ON THE THERMODYNAMIC EQUILIBRIUM IN THE UNIVERSE

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With the establishing of the second law it was realized that all the actual processes on earth are irreversible and unidirectional in the sense of this law. The same is true for the solar system as the sun is radiating energy continually in an irreversible way. Because of the same phenomenon being connected with all the stars it seemed to be justified to extrapolate and to consider the actual universe as a unique one, being far from a state of thermodynamic equilibrium and running down irrevocably toward a state of highest entropy. This seems to be the general opinion up to date.[1]

However, several attempts have been made to deduce special conclusions from the postulate of a thermodynamic equilibrium in the universe. (This postulate we denote by P.)

The relativity relation between mass and energy, phenomena connected with the evolution of the stars, and the existence of the penetrating radiation, had made it probable that mass can be converted into radiant energy. Stern,[2] therefore, applied (P) to the following reaction.

$$\text{Radiation} \rightleftarrows \text{Particles (of mass } m) \qquad (1)$$

He found that the radiation is favored by a factor $e^{mc^2/KT}$ which is of the order $e^{10^{13}/T}$ for $m = m_H$. This would mean that for possible temperatures of the universe practically all the matter would disappear into radiation. Lenz[3] then considered the reaction from another point of view, taking into account the change of volume of an Einstein universe connected with the disappearence of mass into radiation. His result is that the amounts of radiation and matter are equal. But Tolman[4] afterwards showed that Lenz's considerations cannot be justified on a more general basis. He on the contrary shows, for the case considered by Lenz, that Sterns conclusions are still approximately valid, a result which is in clashing contradiction with the actual facts.

Some other considerations related to our problem were given by R. C. Tolman[5] in a paper treating the following reaction

$$4H \rightleftarrows He$$

He showed that the ratio of the concentrations of He and H in equilibrium in the universe should then be of the order $e^{\Delta m \cdot c^2/KT}$. With $m = 0.008 \times m_H$ this is approximately $e^{10^{10}/T}$. This again seems to be in strict contradiction with the ratio of the concentrations of the two elements in the stars.

However, reasons might be advanced for the view that the conditions in the stars can hardly be considered as appropriate for testing the theory. In any case a review of the results obtained so far fails to reveal any positive confirmation of the postulate (P).

It appears however to the writer, that the basis of the problem needs to be extended if it is to conform with the actual conditions. Indeed an equilibrium involving many products all of which can react with each other cannot be treated by considering the equilibrium in regard to an insufficient number of partial reactions only. Now one of the most conspicuous features of the universe lies in the phenomenon of the agglomerations of mass, which shows regularities as perfect as might be expected if postulate (P) were realized. The surprising uniformity in the characteristics of stars of the same class (age) is a fact so fundamental that we propose to treat the equilibrium between stars and free atoms in the universe precisely as we treat that between different kinds of molecules, as for instance S, S_2, S_6, S_8 in the case of sulphur vapor. There are also agglomerations of another kind like gaseous nebulae, star clusters and galactic systems, which, in the analogue of the sulphur vapor would have to be compared with swarms of molecules. Since, however, they are not units of a definite kind as are molecules they show less uniformity. Their general characteristics, however, are sufficiently alike to justify the view that they might be considered as swarms in the strict meaning of statistical mechanics. The postulate (P) then has to be applied simultaneously to the following chain of reactions.*

$$\begin{gathered}\text{Radiation} \rightleftarrows \text{Protons Electrons} \rightleftarrows \text{Higher nuclei} \rightleftarrows \\ \rightleftarrows \text{Dust Particles of all sizes} \rightleftarrows \text{Gaseous Nebulae} \rightleftarrows \\ \rightleftarrows \text{Stars} \rightleftarrows \text{Swarms of stars (Galactic systems)}\end{gathered} \quad (1)$$

Let us first consider the following process

$$\nu \text{ atoms} \rightleftarrows \text{one star} \quad (2)$$

A rough preliminary estimate as to the equilibrium concentration may be obtained in the following way. Let us consider stars of a certain size only and use the data known for the sun

$$M = 2 \times 10^{33} \text{ gr.} \quad R = 7 \times 10^{10} \text{ cm.} \quad f = 6.68 \times 10^{-8}$$

we obtain a gravitational potential energy approximately equal to

$$\Omega = -f\frac{M^2}{R} = -3.81 \times 10^{48} \text{ ergs.}$$

Assuming an average atomic weight of 50 for the particles constituting the star we obtain for the number of atoms in the star $\nu = 2.1 \times 10^{55}$.

This means that the average potential energy of one atom in the star amounts to

$$\Omega/\nu = 1.8 \times 10^{-7} \text{ ergs.}$$

The average kinetic energy of approximately $kT = 1.37\ 10^{-16}\ T$ ergs will actually always be small compared with Ω/ν (even for $T = 10^7$ degrees). As a first approximation we, therefore, may consider all the degrees of freedom in our star frozen in. Then we make use of the statistical treatment of a chemical reaction in the form given by Ehrenfest and Trkal.[6] ν_i of the molecules A_i are entering the reaction

$$\sum \nu_i A_i = 0.$$

The equilibrium constant is expressed as follows (with concentrations in numbers of molecules per cm.[3])

$$lnK_c = -\frac{1}{KT}\sum \nu_i \epsilon_i + \sum \nu_i \frac{f_i}{2} lnKT + \sum \nu_i lna_i. \qquad (3)$$

ϵ_i is the potential energy of a molecule of the ith kind. f_i represents the number of fully excited degrees of freedom in this molecule. a_i is the chemical constant with respect to the molecule i. For monoatomic molecules it would be $a_i = (2\pi m_i)^{3/2}/h^3$. It can easily be seen that in our case only the first term on the right side of (3) is of importance. We have A_1 = atom, A_2 = star, $\nu_1 = \nu$, $\nu_2 = -1$. $\epsilon_1 = 0$, $\epsilon_2 = \Omega$. Therefore,

$$-\frac{1}{KT}\sum \nu_i \epsilon_i = \frac{\Omega}{KT} = -2.8 \times 10^{64}/T.$$

The second and the third term of (3) are of the same order of magnitude as $\nu = 2 \times 10^{55}$. They can therefore be neglected as compared with the first term, at least for all possible equilibrium temperatures of the universe. We have then essentially

$$lnK_c = ln\left(\frac{N_1}{V}\right)^{\nu}\left(\frac{N_2}{V}\right)^{-1} = -2.8 \times 10^{64}/T$$

where N_1 and N_2 are the total number of free atoms and of stars, respectively, in the universe. (V is the volume of the universe.) Denote the total number of atoms with N, then

$$N = N_1 + \nu N_2$$

Introducing the following concentrations $n = \frac{N}{V}$, $n_1 = \frac{N_1}{V}$, $n_2 = \frac{N_2}{V}$. Making use of the ratio

$$x = n_1/n$$

our relation will be

$$x^{\nu}n^{\nu} = \frac{(1 - x)n}{\nu} e^{-2.8 \times 10^{64}/T}$$

$$x^{\nu} = (1 - x)e^{-2.8 \times 10^{64}/T - ln\, \nu - \nu\, ln\, n}.$$

To determine n we make use of the mean values for the density of matter in the universe as estimated by Hubble, $\rho = 1.5 \times 10^{-31}$ gr./cm.[3] This leads to $n = \frac{\rho}{m} = 1.6 \times 10^{-9}$. Therefore, we have only to consider the first term in the exponential and we obtain as an order of magnitude

$$x = e^{-2.8 \times 10^{64}/T\nu} = e^{-1.3 \times 10^{9}/T}. \qquad (4)$$

The vapor pressure in the interstellar space, therefore, is extremely small. The practical limits for the size of stars, on the other hand, are given as follows. According to the accepted views the upper limit is determined by the instability of larger agglomerations. For decreasing mass the probability according to (4) is decreasing so rapidly that practically only stars near to the possible upper limit will be formed. The statistical treatment on the basis of postulate (P) therefore accounts readily for the two fundamental facts of relative emptiness of space and the existence of stars of a certain size only.

The high temperatures of the stars are not necessarily in contradiction with a much lower average temperature of the universe, as the formation of highly probable reaction products involves always excessively large kinetic energies for the individuals in the transition state.

In regard to the translational velocities of the stars it should be mentioned that they have nothing to do with the immensely small velocities corresponding to $\frac{3}{2}kT$. They are really determined by the mutual interaction of the masses. The fundamental difference of the "gas" made up by the stars and a usual "van der Waal's gas," however, lies in the fact that for the first no equation of state in the ordinary sense can exist because of the slow fading of the mass attraction with distance. The star gas might be compared with a space charge made up by ions of one sign only in which case it is known that correct results can be obtained only by considering the system as a whole.

The statistical treatment given above corresponds to an application of Berthelot's principle to a chemical reaction. It would be easy to improve this procedure by introducing the free energy instead of operating with the energy or heat of reaction. It can be shown that the value for x would be multiplied by a factor $(v)^{c\nu}$ where v is the volume of the star and c is a number of the order 1 to 10. Also one would have to take into account the actual distribution of gravitational potential energy and of kinetic energy over the star. All these factors tend to increase the concentration x of free atoms in space, but still leave it quite small.

The question of the existence of dust particles can be treated as an evaporation equilibrium. Assuming that all the matter in the universe exists either in the form of free atoms or of dust, the vapor pressure equation shows that for temperatures below 1000° dust would exist in a considerable relative amount. This argument, however, is fallacious when applied to actual conditions. Considering the following reactions simultaneously

$$\nu_1 \text{ atoms} \rightleftarrows \nu_2 \text{ dust particles} \rightleftarrows \text{star}$$

it can be seen immediately that the possibility of stars decreases the total amount of matter in the form of atoms and dust by a very large factor. This means then that the remaining solid phase has to evaporate entirely. From this argument it can be seen how necessary it is not to consider partial equilibria only but to treat the interchange between all the possible reaction products simultaneously. Matter then in the universe, according to the above, should exist either in the gaseous form or else concentrated in stars only. This of course cannot mean that local conditions like the vicinity of stars cannot make the existence of dust particles more probable (dark clouds in interstellar space?).

In relation to the reaction (2) it should be said that it might be necessary to modify it in the following way.

$$\nu \text{ atoms} \rightleftarrows \text{one star} + \nu^1 \text{ atoms (as radiation)}$$

because of the fact that the final product star does not contain the same number of atoms it started with. The correct treatment of the above reaction might also remove Stern's difficulty. It seems to the writer that there must be involved a serious inconsistency in the present statistical treatment of radiation and matter. In Stern's result radiation seems to enter like a state of matter of high negative potential energy. In the usual considerations of equilibria between different forms of matter, however, radiation like kinetic energy represents a state of positive potential energy. Indeed, it does not matter whether the heat of reaction is liberated in the form of radiation or if it causes an increase in kinetic energy.

We then arrive at the following conclusions: (*a*) Postulate (*P*) is not justified by the facts as far as the distribution of radiation in the universe and the equilibrium between matter and radiation is concerned. It is desirable however to reconsider the problem on a broader basis as suggested in this paper.

(*b*) A consistent statistical treatment of the equilibrium of different forms of matter in the universe on the basis of postulate (*P*) promises to furnish results in agreement with the facts, as has been shown above.

* Evidence for the second partial reaction going on from left to right has been obtained recently by Millikan and Cameron. As the intensity of the cosmic radiation is of the same order of magnitude as the total intensity of star light, the building up process of matter from simple nuclei seems to go on at the same rate as the burning up of matter in the stars.

1 See, for instance, Jeans, *Nature*, April 28, 1928.

2 O. Stern, *Zeitschr. Elektrochemie*, **31**, 448, 1925. R. C. Tolman, these PROCEEDINGS, **12**, 670, 1926.

3 Lenz, *Physik. Zeitschr.*, **27**, 642, 1925.

4 R. C. Tolman, these PROCEEDINGS, **14**, 353, 1928.

5 R. C. Tolman, *J. Am. Chem. Soc.*, **44**, p. 1902.

6 Ehrenfest and Trkal, *Proc. Amst. Acad.*, **23**, 162, 1920.

ALGAL DEPOSITS OF UNKAR PROTEROZOIC AGE IN THE GRAND CANYON, ARIZONA

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The Algonkian Proterozoic of the Grand Canyon consists of two groups of sedimentary formations about 12,000 feet in aggregate thickness, and collectively separated by one or more periods of mountain building and profound erosional effacement both from the underlying Archean Vishnu schist and the overlying Cambrian of the Paleozoic. The upper group, the Chuar, composed mainly of shales, sandstones and thin limestones, bluish, greenish gray or red, and aggregating 5120 feet, was found by Walcott to contain "a Stromatopora-like form," later described as *Collenia*, and, in the upper division, several obscure organic traces, one of which, first characterized as Discinoid, was subsequently designated as *Chuaria.*

The lower group, the Unkar, over 5500 feet thick, separated from the Chuar by a minor unconformity, embraces sandstones and shales, mainly red or purple in color, with a relatively small proportion of limestone. No traces of life have heretofore been recognized in the Unkar group. On the basis of the general characters of these two Proterozoic groups and the diastrophic evidence, Van Hise suggested the tentative correlative reference of the Unkar, which is rather heavily charged with iron, to the Lower Huronian, notwithstanding its relatively slight metamorphism on account of which he called attention to this group as a most promising series of sediments in which to search for traces of life in this ancient period.

As the result of downfaulting of masses of sediments into the Archean schist, portions of several blocks of Unkar escaped complete pre-Cambrian erosion and now lie almost entirely below the level of the Tonto platform at or near the mouth of Bright Angel Creek.