ENTROPY AND THE SOLID STATE

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Entropy is discussed from the viewpoints of classical thermodynamics and statistical mechanics.

To better understand the effect of increasing entropy on the cursed creation, the effect of entropy on the solid state is discussed. Crystalline solids are considered to be structurally ordered. Such a concept is far from the truth. Crystalline solids are actually structurally disordered. There are atomic imperfections in the lattice structure and these imperfections, such as vacant lattice sites, are thermodynamically stable because the entropy of the solid is increased by their presence.

The principle of increasing entropy is considered to be opposed to the theory of evolution and certain aspects of the ruin-reconstruction theory.

Introduction

The thermodynamic quantity of entropy plays a role as important as that of energy in every field of physics, chemistry, and technology but is generally not very well understood. The effect of entropy on solids, particularly metals, has been investigated by many scientists.

To give a better understanding of entropy, this article is a discussion and review of the disordering effect of entropy on the structure of crystalline solids. It is well to keep in mind that this tendency toward disorder and randomness is universal because of the principle of entropy increase.

Entropy can be considered from two standpoints. First, in classical thermodynamics entropy is described in a rather abstract manner as a thermodynamic variable of the system under consideration; secondly, in statistical mechanics it is defined as a measure of the number of ways in which the elementary particles (for instance atoms or molecules) may be arranged in the system under the given circumstances.[1] The latter method applies to the solid state.

Entropy in Classical Thermodynamics

The concept of entropy originated in classical thermodynamics under conditions where heat can be converted into work.[1] The quantity of heat $\int_1^2 dQ$ necessary to bring a system from state 1 to state 2 is not uniquely defined since it depends on the path followed from 1 to 2.

However, the thermodynamic quantity $\int_1^2 \frac{dQ}{T}$, where T is the absolute temperature, has a value which is independent of the path followed. This is only true if the path is reversible and the integration is carried out so that each quantity of heat is divided by the temperature at which it is introduced.[1] This quantity calculated from a temperature of absolute zero is called the entropy (S) of the system

$$S = \int_0^T \frac{dQ_{rev}}{T} \qquad (1)$$

Some systems, such as solid solutions, have a finite value of entropy even at absolute zero and S in equation 1 must be replaced by $S - S_0$. The measurement of the entropy of a system in classical thermodynamics depends on the measurement of quantities of heat. Entropy is the central concept in classical thermodynamics.[1] Considering the second law of thermodynamics, the entropy of an isolated system tends to a maximum; therefore this quantity is a criterion for the direction in which processes can take place.

This is the principle of the increase in entropy. Although it refers to an isolated system, it is nevertheless of extremely general application because all materials that are in any way affected by a process may be included within an isolated system.[2]

Entropy in Statistical Mechanics

Classical thermodynamics is concerned only with macroscopic systems, and such systems can be described by temperature, pressure, volume, chemical composition, etc. However, classical thermodynamics is not concerned with what happens on an atomic level.

This can be illustrated as follows. If the energy content of a particular system is known, then each of the molecules in the system will not necessarily have the same energy (total energy of system divided by the total number of molecules). Some molecules will have more or less energy than this average energy per molecule, but taken as an entirety all of the molecules will have an energy corresponding to the energy of the system. If the temperature of the system is raised from T_1 to T_2, thermodynamically, this is considered a single event. On the atomic level an immense number of collisions of the molecules occurs, and this change is considered an average value of very many events.[3]

Thermodynamics can be applied to the atomic level if the methods of statistical mechanics are utilized. When dealing with such a large number

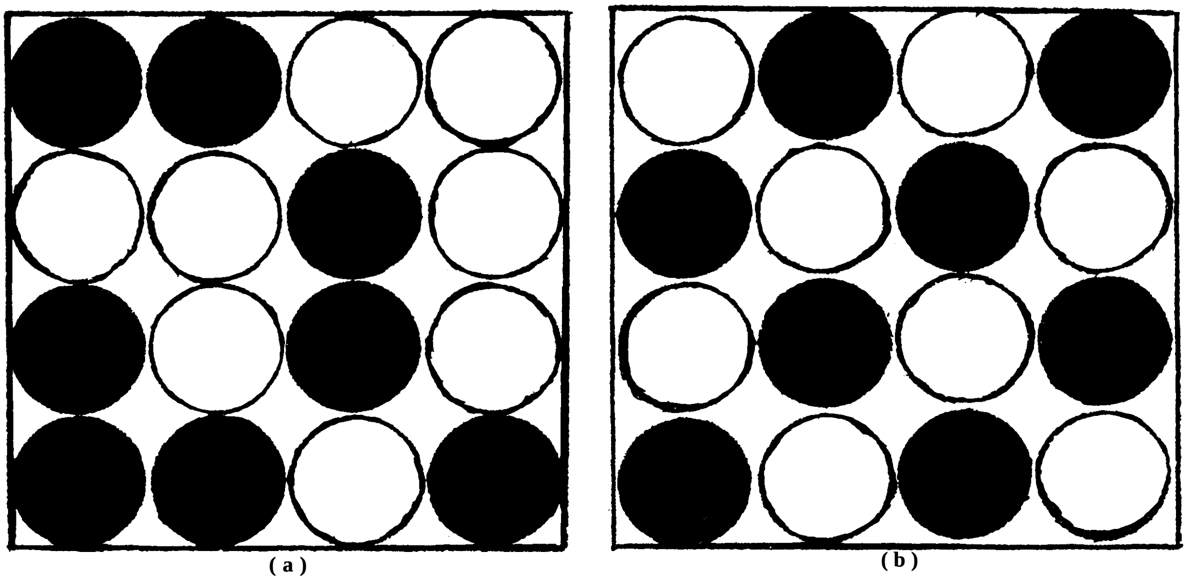

Figure 1. Some possible arrangements of balls in a box.

of molecules the specification of the state of each separate particle is impossible, and it is necessary to resort to statistical methods.

Also it should be realized that a thermodynamic state is comprised of many states on the atomic scale, or a thermodynamic state can be realized in many ways. These possibilities of realization are called micro-states.[1] Let the number of micro-states be denoted by w, then the statistical definition of entropy (S) is

$$S = k \ln w \qquad (2)$$

where k is Boltzmann's constant, and

$$k = \frac{R}{N_o} \qquad (3)$$

where R is the gas constant per mole, and N_0 is Avogadro's number.

Entropy tends to a maximum, and this means according to equation (2) a tendency towards the most probable state, According to this statistical interpretation of entropy the second law does not hold entirely rigidly.[1] It is not absolutely certain, but only highly probable, that the entropy will increase in each process spontaneously taking place in an isolated system.

A logical question to ask is, what is the most probable state? The state which can be described by the largest number of micro-states will be the most probable since it has the greatest possibility of appearance. When considering the internal configuration of a system there are really only two different states, ordered and disordered.

Since entropy is determined a different way in statistical mechanics than in classical thermodynamics (counting micro-states vs. measuring quantities of heat) it would be well to ask the question, how close do the results calculated by each method check? Fast[1] states that "one of the finest achievements of physics and chemistry is that these two paths generally lead to the same result, while divergences which appear can be explained by the theory in a completely satisfactory manner and even serve to endorse it."

The concept of entropy has become as fundamental as the energy concept. Emden[4] writes,

> As a student, I read with advantage a small book by F. Walk entitled ***The Mistress of the World and Her Shadow.*** These meant energy and entropy. In the course of advancing knowledge the two seem to me to have exchanged places. In the huge manufactory of natural processes, the principle of entropy occupies the position of manager, for it dictates the manner and method of the whole business, whilst the principle of energy does the bookkeeping, balancing credits and debits.

Entropy and Probability

To illustrate the relationship of entropy and probability a simple example will be discussed.[5] The aim is to deduce the macroscopic properties of a system as statistical resultants of the properties of its particles,

A man is blindfolded and has to pack 16 equalized balls in a flat, square box; eight of the balls are white and eight are black. He is able to arrange the balls in a square pattern in the box but will have no control over the distribution of the colors. The kind of arrangement that might result is shown in Figure 1 (a) when the distribution is random or disordered. An ordered distribution as shown in Figure 1 (b) may turn up, but is very unlikely.

There are approximately 13,000 different ways of arranging the balls in the box. This is calculated as follows:[1] If only the white balls are numbered, then each of the N arrangements would be realizable in 8! different ways, because eight unnumbered white balls can be distributed over eight positions in only one way, while eight numbered balls can be distributed in 8! distinguishable ways. The same reasoning applies to the black balls, and the number of possible arrangements would be multiplied by 8!, Considering 16 possible positions for the balls then N X 8! x 8! = 16!, and N = 13,000 (approximately).

(Note: 8! is read the "factorial of 8," and means the product of 8 and all the lower integers, including 1; i.e., 8 X 7 X 6 X 5 X 4 X 3 X 2 X 1.)

Therefore the chance of the distribution in Figure 1 (b) appearing is only about 1 in 13,000. The improbability of this particular arrangement is not due to the ordered distribution of the colors, but to the fact that this is only one of many possible distributions all with the same probability of appearance. The particular arrangement shown in Figure 1 (a) is equally improbable.

The essential difference between 1 (a) and 1 (b) is that 1 (a) is in a large class of distributions all of which are disordered. Almost all of the 13,000 distributions fall into this category so that the chance of some disordered distribution appearing is practically unity. The arrangement in 1 (b) is ordered, and it is unique in this respect. Thus the chance of some ordered distribution appearing is very small.

In any rearrangement of the balls in the box the "system" remains the same, only the internal configuration changes. Any natural rearrangement that may occur will normally be to a disordered state, because of the high number of disordered states as compared to the ordered states.

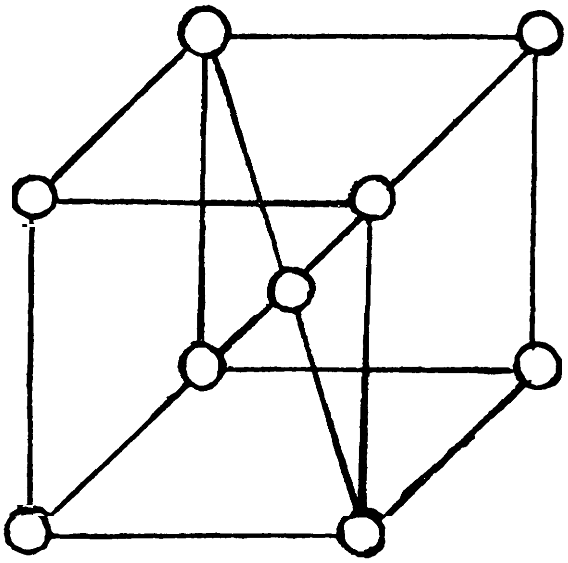

Figure 2. (a) Body-centered cubic

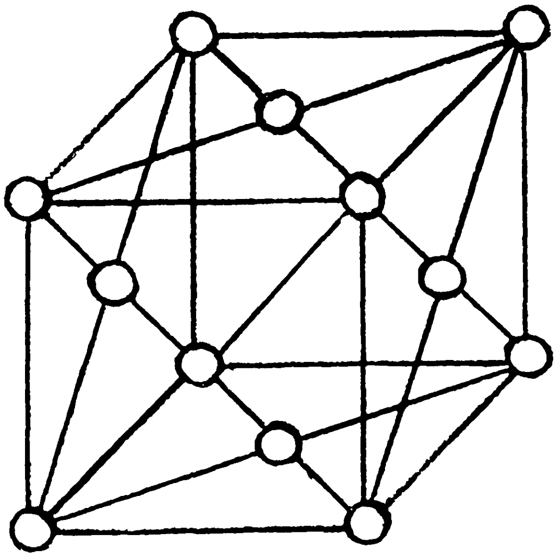

Figure 2. (b) Face-centered cubic

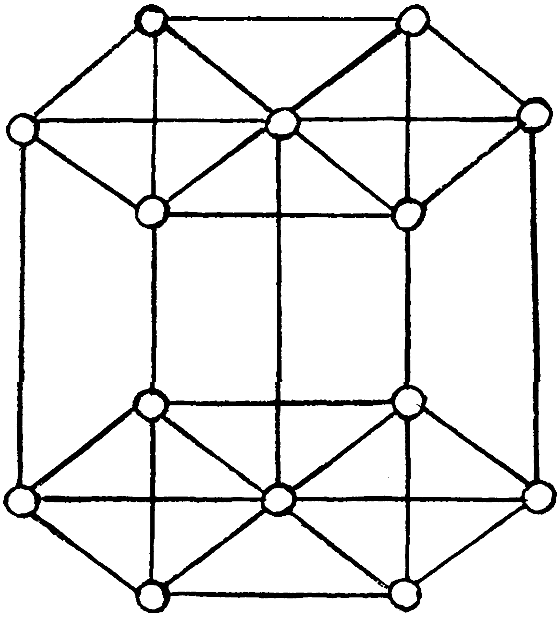

Figure 2. (c) Simple hexagonal

It should be realized from this discussion that many different arrangements of atoms in a system may give the same total system energy content. A given temperature, pressure, volume, etc. does not necessarily mean the same exact atomic arrangement every time this temperature, pressure, volume, etc. are attained. Many different atomic configurations are possible within a system at a constant temperature, pressure, volume, etc. This is particularly true of the solid state when considering the number of different ways the atoms and vacancies can be arranged on the various lattice sites.

Considering again equation (2), if according to the second law of thermodynamics, S increases in any spontaneous process, then w increases; which means the arrangement of the particles in an isolated system goes toward a more probable distribution. Since the number of micro-states (w) is greater for the disordered arrangements (more possible disordered arrangements), the system goes to a more disordered state. Therefore it can be seen when considering configuration entropy, it is a measure of the disorder in a system, and the system tends to go to a more disordered state since there is an entropy increase.

The Effect of Entropy on the Solid State

Considering crystalline solids, their atoms or molecules are arranged in a regular pattern with a definite periodic repeat of a basic unit cell.[6] There are several types of basic unit cells.

Three types of unit cells are shown in Figure 2; (a) is body-centered cubic, (b) is face-centered cubic, and (c) is simple hexagonal. The white spheres represent atoms and the lines between the spheres simply help to visualize the basic unit structure. Actually the spheres should be glued together for, as in the case of metals, the outer electron clouds of the atoms overlap and the spheres are "touching."

The resultant crystal structure is imagined by stacking in three dimensions these unit cells around and on each other. This symmetrical arrangement is grossly misleading for it implies a perfect static pattern whereas the crystalline state is *neither static nor perfect.*[6]

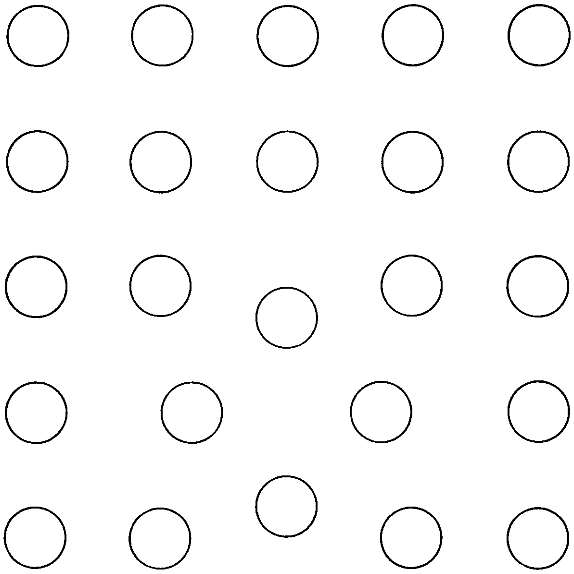

Figure 3. Illustration of a vacant site causing nearest neighbor lattice distortion.

Disorder in solids results from vibration of the atoms, presence of impurities, and presence of structural defects. For this discussion, only structural defects such as vacant lattice sites and dislocations are considered. Vacant lattice sites are classified as point defects and are illustrated in Figure 3. The atomic distances around the vacant site are distorted because of the missing atom and lattice strain is present for some distance away from the vacancy.[7]

Dislocations are line defects, and a very simple representation of a dislocation is shown in Figure 4. This is an edge dislocation and may be considered in the simplest sense a missing row of atoms in part of the crystal lattice, or as an extra row of atoms in the other part of the crystal lattice that is shown.

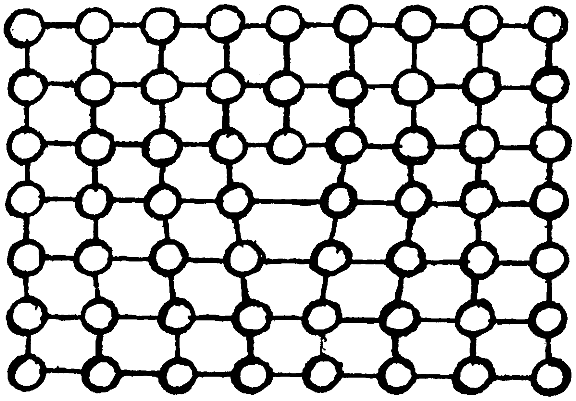

Figure 4. Representation of an edge dislocation.

The question may be asked: why are these imperfections present in solids? Their presence causes disorder in the crystalline lattice, and disordered states are more probable statistically. Thus the entropy of the solid is increased by having imperfections present, since the solid tends toward the most probable state.

The same argument as developed with the 16 colored balls can be applied to crystals containing 10^{20} atoms or more, and the only difference is to increase enormously the number of distributions of the disordered kind, but not of the ordered, so that the chance of finding a crystal in a disordered state becomes almost certain.[5] From equation (2) any state that is more probable statistically will cause an increase in entropy, and this is the factor that inclines the system towards disordered states. Therefore the second law of thermodynamics is satisfied.

The stability of crystalline disorder is illustrated as follows:[8] Consider an elemental crystal containing vacancies. There are N atoms arranged on N atom sites in the crystal. The free energy of the perfect crystal is G_p. Remove n atoms from the crystal and place them on the surface forming n vacant sites. Each of these vacancies has an enthalpy of formation ΔH_v and a vibrational entropy ΔS_v resulting from the disturbance of the nearest neighbor atoms in the lattice.

There is a configurational entropy change associated with the formation of n vacancies given by

$$\Delta S_c = S_n - S_p = k\ln w - k\ln w' = k\ln\left(\frac{w}{w'}\right)$$

where S_n is the entropy of the crystal with n vacancies, S_p is the entropy of the perfect crystal. The number of possible micro-states for the crystal with vacancies is w, and w' is the number of possible micro-states for the perfect crystal. Since w' = 1 for the perfect crystal, and there are n vacancies and N atoms arranged among (N + n) sites, then

$$\Delta S_c = k\ln w = k\ln\left[\frac{(N+n)!}{N!n!}\right].$$

Using Stirling's approximation

$$\Delta S_c = -k\left[N\ln\left(\frac{N}{N+n}\right)+n\ln\left(\frac{n}{N+n}\right)\right]$$

and

$$\Delta G = G_n - G_p = n\Delta H - T(\Delta S_c + n\Delta S_v)$$

where G_n is the free energy of the crystal with n vacancies, G_p is the free energy of the perfect crystal, and $\Delta G = \Delta H - T\Delta S$.

Substituting

$$G - G_p = n\Delta H_v + kT\left[N\ln\left(\frac{N}{N+n}\right)+n\ln\left(\frac{n}{N+n}\right)\right] - nT\Delta S_v \quad (4)$$

Separating equation (4)

$$G - G_p = n(\Delta H_v - T\Delta S_v) + kT\left[N\ln\left(\frac{N}{N+n}\right)+n\ln\left(\frac{n}{N+n}\right)\right] \quad (5)$$

Figure 5 is a plot of $n(\Delta H_v - T\Delta S_v)$, ΔS_c and G as a function of n. The entropy contribution, ΔS_c, is always negative. As can be seen, G is a function of n, From Figure 5, G = f(n) is simply the algebraic addition of $n(\Delta H_v - T\Delta S)$ and $kT\left[N\ln\left(\frac{N}{N+n}\right)+n\ln\left(\frac{n}{N+n}\right)\right]$.

Notice that the introduction of vacancies lowers the free energy of the crystal until an equilibrium concentration is reached, after which G increases. Therefore, it is seen that a certain number of vacancies are thermodynamically stable in crystalline solids (minimum free energy is at a point where there are a definite number of vacancies present in the solid). As an example, using equation 4 in a somewhat simpler form, the equilibrium amount of vacancies at a given temperature can be calculated. Considering copper at 1000° K for a cubic centimeter of crystal (5×10^{22} lattice sites) there should be about 10^{16} vacancies.[8]

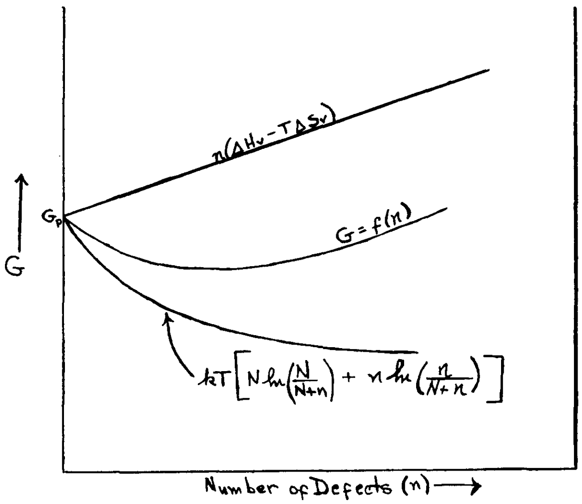

Figure 5. Free energy of a crystal as a function of defect concentration.

Dislocations are thermodynamically unstable. A simple calculating shows that the entropy term for a dislocation is small, Therefore the free energy is minimized only if all of the dislocations are removed from the crystal. However the presence of other lattice defects and their action in crystals can cause the generation of dislocations.

Also, an imperfect solid crystal can grow by a dislocation mechanism easily from the liquid state, whereas the growth of a perfect crystal from the liquid is extremely difficult, if not impossible. Even if dislocations are considered thermodynamically unstable they always have been found in solid crystals,[9] and the mechanisms of dislocation generation generally depend on other existing lattice defects.

Solids, particularly those that are crystalline, are often looked upon as having a regular structure. This is **not true,** since imperfections in the lattice of the solid cause disordering of the structure. This causes an entropy increase in the solid, making it more stable thermodynamically. This is also the reason it is impossible to obtain materials that are absolutely pure.

The same line of reasoning could be used when introducing foreign atoms into a perfect crystal as when introducing vacancies. Besides increasing the entropy of the crystal by the number of possible ways the foreign atoms can be statistically arranged, the size difference of the foreign atom causes lattice strain within the crystal which also disorders the parent lattice.

If a perfectly pure crystal could be made, the first time it touched a foreign substance, it would tend to absorb and dissolve impurity atoms. The only way a perfectly pure substance could be produced and maintained would be in a perfect vacuum, touching nothing.

It should be realized that imperfections in solids are of more than minor importance, since they actually control many of the properties of the solids. Such phenomena in metals as elastic and plastic deformation, diffusion, precipitation hardening, radiation damage, etc. can be explained by the presence of various lattice imperfections, Then, to explain many observed effects in solids, it is necessary to assume lattice disorder rather than lattice perfection.

Again, it needs to be stressed that *crystalline solids are disordered,* since many people—including some scientists—have an idea that crystals have highly ordered, regularly arranged atomic structures; thus violating the second law of thermodynamics. Such a concept is far from the truth. Crystalline solids are more ordered than gases and liquids, but they are interlaced with structural defects that destroy lattice regularity.

The Entropy Principle as a Universal Law

This very simplified discussion of the effect of entropy on the solid state can be applied to other natural systems to illustrate the stability of disorder and randomness.

Dr. H. M. Morris[10] has suggested that the principle entropy increase is a direct result of the curse God placed on the creation as a result of Adam's sin (Genesis 3:17-19). The creation process would be of course directly opposite to the entropy principle of present scientific processes. In looking over His newly-finished creation the Lord saw that it was very good (Genesis 1:31).

If the perfect holy God created; then the creation would be perfect. Here would be perfection in nature, perfection in the universe, and as for the solid state, perfect crystals. However, today we find very little, if any, perfection in nature, and this change from order to disorder must have occurred by divine edict later than Genesis 1:31. He spoke all nature into being, and then cursed His perfect creation because of man's sin.

Thus the perfectly ordered crystalline materials that God created have degenerated into atomically disordered materials because of the operation of the second law of thermodynamics. The crystalline lattices in solids no longer exhibit order but are filled with defects that interrupt order and cause disorder.

Evolution is statistically highly improbable if not impossible. From the statistical approach of considering entropy increase, an occasional process that results in a more ordered, more complex product would be possible. However, millions and billions of years of constant violations of the second law of thermodynamics are impossible if this law is valid. Every time a simpler organism becomes more ordered and more complex, the statistically improbable event occurs. And such events are *highly* improbable. The second law of thermodynamics has not been proven wrong in any experiments conducted to verify it.

Creation requires a Creator, and the Creator controls His creation and the principles that govern it. Evolution does not require a creator, and depends only on chance and natural selection (both are statistical processes). Also all laws of science now operating would have always been operating, and evolution is supposed to operate under present scientific processes.

However present processes do not favor any type of evolutionary development. The question of logic may enter the argument; what is more logical; a Creator as revealed in His Word doing what He said He did, or a process of statistical chance always occurring in such a way so as to favor the statistically improbable and violate a basic scientific law? Romans 1:19-22 has the answer to those who choose to believe the latter.

The Ruin-Reconstruction Theory

The ruin-reconstruction theory in the Scofield Reference Bible (page 3, footnote 3; page 4, footnote 3) brings up an interesting point concerning entropy. The "first" creation had undergone divine judgment, and the earth and all of the remains would then have a high entropy content because of the supposed disorder and death.

Then God places another creation on this one, and this new creation would have a low entropy content because it was perfect at the end of this "new" creation period. The two systems could not stay in equilibrium with each other without the "latter" creation increasing in entropy.

Here is a paradox, an old disordered system in intimate contact with an ordered system. What happened when the newly-created animals and man breathed in dust or ate anything from the disordered system? The intake in any way of any disordered material would destroy the ordered perfection of the newly-created creatures.

Therefore, God would not have had to curse His new creation, it was already becoming disordered immediately after creation. Did God then lie to us about the necessity of the curse? The disordered system in contact with the new creation would have eventually disordered it.

Would the seeds possibly left over from the previous judgment, being disordered (higher entropy content), yield disordered or perfect plants? If the ground was already cursed from the previous judgment, why did God have to curse it again? Was He deceiving us? One could ask many questions like this.

Possible explanations could be given, such as God perfecting the earth before the "second" creation by ordering the rocks, dirt, fossils, etc. before placing the "new" creation on this. However the Scriptures give no indication of this. Any time Christians deviate from the Word of God to try to justify the Word in the light of modern science, their theories demand explanation after explanation and never solve the problem.

Why not believe what God said? The Scriptures plainly state the heavens and earth were created in six days, and because of Adam's sin this creation was cursed, and the principle of entropy increase became operative.

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BOOK REVIEW

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Mechanism and Vitalisrn: Philosophical Aspects of Biology by Rainer Schubert-Soldern and edited by Philip G. Fothergill, F. R. S. E., University of Notre Dame Press, Notre Dame, Indiana, 1962, 244 pp., $6.50.

Introduction

The purely mechanistic philosophy of life is so prevalent, not only in scholarly works but in productions written for children in the public schools, that study of the matter from the point of view of pure science seems wise. Rainer Schubert-Soldern, Professor at the Vienna Institute for Experimental Zoology, Anatomy and Physiology, approaches the problem as a physiologist and a mechanist. This review will present the position that his mechanistic approach resulted in vitalistic conclusions.

According to the author, the purpose for writing the book "is to conduct a scientific enquiry into the nature of life." (p. xv) He further asserts that the **crux of the problem** lies in whether the phenomena of life can be explained entirely in terms of chemistry and physics. To solve this problem Schubert-Soldern states, "Objective, observable facts alone can be the basis of any scientific theory of life," (p. xviii) He then sets up two criteria upon which to base conclusions, namely:

1. "Every statement we are entitled to must be based on sense experience."
2. "Dualistic views are not admissible unless they can be proved lineally upon this one level of knowledge." (p. 10)

Biochemistry: Mechanism and Vitalism

Since both living and non-living materials are composed of elements, Schubert-Soldern states that a study of inanimate and animate matter must be based on a comparison of the chemistry of the two classes of substances. Also, the characteristics of life will be found in any qualities which distinguish animate from inanimate substances.

Defining a **vitalist** as one who considers life as something which exists in and through matter and a **mechanist** as one who regards matter itself alive, the author begins his study of these two ancient philosophies by examining elements and compounds. This is the mechanistic approach and could be expected to result in mechanistic conclusions.

Schubert-Soldern expects to arrive at one of three theoretical possibilities, namely:

1. "A merogenous system consisting of parts, which is nothing but the sum of the laws operating in the parts and which rests upon a merogenous principle.
2. "A halogenous system, a whole which is nevertheless based upon a merogenous principle. The forces inherent in the parts generate a whole; but the whole is an agglomeration of particles and becomes whole, halogenous, through the operation of particles.
3. "A halogenous system, a whole which is constituted by a halogenous principle. Here the principle is a whole which produces a complete entity from its parts; by themselves, however, the parts could never produce a whole." (pp. 20, 21).

Using the principle that all things are described in terms of the laws governing them the author states that an investigation of life must begin with the basics, or electrons, and the laws governing them. After noting that the same laws governing the neutralization of electrons forming an atom also govern the formation of molecules from atoms, the author observed that elec-