# 8 Transport Properties

## 8.1 Planets have Transport

Thermodynamics tells you about <u>equilibrium</u>: the state (phase) that a medium prefers to have at a specified P and T. However, planets are continuously driven out of equilibrium: Heat flows from one place to another, materials flow and sometimes react chemically, electrical currents flow, etc. So it is of great importance to understand the transport properties of planet-forming materials.

## 8.2 The Nature of Microscopic Transport Properties

These properties have a far less secure theoretical framework than the thermodynamic properties. Moreover, they are often harder to measure. They are also far more susceptible to "dirt" effects (minor constituents or imperfections). On the other hand, our expectations (the desired accuracy with which we need to know the parameters) are often less. Here we wish to focus on three questions: Is the process important? How does it work at the microscopic level? How does it scale to other (unmeasured) thermodynamic conditions?

We deal much later in the course with macroscopic transport, specifically fluid flow, such as convection, but we do deal here with parameters that are input into fluid dynamics, e.g., viscosity.

# 8.3 Which Transport Processes?

Diffusion of Heat is governed by an equation of the form

$$F = -k\nabla T = -\rho C_v \kappa \nabla T \tag{8.1}$$

(Fourier's law) where F is the heat flux (energy per unit area per unit time), k is called the thermal conductivity and  $\kappa$  is called the thermal diffusivity. For constant material properties, the resulting continuity equation  $\nabla .F = -\rho C_p \partial T/\partial t$  becomes the well-known diffusion equation (assuming no internal heat sources)

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T \tag{8.2}$$

and  $\kappa$  accordingly has units of (length)<sup>2</sup>/time. The existence of a continuum equation is contingent on a short mean free path for the entity carrying heat (phonons, photons). So this equation can also describe radiative transfer <u>but only in the limit just described.</u> (In practice, this limit works fine for radiation inside planets and works poorly in atmospheres. However, it should be noted that radiative "conductivity" is highly temperature-dependent and so the diffusivity cannot be brought outside the gradient operator as has been done in the above equation. The correct equation is then  $\frac{\partial T}{\partial t} = \nabla \cdot (\kappa(T)\nabla T)$ .

By dimensional analysis, there is a characteristic <u>diffusion length</u>  $(\kappa t)^{1/2}$  which describes the distance within which a heat disturbance will modify its surroundings in an elapsed time t.

Diffusion of composition is governed by an equation which has the same underlying physical origin (a random walk):

$$J = -\rho D\nabla C \tag{8.3}$$

where J is a mass flux (mass per unit area per unit time), D is a diffusivity and C is a concentration of a diffusing species (which could even be the only species in the case of self-diffusion... e.g., as in diffusion of isotopes.) The differential equation for time evolution has the same form as for heat.

*Diffusion of Momentum* is governed by the divergence of the stress tensor. The constitutive equation for the stress tensor depends on the nature of the material and can in principle very complicated (unlike the preceding examples of diffusion). For an incompressible Newtonian fluid, it has the form:

$$\sigma_{ij} = \eta(\frac{\partial u_i}{\partial x_i} + \frac{\partial u_j}{\partial x_i}); \qquad \eta \equiv \rho v \tag{8.4}$$

where  $\sigma$  is the deviatoric stress tensor, u is the fluid flow,  $\eta$  is the dynamic viscosity (sometimes written as  $\mu$ , though this symbol is more often reserved for shear modulus) and v (nu) is the kinematic viscosity and has units of diffusivity, i.e., (length)²/time. "Deviatoric" means that the mean stress state (the pressure term) is omitted. We will not make explicit use of this formula until later in the course.

Although there exist fluid dynamical problems where a diffusion-like equation (similar to those mentioned earlier) arises, we are usually concerned with quasi-steady state applications of the viscous stress. The reason is that most problems where viscosity is of great interest (e.g. mantle convection) are also problems where steady state has been established (i.e., no net force).

Electrical Conductivity is defined by the equation

$$J = \sigma E = -\sigma \nabla V \tag{8.5}$$

where J is the current density, E is the electric field and V is the electric potential. As we shall see in due course, the electrical conductivity is most often seen in planetary problems as a "magnetic diffusivity", describing the Ohmic decay of electrical currents and associated magnetic field.

# 8.4 A Simple View of these Transport Coefficients (Motivated by the Kinetic Theory of Gases).

Recall that for a diffusive process, if the single diffusion step has length a and takes a typical time  $\tau$ , then after N steps (elapsed time N $\tau$ ), the distance gone is N<sup>1/2</sup>a. This is what is meant by a random walk. For a diffusivity D, we thus must have

$$\sqrt{Dt} = a\sqrt{N}$$
 when  $t = N\tau \Rightarrow D = a^2 / \tau = av$  (8.6)

where  $v = a/\tau$  is the velocity of the entity that is diffusing. For heat transport in an insulator or diffusion in a liquid or viscosity in a liquid, v should naturally be identified as the sound speed, and a as the distance between atoms. So we get the result that

$$\kappa \sim D \sim v \sim (10^{-8} cm)(10^{6} cm/s) \sim 10^{-2} cm^{2}/s$$
 (8.7)

This is actually correct to within an order of magnitude, for materials where the transport is done by atoms and there is no strong bonding of the atoms to particular sites. It is also roughly true for heat diffusion in <u>insulating solids</u>, where the heat is actually carried by phonons. (The mean free path a is in that case best thought of as the scattering distance for phonons. If the material were perfectly harmonic then it would have "infinite" thermal conductivity!)

Electrons are more efficient carriers of heat (or electrical current) and will dominate if they are free to move, so metals typically have higher thermal diffusivities than that given above by an order of magnitude or two.

## 8.5 Does Diffusion Matter?

In the age of the solar system, a diffusivity of  $0.01 \mathrm{cm}^2/\mathrm{sec}$  implies a possible diffusion distance of

$$\sqrt{(0.01cm^2/s).(4.5x10^9 yr).(3.15x10^7 \sec/yr)} \approx 400km$$
 (8.8)

and this is small compared to the size of most planets. So diffusion of heat in insulators is often unimportant on the planetary scale. An example of where it would matter is in small bodies (e.g., asteroids or small icy satellites or Kuiper belt objects). Even in small bodies, you need to ask whether the relevant time scale is the age of the solar system or some other time scale, e.g., the decay of a short-lived isotope such as  $^{26}\text{Al}$  (half life  $\sim$  one million years). Thus, a body larger than  $\sim$  5 or 10km, the diffusion length for 1 million years, might be expected to get very hot internally if it formed very early in the solar system.

Diffusion of atoms is less important, because the relevant diffusivity is typically even smaller, e.g.,  $10^{-4}$  cm<sup>2</sup>/sec in a liquid, much smaller still in a solid. It is almost universally true that large scale transport of atoms in a planet is accomplished by fluid dynamical processes (convection) and not by diffusion.

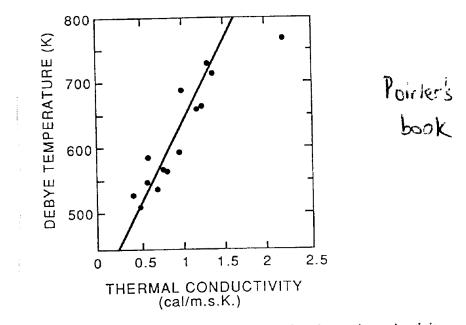
Diffusion of heat in a <u>metallic</u> core is obviously somewhat more important because of the higher thermal conductivity of a metal. It is even important in Earth's core (despite its size). But diffusion is not important in Jupiter's core (despite being a metal).

#### 8.5.1 General Comments about the Diffusion of Heat

Typically, <u>radiation</u> is not important deep within planets. There are two reasons for this: The mean free path of photons is small and the energy in the radiation field (which scales as T<sup>4</sup>) is small compared to the thermal energy in atomic motions. So atoms carry the heat, and in solids, the scattering of phonons is what matters. It has nonetheless been suggested that radiation might matter near the bottom of earth's mantle because the mean free path of the photons is substantial. This is based in large part on potentially unrealistic notions about the mineralogical "cleanliness". (Multiphase systems loaded with impurities tend not to be very transparent.) But it remains an unanswered question.

In materials with large Debye temperature, the crystal is very stiff and harmonic, so the scattering is weak and the thermal diffusion is high (see figure). The thermal conductivity

is <u>higher at high pressure</u> if the crystal is more harmonic (but recall that  $T/\theta_D$  is constant along an adiabat.)



. Correlation of Debye temperature and lattice thermal conductivity for silicates (after Horai and Simmons 1970).

Figure 8.1

In <u>metals</u>, it is still scattering by phonons that matter, but the actual carriers are more effective (i.e. move faster). In liquids, there is no profound change in how heat is carried, although the transport tends to be somewhat diminished (scattering is stronger).

# 8.5.2 General Comments about the Diffusion of Atoms

In solids, this diffusion is limited severely by the high energy involved in moving an atom, e.g., creating a vacancy. As a consequence, it is usual to find that

$$D = D_0 \exp\left[-\frac{\Delta H}{kT}\right]; \qquad \Delta H = \Delta E + p\Delta V \tag{8.9}$$

where  $\Delta H$  is an activation enthalpy for the process required to accomplish diffusion. Notice that this is now fundamentally different from heat because a physical entity (rather than merely a package of energy) has to be moved from place to place. Naturally, the expression inside the exponential is the ratio of an atomic energy to a thermal energy and you should know by now that this is usually a big number, hence this diffusion is small

even at high temperatures. Of course, there is an enormous discontinuity in diffusivity at the melting point. Note the explicit pressure dependence inside the exponential.

#### 8.5.3 General Comments about Electrical Conductivity

In a metal, there is a very simple classical theory, which goes like so: The mean velocity  $\langle v \rangle$  attained by an electron due to an electric field E is acceleration multiplied by the time  $\tau$  that the acceleration acts (before a collision), or  $\langle v \rangle = eE\tau/m$ . The current density is ne $\langle v \rangle$ . Accordingly, from  $J = \sigma E$ , one has:

$$\sigma = \frac{ne^2\tau}{m} \tag{8.10}$$

where n is the electron number density (counting only those electrons free to move) and m is the electron mass. In SI units, typical numbers for a good metal (e.g., Cu at room temperature) would be  $n \sim 10^{29}$  m<sup>-3</sup> and  $\tau \sim 10^{-14}$  sec. Together with  $e = 1.6 \times 10^{-19}$  Coulombs and  $m = 9.1 \times 10^{-31}$  kg, this gives  $\sigma \sim 10^7 \, \Omega^{-1}$ . (This is usually written S/m where S stands for Siemen, which is the same thing as inverse Ohm. Don't ask me why it was considered necessary to give the inverse of something a special name!)

The "relaxation time"  $\tau$  is related to the Fermi velocity, but depends on electron-phonon scattering.... the same process that determines thermal diffusion. So it is not surprizing that there is a fundamental relationship between thermal and electrical transport in metals called the *Wiedemann-Franz law*:

$$\frac{k}{\sigma T} = 2.45 \times 10^{-8} W.\Omega. \text{deg}^{-2}$$
 (8.11)

(where the parameters are in SI units).

Of course a semiconductor will have a much lower electrical conductivity dictated by the energy gap in the material, i.e. conductivity  $\propto \exp[-\Delta E/2kT]$ , where the factor of two in the denominator arises from fundamental statistical mechanics, according to which the product of electron density and hole density scales as  $\exp[-\Delta E/kT]$  and these densities are equal. This is presumably relevant to Jupiter (cf. chapter 4), as well as to electromagnetic sounding in terrestrial planets.

#### 8.5.4 General Comments about Viscosity

In liquids, one finds that the simple rule given above (yielding  $v\sim0.01~\text{cm}^2/\text{sec}$ ) is not a bad guide for simple liquids, e.g. water, liquid iron. Silicate liquids are not simple; they are polymers and have viscosities with substantial activation energies.

$$v = v_0 \exp\left[\frac{\Delta H}{kT}\right]; \qquad \Delta H = \Delta E + p\Delta V$$
 (8.12)

and this is like the expression for diffusion but with a positive sign in the exponent. Why? Well, high viscosity implies low creep, i.e. in a one dimensional version of the governing equation one ought to think of the equation as having the form strain rate (same thing as velocity gradient) proportional to deviatoric stress divided by viscosity.

$$\dot{e} = \frac{\sigma}{n} \tag{8.13}$$

One then realizes that conceptually, high viscosity is like low atomic diffusivity, i.e. if there is a high activation energy for allowing the material to creep then it will have an exponentially high viscosity. If the viscous flow arises from the same physical mechanism as diffusion of atoms then the product Dv (or  $D\eta$ ) will be weakly dependent on temperature (the exponential dependences will cancel). The most striking (but complicated) example of this arises when it comes to thinking about the viscosity of solids.

#### 8.5.5 The Viscosity of a Solid

A perfect crystal has a purely elastic response, meaning that strain  $\infty$  (stress)/(elastic modulus). But perfect crystals don't exist in nature, if only because there will be a finite thermal excitation of impurities (e.g. voids and dislocations). Under stress, the material may undergo irreversible strain (meaning that the strain is finite even when the stress is reduced back to zero). At fixed stress, there may (in steady state) be some finite strain rate. This is observationally true: In polycrystalline materials in the lab, one typically finds something like this:

$$\dot{e} = A\sigma^n d^{-m} \exp\left[-\frac{\Delta H}{kT}\right] \tag{8.14}$$

where d is the grain size, n and m are often (but not necessarily) integers, and A is some constant (usually insensitive to temperature and pressure but possible dependent on other things such as oxygen fugacity). If one tries to define a viscosity (stress divided by strain rate), one gets

$$\eta = A^{-1}d^m \sigma^{-(n-1)} \exp\left[\frac{\Delta H}{kT}\right]$$
(8.15)

but this is only independent of stress in the special case n=1 (the Newtonian fluid case). We can always define an effective viscosity for some flow but it's important to remember that in general the flow is non-linear (i.e., stress and therefore effective viscosity varies from place to place), so that this is a definition of convenience rather than a correct characterization of the rheology. In solids, the two most important mechanisms for creep are likely to be Nabarro-Herring (diffusion) creep, for which n=1, m=2 and dislocation creep, for which  $n\sim3$  (but may not be an integer or even constant) and m=0. To the extent that the grain size also depends on stress, it could be argued that there is never any truly Newtonian creep. Generally, non-Newtonian creep will dominate at high stress, because n>1 for that process and the mechanism that predicts the largest strain rate will tend to dominate.

In either case, one expects that the activation energy is much larger than kT. In fact, it is often found that the parameter inside the exponential is rather similar among different materials provided it is evaluated at the melting point. This makes sense if one thinks (naively) of the melting point as being high in materials where it is difficult to make voids or diffuse atoms and low when it is easy. The following table quantifies this.

Table 8.1

Material	ΔH/RT <sub>m</sub>
Silicates & oxides	25 to 30
water ice	~25
metals	15-20

(Note: There is of course no difference between using RT and kT in evaluating the RHS column, provided one remembers that the enthalpy is per mole in the first case and per atom or molecule in the second case). The following figures show (crudely) two mechanisms for creep. The first figure shows how atoms can diffuse away from a region of high stress (compression) to a region of low stress (extension) thereby allowing the block of material to continuously deform. This is possible because all materials have a finite vacancy level at finite temperature. It is a linear (i.e., Newtonian) mechanism because the process is thermally activated at all stress levels.

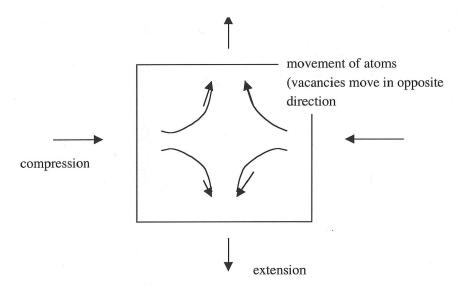


Figure 8.2

The next figure illustrates several layers of atoms. In the process of dislocation creep, a truncated layer of atoms connects to an adjacent layer, thereby shifting the dislocation (and the material) over. By a sequence of such steps there will be a net strain. Although dislocations are thermally activated, the stress required is finite and the overall process is nonlinear. (A and B indicate a line of atoms perpendicular to the plane of the figure).

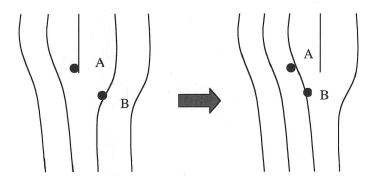


Figure 8.3

## 8.6 Implications for Planetary Materials

Let's write the effective viscosity in the form

$$\eta = \eta_0 \exp[g(\frac{T_m}{T} - 1)]$$
(8.16)

so that  $\eta_0$  is the viscosity at the melting point and g is dimensionless. Table 8.1 gives g (approximately). The ratio of  $T/T_m$  is known as homologous temperature. In some materials, we think that  $\eta_0$  does not vary much with pressure, but in general this is not known. In a polycrystalline assemblage, one must interpret  $T_m$  as the melting point of the major phase... the one that dominates in the deformation (e.g. olivine in Earth's upper mantle). So  $T_m$  is <u>not</u> the solidus! This makes sense, since the ability to form a low melting point component is usually governed by minor constituents that are not inside the olivine crystals. (Actually, this is an oversimplification; for example, the presence of water lowers the viscosity of olivine and also lowers the solidus.)

Of course,  $\eta_0$  is not independent of the stress level associated with the convection. Roughly speaking, convective stress levels are of order  $\rho g\alpha\Delta T.\delta$  where  $\Delta T$  is the temperature fluctuation driving the convection and  $\delta$  is some characteristic lengthscale associated with these motions (e.g. boundary layer thickness, <u>not</u> the depth of convection). We will discus this more in a later chapter. For Earth, this gives (3).(1000).(2 x 10<sup>-5</sup>).(500K).(10<sup>7</sup>) = 3 x 10<sup>8</sup> cgs = 300 bars (but actually 100 bars is a better mean value). For Ganymede, this gives (1).(160).(1 x 10<sup>-4</sup>). (20K). (2 x 10<sup>6</sup>) = 0.2 bars.

With this parameterization, one finds roughly the following things:

(i) In terrestrial mantles,  $g \sim 30$ ;  $T_m \sim 1950 K$  and  $\eta_0 \sim 10^{18}$  Poise at a stress level of around 100 bars. This means that  $\eta \sim 10^{21}$  Poise ( $10^{20}$  Pa.s) at the uppermost mantle condition of  $T \sim 1600 K$ . Actually, observations suggest a value that is

about one order of magnitude lower for Earth.. This is believed to be due to "water" (dissolved hydrogen in the olivine crystals).

- (ii) In water ice, g~25 again;  $T_m \sim 273$ K and  $\eta_0 \sim 10^{15}$  Poise at  $\sigma \sim 1$  bar.
- (iii) It is important to remember that because viscosities can vary over many orders of magnitude, it is easy to get (or assume) the "wrong" value by an order of magnitude or more.

#### 8.7 Newtonian vs. Non-Newtonian?

In general, we expect the strain rates of different mechanisms to be additive, i.e.,

$$\dot{e}_{total} = \dot{e}_{diffusion} + \dot{e}_{dislocation} \tag{8.17}$$

with the result that the dominant mechanism will change as stress changes.

In terrestrial mantles, the stress level at which diffusion (Newtonian creep) begins to dominate depends on grain size and mineral phase. Most probably it is around 10 bars. In the lower mantle, Newtonian creep may be more important but this is not well known. In ice, the transition is probably around a bar or a little less. It follows that most planetary bodies are non-Newtonian in most places. Remember also that since grain size depends on stress, even a Newtonian mechanism can yield a non-Newtonian response.

## 8.8 Viscoelastic Rheologies

Solid planets have outer regions that are so cold (e.g., temperature less than half the melting point) that their response is not viscous even on geologic timescales. These regions may respond elastically for modest stresses but then fail at stresses exceeding a few hundred bars to a few kilobars (rock) or a few tens of bars or less (ice). In some cases, it is necessary to consider a more complete rheological description, one where the material has both viscous and elastic properties depending on the timescale on which it is stressed. We will return to this when we talk about lithospheres and when we consider how satellites respond to tides (Ch 17).

#### 8.9 Dependence on Pressure

If you took the scaling law literally, lines of constant homologous temperature  $T/T_m$  (i.e., parallel to the melting curve) would be isoviscous. Since the melting curve is generally steeper than the adiabat, viscosity should increase with depth in planets (after you get into the adiabatic region). This is widely thought to be true, though subject to the complications of phase transitions. In reality, the argument based on homologous temperature is only a qualitative guide and should not be used quantitatively... if you look back at the more fundamental equation, you see that what really matters is the activation volume in the  $\Delta H$  that governs the rheology. Nonetheless, activation volumes are often qualitatively like the volumes to create melting, e.g., the activation volume for Ice I is negative and the melting point for Ice I decreases with pressure. Most activation volumes are positive in materials with positive melting point gradients.

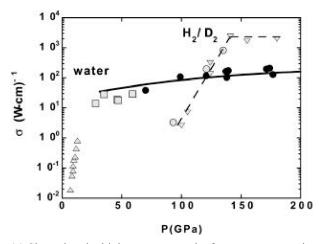
#### 8.10 Viscosity of Partial Melts

When a polymineralic material undergoes partial melting, several factors influence the viscosity of the medium as a whole. For example, the melt may lower the solid-solid contact area of the grains, thus increasing the deviatoric stress (at the scale of individual grains) and increasing the strain rate. In other words, the viscosity will go down. In some cases, this effect is large; an order of magnitude even at modest melt fraction. In general, the effect is complicated, however. An example of an opposite effect: The melt may be the favored location for molecules that weaken the crystal (e.g., water in olivine). In this circumstance it is even conceivable for the viscosity to go up. As an additional complication, the melt may migrate (under the action of gravity, given it has a different density from the solid). We will discuss this in a later chapter.

It has sometimes been argued that Earth's asthenosphere (the weak upper most part of the mantle) owes its existence to partial melt, but it might in part be the weakening of olivine arising from water molecules within the crystals.

#### Ch. 8 Problems

- 8.1) In hydrogen planets more massive than Jupiter, the radius R decreases with increasing mass M,  $R \propto M^{-1/3}$ . At the same time, the thermal diffusivity  $\kappa$  (and other diffusivities) might be expected to change in accordance to the scaling discussed in this chapter, i.e., particle spacing times sound speed. What does this suggest about the dependence of characteristic diffusion time  $R^2/\kappa$  as a function of mass (all the way up to the masses of white dwarfs ~1000 Jupiter masses).
  - Solution:  $\kappa \propto v.a \propto (K/\rho)^{1/2} \rho^{-1/3} \propto \rho^0$  because  $K \propto \rho^{5/3}$  in that limit. So the only effect on  $R^2/\kappa$  is in R. This can be large effect when one gets up to white dwarf masses (objects the radius of Earth). Even then, it would seem that diffusion times will be longer than the age of the universe unless  $\kappa$  is substantially larger than this scaling suggests(i.e., >> 0.1 cm²/sec.) The shortcoming of this argument is that it does not explicitly address the scaling for heat conduction by electrons in a metal. This can be large if the body is cold enough; and this depends in turn on the ratio of actual to Debye temperature. To appreciate this effect, we would have to analyze the thermal structure of the body.
- 8.2) Shown here are the Livermore shock wave experimental results for the electrical conductivity of H<sub>2</sub>O and H<sub>2</sub>, as a function of pressure (but temperature also changes of course). Under the highest pressure conditions of these experiments, the temperature is several thousand degrees. The units of conductivity are (ohm.cm)<sup>-1</sup>.



- (a) Show that the high pressure results for water are consistent with the formula derived in this chapter, provided it is assumed that the charge carriers are protons, there is about one free proton per water molecule, and the free protons go about one intermolecular spacing before colliding. You can assume the protons have a thermal velocity, with T=5000K. The water density is about 2 g/cm³. You're only looking for approximate consistency, not exact reproduction of the observed value.
- (b) Try to do the same thing for the hydrogen results, but here the question becomes: What fraction of the electrons are "free"? To get the relaxation time, you should assume that the electrons move at a Fermi velocity  $v_F$ . and scatter after one intermolecular spacing. (Fermi energy can be written as  $mv_F^2/2$ , where m is the electron mass.) Hydrogen density  $\sim 1 \text{g/cm}^3$ . (The fact that some experimental work is on  $D_2$  is irrelevant because electrons are the current carriers, but when I say hydrogen density, I mean  $H_2$  of course).

*Important*: You can easily get into trouble with units in this problem (as is so often the case in E & M.) For historical reasons, conductivities are often given in non-standard units, and  $(ohm.cm)^{-1}$  is not an SI unit, nor is it esu or emu units! To calculate consistently in SI units, use e (charge of electron or proton) = 1.6 x  $10^{-19}$  Coulombs, n is per cubic meter, m is in kilograms  $(1.6 \times 10^{-27} \text{ kg for a proton})$  and the answer will be in  $(ohm.meter)^{-1}$ .