpha_c C_c\frac{dr_\mathrm{i}}{dt}.$$

Combining and using eq. (10) for dr_i/dt gives

$$Q_g = \left[\int_{\mathrm{oc}}\rho\psi\,dV - M_{\mathrm{oc}}\psi(r_\mathrm{i})\right]\alpha_c C_c C_r\frac{dT_\mathrm{c}}{dt} = \tilde{Q}_g\frac{dT_\mathrm{c}}{dt}, \tag{39}$$

where ψ is the gravitational potential referred to zero at the CMB: it was found from PREM by integrating g downwards from the CMB.

The entropy E_g is simply Q_g/T_c.

4.2 Entropy of heat of solution

R_H is assumed to be independent of radius. The total heat of reaction is then zero for constant R_H, however, the entropy is not because of the vertical variation in temperature. Eq. (27) gives

$$E_H = -R_H\int\frac{\rho}{T}\frac{Dc}{Dt}\,dV = -R_H\left[\int_{\mathrm{oc}}\frac{\rho}{T}\,dV - \frac{M_{\mathrm{oc}}}{T_\mathrm{i}}\right]C_c C_r\frac{dT_\mathrm{c}}{dt}. \tag{40}$$

There is an efficiency factor entering here: it differs from the one applying to cooling because heat is absorbed (or possibly released, depending on the sign of R_H) at the ICB rather than through the CMB. This explains the presence of the temperature T_i here in place of T_c in E_S (eq. I36).

4.3 Entropy of molecular diffusion

Entropy gain as a result of diffusion of light material is given by eq. (26) and the flux $\imath$ by eq. (33). Assuming constant α_c and α_D, which should be a reasonable approximation,

$$E_\alpha = \alpha_c^2\alpha_D\int\frac{g^2}{T}\,dV. \tag{41}$$

The integral was performed numerically using the adiabatic temperature of the model CORE and PREM values. Separate calculations are required for oxygen, sulphur and silicon because all three components diffuse in the outer core, even though only oxygen separates at the ICB. Results are given in the last line of Table 3; the total is $E_\alpha = 4.8$ MW K^{-1}. This value is more than an order of magnitude smaller than E_k: molecular diffusion, therefore, appears to be negligible.

5 RESULTS

Table 4 gives numerical values for all entropies and heats. Quantities with a tilde must be multiplied by the cooling rate (or by the heat source h in the case of $\tilde{Q}_R$ and $\tilde{E}_R$) to give actual model values in W and WK^{-1}. The heat and entropy equations are then

$$Q = \tilde{Q}_R h + \tilde{Q}_c\frac{dT_\mathrm{c}}{dt}, \tag{42}$$

$$E = \tilde{E}_R h + \tilde{E}_c\frac{dT_\mathrm{c}}{dt}, \tag{43}$$

where

$$\tilde{Q}_c = \tilde{Q}_S + \tilde{Q}_L + \tilde{Q}_P + \tilde{Q}_g, \tag{44}$$

$$\tilde{E}_c = \tilde{E}_S + \tilde{E}_L + \tilde{E}_P + \tilde{E}_g + \tilde{E}_H. \tag{45}$$

Setting $E = 10^9$ W K^{-1} as in Paper I gives a cooling rate of 123 K Gyr^{-1}, total heat flux $Q = 15$ TW and projected inner core age 345 Myr. This cooling rate has been used to compute the individual terms in Table 4. The relevant columns show the relative contributions of each effect to the overall heat and energy budgets. E_g makes the largest contribution to the entropy, 57 per cent, reflecting its high efficiency in driving convection and the dynamo. It only contributes 15 per cent of the heat flux.

The results in Table 4 show a rapid cooling rate and very young inner core for the rather arbitrarily chosen dissipation entropy of 10^9 W K^{-1}. The young inner core poses very serious problems for maintaining the Earth's magnetic field in early times because of the inefficiency of thermal convection in driving the dynamo, as discussed in Paper I. We, therefore, consider the following range of models and a combination of cooling and radioactive heating. The calculations are a simple application of eqs (42) and (45); the results are summarized in Table 5 for three values of the density jump: 0.59 (PREM), 0.82 (Masters & Gubbins 2003) and 1.00 (one standard deviation above the preferred value of Masters & Gubbins 2003).

(i) $E = 10^9$ W K^{-1}. As detailed in Table 4.

(ii) $Q = Q_k$. This choice of heat flux means convection continues to be driven thermally throughout the core. In paper I, which did not consider compositional convection, this condition required the top of the core to become subadiabatic. In this case, compositional convection can continue to drive convection against an unfavourable temperature gradient: heat is convected downwards at the top of the core. Heat is still conducted upwards by conduction down the steep adiabatic gradient and the net heat flux remains outwards into the mantle.

Table 4. Numerical values of the $\tilde{Q}$ and $\tilde{E}$ and corresponding values of Q and E for a total entropy production of 10^9 W K^{-1} for the three chosen values of the inner-core density jump. Of the tilde quantities, only $\tilde{Q}_g$, $\tilde{E}_g$ and $\tilde{E}_H$ depend on the density jump. The first column denotes the subscript in eqs (42–45). The last line gives the total heat and entropy budgets for cooling. Pressure effects resulting from compositional rearrangement have been ignored.

	$\tilde{Q}(10^{25})$		Q TW		$\tilde{E}(10^{21})$		E MW K^{-1}	
$\Delta\rho$		0.59	0.82	1.00		0.59	0.82	1.00
s	161	6.3	4.97	4.24	54	211	167	142
L	164	6.4	5.05	4.31	99	388	306	262
P	6	0.2	0.18	0.16	3	13	10	8
g	(60,102,135)	2.3	3.13	3.55	(145, 245, 326)	569	758	862
H	0	0	0	0	(−46, −78, −104)	−181	−241	−274
c		15.3	13.3	12.3		1000	1000	1000

(iii) $E = E_k + E_\alpha = 283$ MW K^{-1}. Nothing is left for magnetic dissipation and the dynamo fails. This gives the lower bound for cooling or radioactive heating.

(iv) A model containing enough radioactive heating to give an inner-core age of 3.5 Gyr and $E = 1000$ MW K^{-1}.

(v) As model (iv), however, with $Q = Q_k$, the point where compositional convection becomes essential in maintaining the adiabat.

(vi) As model (iv), however, with $E = 283$ MW K^{-1}, the point where dynamo action fails.

The results in Table 5 show that, if the core parameters of the model are correct, it is only possible to sustain a dynamo and an inner core throughout most of Earth's history if the core contains a substantial concentration of radioactive isotopes and a large fraction of the Earth's surface heat flux (20 per cent) originates in the core.

Table 5. Results for the range of models (i)–(vi) described in the text. Units are MW K^{-1} (E), K Gyr^{-1} (dT_c/dt), Myr (IC age), pW K^{-1} g (h), TW (Q's). h and Q_R are alternatives to cooling for models (i)–(iii) and are shown in brackets, the total heat flux is either Q_R or Q_c. Models (iv)–(vi) have both heat sources and the total heat Q is their sum.

Model	(i)	(ii)	(iii)	(iv)	(v)	(vi)
$\Delta\rho = 0.59$						
E	1000	562	283	1000	325	283
dT_c/dt	123	69	35	12	12	12
IC age	345	614	1220	3500	3500	3500
h	(16)	–	(4)	14	4	3
Q_c	15	9	4	2	2	2
Q_R	(31)	–	(8)	28	7	6
Q				30	9	8
$\Delta\rho = 0.82$						
E	1000	644	283	1000	351	283
dT_c/dt	97	63	28	12	12	12
IC age	438	680	1546	3500	3500	3500
h	(16)	–	(4)	14	4	3
Q_c	13	9	3	2	2	2
Q_R	(31)	–	(8)	27	7	5
Q				29	9	7
$\Delta\rho = 1.00$						
E	1000	700	283	1000	373	283
dT_c/dt	83	58	24	12	12	12
IC age	512	732	1811	3500	3500	3500
h	(16)	–	(4)	14	4	2
Q_c	12	9	2	2	2	2
Q_R	(31)	–	(8)	27	7	4
Q				29	9	6

6 CONCLUSIONS

(i) Compositional convection helps drive core convection and the geodynamo. For PREM densities, about half the entropy comes from gravitational energy changes caused by expulsion of oxygen from the ICB and its redistribution throughout the outer core. This gravitational energy contributes a much smaller proportion of the heat flux (15 per cent). This alleviates the problem of high heat flow found for thermal convection in paper I, however, only by a factor of approximately 2.

(ii) The higher density jumps raise the contribution of compositional convection. For the highest jump considered, Q_g and E_g are raised by a factor of 2. Compositional convection then provides two-thirds of the entropy balance rather than one half. This reduces the heat flux and heat sources somewhat, however, not by enough to change the conclusions qualitatively.

(iii) Ideal-solution theory gives accurate results for density: it predicts well the compositional expansion coefficient and, therefore, the gravitational energy change. Ideal-solution theory requires knowing only the density jump at the ICB, which is determined by seismology, the change in volume on melting and the mean atomic weight of the outer core. The exact chemical composition of the light component is, therefore, rather unimportant for calculations of the density and gravitational energy and will remain so for future calculations unless an element is introduced with drastically different chemical effects.

(iv) Ideal-solution theory does not predict the chemical potential or its gradients well. The heat of solution makes a significant contribution to the overall thermal budget and nullifies the latent heat's contribution to powering the dynamo for the larger density jump.

(v) Molecular diffusion of light material in the outer core is also a potentially significant chemical effect: its contribution to the entropy budget may be comparable with that of the magnetic field. All light constituents (S, Si, O) contribute to this entropy because they all diffuse, even though S and Si do not separate on freezing. It is tempting to think of molecular diffusion as analogous to thermal diffusion: light material diffuses down the pressure gradient and is not, therefore, available to drive convection in the same way as heat is lost by conduction down the adiabatic temperature gradient and does not drive convection. This is not quite right because molecular diffusion reduces the dynamo efficiency regardless of whether material diffuses up or down. It is better to think of the convection as stirring the core to uniform composition, while diffusion produces an imbalance that must be continually corrected.

(vi) For the PREM model, a cooling rate slower than 69 K Gyr^{-1} requires convection at the top of the core to be driven compositionally against a subadiabatic temperature gradient, as originally envisaged by Loper (1978a). Heat is convected downwards by the convection in a refrigerator-like mechanism. Heat continues to be conducted upwards along the adiabat, which is maintained by vigorous compositional convection, however, the heat emerging from the core is less than that conducted down the adiabat. A cooling rate slower than 35 K Gyr^{-1} fails to meet the entropy requirements. Either the dynamo fails or the temperature gradient falls below the adiabat and the upper part of the core becomes stably stratified and ceases to convect. The heat-flux requirements under these conditions are reduced somewhat provided the latent heat continues to be provided at the ICB, driving convection at the base of the outer core. The corresponding cooling rates for higher density jumps are given in the tables.

(vii) The cooling models predict a young inner core with an age range 0.3–1.8 Gyr, all younger than the geomagnetic field and, therefore, the age of the dynamo, in agreement with other recent calculations (Labrosse *et al.* 2001). A young inner core presents quite serious problems for explaining the presence of a magnetic field in early times because the geodynamo would have to be driven by thermal convection with no latent heat or compositional effects, which requires a large cooling rate. A proper thermal history calculation is needed to address the early evolution of such a model, however, it will be hard to maintain core temperatures below the lower-mantle liquidus in the distant past.

(viii) The heat flux across the CMB is a large fraction of the Earth's surface heat flux: at least 5 per cent and possibly 50 per cent. Radioactive heating in the core exacerbates the heat-flux problem, however, it maintains an old inner core. Lower heat fluxes require a subadiabatic temperature profile at the top of the core; such a hidden ocean (Braginsky 1999) seems quite likely in view of these calculations.

(ix) There is a consensus about core properties relevant to convection and the geodynamo: our results appear to be robust and will only change substantially if radically different chemistries or physical properties are proposed for the core. Even changing the density jump at the inner-core boundary makes little difference to the qualitative conclusions.

(x) Our favourite model is (v) in Table 5. The core heat flux is reasonably low, it retains compositional convection throughout most of Earth history, the cooling rate is low so that early temperatures are not too high and the radioactive heating could perhaps be supplied by the presence of potassium in the core. This amount of heat requires approximately 1000 ppm of potassium, a very large amount. These calculations assume constant cooling rates, which is unrealistic over the long term. Further refinement needs a proper thermal history that allows for changing cooling rates determined by mantle convection. A new study is underway (Nimmo *et al.* 2004).

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