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THE RATE OF ENTROPY GENERATİON ON THE EARTH

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Abstract

In this study, beginning with the structure of atmosphere and irreversible processes of the Earth, the rate of entropy generation mainly based on solar radiation was considered. Absorption of the solar radiation, is one of most effective irreversible process on the Earth, therefore it has been examined in more detail than other irreversible processes. General information about radiation was given for clear perspective with regard to absorption and the irreversibility it caused. The effects of solar radiation on the atmosphere and the Earth's surface were discussed in terms of flux and their contribution to the rate of entropy generation is discussed. Overall amount of the rate of entropy generation was then estimated on the context of the Earth's entropy generation budget. As a result, it is recommended to examine the entropy issue in detail in terms of the future of the Earth and the Universe in future studies.
Keywords: Entropy; Irreversibility; Entropy generation.

ÖZ
Bu çalışmada, atmosferin yapısı ve Dünya'nın tersinmez süreçlerinden başlayarak, esas olarak güneş ışınımına dayalı entropi oluşum hızı ele alınmıştır. Güneş radyasyonunun absorpsiyonu, Dünya'daki en etkili geri dönüşü olmayan işlemlerden biridir ve bu nedenle diğer geri dönüşü olmayan işlemlere göre daha ayrıntılı olarak incelenmiştir. Radyasyon hakkında genel bilgiler, absorpsiyon ve neden olduğu tersinmezlik ile ilgili net bir bakış açısı sağlanmıştır. Güneş radyasyonunun atmosfere ve Dünya yüzeyine etkileri akı açısından tartışılmış ve entropi oluşum hızına katkıları tartışılmıştır. Entropi üretim hızının genel miktarı, daha sonra Dünya'nın entropi üretim bütçesi bağlamında tahmin edilmiştir. Sonuç olarak, gelecek çalışmalarda entropi konusu Dünya'nın ve Evrenin geleceği açısından ayrıntılı olarak incelenmesi önerilmektedir.
Anahtar kelimeler: Entropi; Tersinmezlik; Entropi üretimi.

1. Introduction

The exchange processes on the Earth system occur by means of closed loops called cycles. They constantly interact with each other in accordance with certain natural laws. The Sun is the main energy source of these exchange processes and it enables the flow of matter through the whole system. Some cycles must be maintained in order for the Earth to continue its existence. These global cycles are accompanied by some irreversibilities. The Sun triggers an irreversible process, since it is an integral part of these cycles. For this reason, it contributes to entropy generation on the Earth. To look at the broader framework of entropy on the Earth, it is necessary to consider its whole structure. The part that contributes most to the entropy generation of the Earth is obviously solar radiation. The laws of nature are supported by thermodynamic laws, and these two are integral parts of each other. The future of the Earth and Universe has been tried to be explained by these laws over the years.Applying thermodynamic laws to natural phenomena is not a new approach. On the contrary, it is a constantly used approach by scientists for better understanding [1].

1.1 Composition of the Earth's Atmosphere

There are some atmospheric gases which are capable of absorbing and trapping radiation and heating up the Earth. These are called the greenhouse gases. The natural component of greenhouse gases are which reasons the heating up; water vapor is about 36-70 %, ozone is about 37 %, carbon dioxide (CO_2) is about 9-26%, and methane (CH_4) is about 4-9 % [1]. The Earth's atmosphere consists of distinct layers switching with altitude:

- ❖ Exosphere (~500km) : The layer where the atmosphere merges with space.
- ❖ Thermosphere (>90km) : The layer where space shuttles and satellites are located.
- ❖ Mesosphere (50-90km) : The layer where meteors burn up.
- ❖ Stratosphere (12-50km) : The layer where stable air exist.
- ❖ Tropopause (11-12km) : The layer which is a cover between troposphere and upper layer.
- ❖ Troposphere (0-11km) : The mixing layer which all weather are limited to this layer.

1.1.1. Ozone layer

Radiation emitted by the Sun ranges from gamma rays (10^{-12} μm) to radio waves (10^{13} μm). The solar radiation has been purified of its most biologically damaging wavelengths at sea level by gases in the atmosphere, most notably water vapor and ozone [2].

Solar radiation has significant impact upon ozone, O_3, the molecule consists of three oxygen atoms, in the atmosphere. Despite O_3 molecules in the stratosphere and the troposphere are chemically same, they have varied roles in the atmosphere. Stratospheric ozone, often called 'good ozone' is advantageous in that it absorbs most of the biologically harmful ultraviolet, called ultraviolet-B (UVB) radiation. Excessive UVB would permeate the atmosphere and would arrive the Earth's surface without the filtering action of the ozone layer. The ozone layer absorbs ultraviolet radiation, creating a heat source that causes the temperature to rise towards the upper layers of the atmosphere (Fig. 1). Therefore, ozone has a significant role in the temperature construction of the Earth's atmosphere.

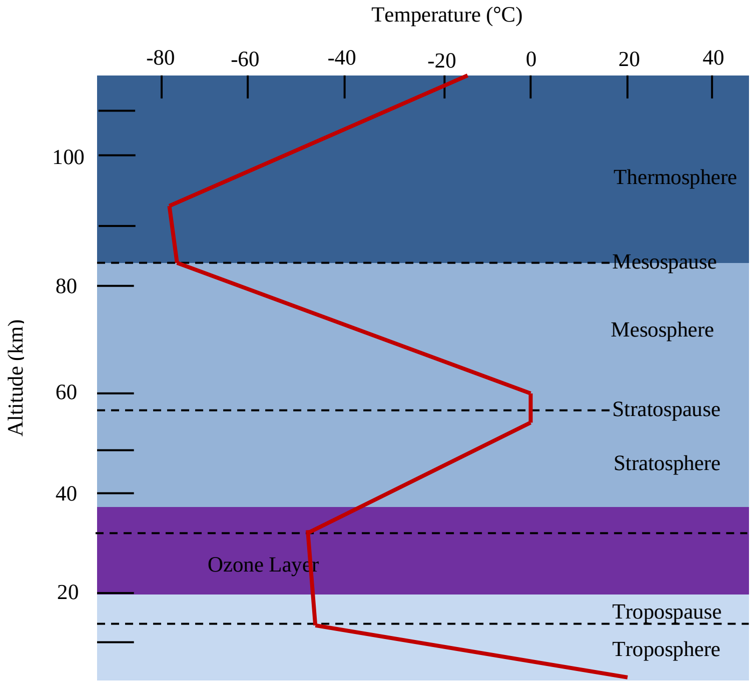

Fig. 1. Vertical temperature profile of the atmosphere based on data of International Civil Aviation Organization [3].

Tropospheric ozone (often referred to as ”bad ozone”) has destructive effects on nature. It reacts exceedingly with other molecules, and its large amounts are very toxic to all living creatures in direct contact. The outermost layers of the atmosphere, the thermosphere and the mesosphere absorb all X-rays and ultraviolet-C (UVC) in the wavelength range of 0.1–0.28 μm and UVB in the the wavelength range of 0.28–0.315 μm. The remaining UVC and most of UVB are filtered out by the stratosphere containing 90% of the ozone in the atmosphere [1].

1.2 Irreversibility, Irreversible Processes, and Irreversible Processes on the Earth

In this section, the notion of irreversibility has been tackled before the irreversible processes on the Earth. Some processes that are discussed at the thermodynamics occurs in a one certain direction. Once these processes occur in a certain direction, they cannot occur reversibly in a opposite direction, thus they cannot turn the system to its initial state. Therefore, they are classified as an irreversible processes. To give an example of the irreversibility: When a glass of hot water cools down, it does not heat up if the heat lost from the environment is restored. In fact, the environment and the system (water) will return to the initial conditions and this will be a reversible process.

Reversible processes are not in a place neither engineering applications, nor in nature. They are only ideal processes that enable us to understand real complicated processes more easily. Despite the fact that all processes in nature of the Earth are irreversible, there are two main reasons why human beings are interested in reversible processes, which are fictitious notion.

The factors that cause a process to be irreversible are called *irreversibilities***.** The irreversibility of a process could be due to (*Non-equilibrium during process*) non-equilibrium during process and/or (*Dissipations*) dissipations [4].

1.2.1 Non-equilibrium during process (external irreversibilities)
Non-equilibrium could be as a mechanical, thermal and chemical between the system and its surroundings causes a spontaneous irreversible changes. Some of these irreversible changes are mentioned below.

1.2.2 Heat transfer through a finite temperature difference

All real heat transfer processes occurs at a finite temperature difference, so they are also irreversible, and the temperature difference is directly proportionate to the irreversibility [4]. Given that the temperature difference between the Sun and the Earth's atmosphere is very large, it can be said the irreversibility is also very large. Due to this high temperature difference, the heat transfer rate from the Sun to the Earth’s atmosphere is also high. According to this; the question of "whether heat transfer between the Earth and the Sun will come to a halt due to global warming thousands of years later " may spring to mind. It is obvious that human beings should continue their investigations in order to be able to answer this question.

1.2.3 Non-equilibrium of pressure within the system or between the system and its surroundings

In the event that there exists a pressure gradient (or difference in pressure) between the system and its surroundings, there is no mechanical equilibrium. In this situation, the system and its surroundings continue to change their states constantly until mechanical equilibrium is established. When mechanical equilibrium is established and pressure gradient is eliminated, it is not no longer possible to reverse without any internal or external impact.

1.2.4 The unrestrained expansion of a gas

According to the law of energy conservation, the heat transmitted from the gas must be equal to the work performed on the gas by the environment. However, initialization of the environment causes this heat to be completely transformed into work and neglected. Therefore, such gas expansions are an irreversible process [5].

1.2.5 *Dissipations (internal irreversibilities)*

Dissipations can be divided into five, and these are friction, mixing of two fluids (viscosity), electric resistance, inelastic deformation of solids and magnetic hysteresis. In this work, only the friction was viewed among the all types of dissipations because of the large proportion of it on the Earth.

1.2.6 Friction

Such irreversibility can be between two moving solid bodies in contact, between a solid and fluid, or between two moving fluids with different velocities. Friction is a type of irreversibility that is frequently encountered on the Earth.
Although the classification of irreversibility is described above, the irreversibility can be classified differently: Irreversibility is called mechanical reversibility if the work is propagated to the increase in the internal energy of a system or due to a limited pressure gradient. If the process is caused by a finite temperature gradient, it is called thermal irreversibility and is called chemical irreversibility if it is caused by a finite concentration gradient or a chemical reaction [4]. The existence of any of these irreversibilities makes the process irreversible.

In 1927, a notion called "arrow of time" emerged. According to this notion: If an arrow is drawn and the arrow is followed and there are more random elements belonging to the world, the arrow extends to the future and if there are fewer random elements, the arrow extends to the past [6]. The word arrow implies a direction only one-way from the past to the future. The notion “arrow of time” means that the time is a one-way property and it is never reversed. The “random element” refers to entropy which a measure of the disorder of any systems. The second law of thermodynamics shows the irreversibility of the processes and consequently presents the notion of "arrow of time ". Note that the time is assumed to flow linearly and irreversibly.

The arrow in the notion “arrow of time” is divided into many types. Some of those with brief explanations: *Thermodynamic arrow* (the entropy of a closed system always increase continuingly, namely the thermodynamic arrow of time generate entropy); c*osmological arrow* (the universe expansions as time slips by); *radiative arrow* (waves, such as electromagnetic and mechanical, never converge uniformly on a point, they often diverge uniformly); *historical arrow* (“the accumulation of information over time”, the accumulation of information is an irreversible process that generates entropy, so the entropy of the universe besides the Earth as a whole still rises); *biological arrow* (every living creature dies after a while, and it can not reverse, thus generate entropy); *psychological arrow* (we perceive time as moving from the past to the future, and as events come towards us in the future, they will move toward our memory from unknown. This is information fixing and generates entropy) [7-9].

The Clasius inequality means that the system, endeavour to return to its initial state, has to be discarded its the entropy. The some amount of heat should be transferred to outer side to achieve this process, but there is no real system in nature which return to its initial state without increasing the entropy of the surrounding, or more generally the "universe". The entropy increase indicates that everything has changed, and it allows the future and the past to be distinguished: that's the "arrow of time" [10].

1.2.7 Irreversible processes on the Earth & Entropy budget of the Earth

Irreversibility and resultant entropy generation results from the Earth system processes. The irreversible processes in relation of the Earth system are illustrated in Fig. 2. As shown in Fig. 2, various gradients within the Earth are consumed by irreversible processes in accordance with the second law of thermodynamics [11].

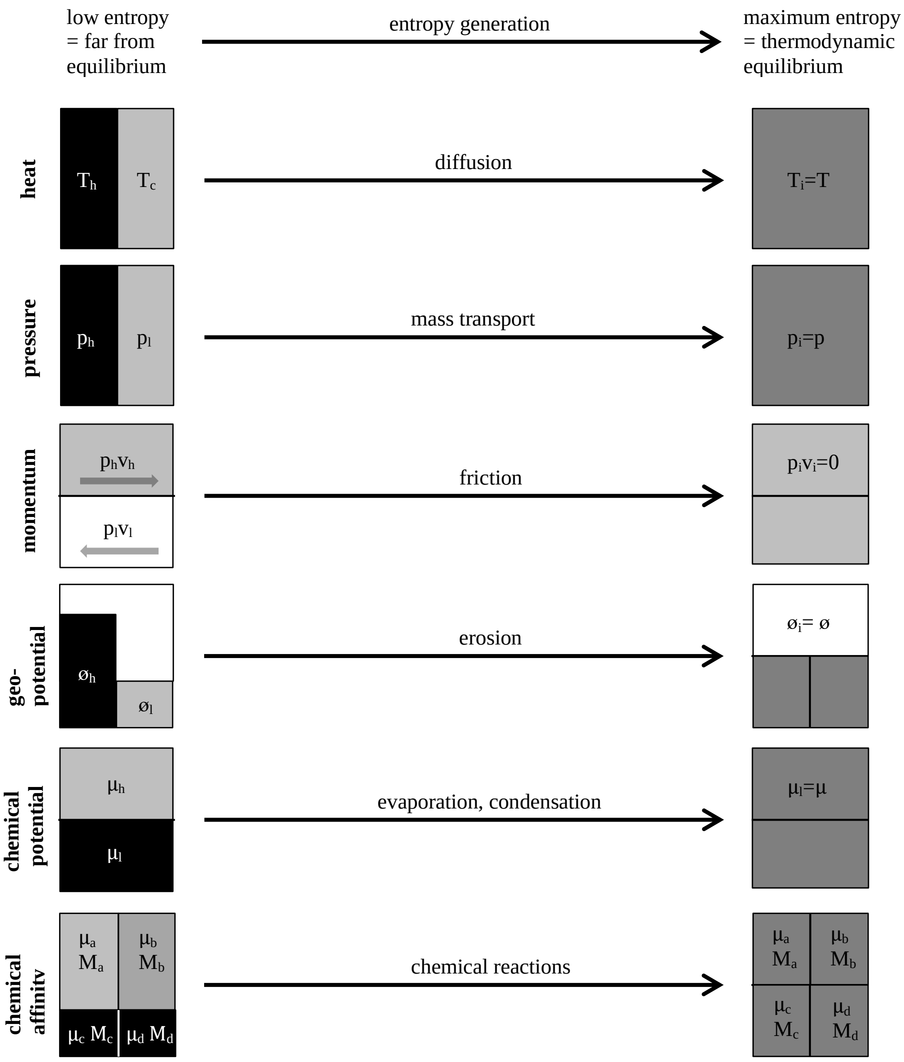

Fig. 2. Representation of irreversible processes in the Earth system and its relation to attenuating gradients, thereby bringing different variables to thermodynamic equilibrium states [11]. In Fig. 2., where T is the temperature, p is the pressure, ø is the gravitational potential, v is the velocity, μ is the chemical potential.

Fundamentally, all studies the Earth system has are releated to irreversibility and therefore entropy generation. Entropy generation based on the irreversibilities can be characterized as the product of a thermodynamic force and flux [12]. Entropy budget of the Earth, as shown in Fig. 2, presents a quantitative perspective of the rate of entropy generation and provides comparing the proportion of irreversible processes with each other at overall rate of entropy generation by the Earth system. While the table shown in Fig. 2 is being established, it has been benefited from the fluxes passing through the upper and lower layers and the temperature values at these boundaries obtained from literature studies [13,14]. The three terms shown by the upward arrow on the top right of the figure indicates the infrared radiation (8.5-11μm) flux that the Earth's surface, the atmosphere and the clouds emit. When all the values of the rate of entropy generation are added together, the rate of total entropy generation within the atmosphere is approximately 4.2406×10^{14} W/K. As it can be seen, the rate of total entropy generation was calculated via some of the irreversible processes in the atmosphere separately. In summary, the values in Fig. 3 show that absorption of solar radiation and the latent heat have biggest proportion within the rate of total entropy generation in the atmosphere. Among the non-radiative processes, the contribution of hydrologic cycle to the rate of total entropy generation is large, while the contribution of the sensible heat and frictional dissipation are relatively small (also see [12]).

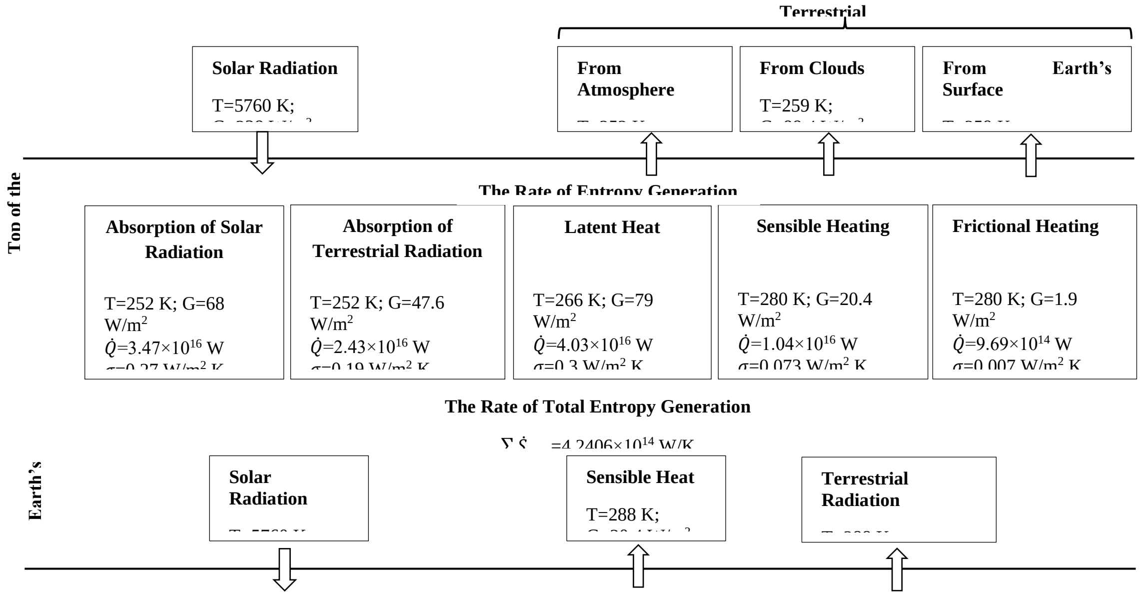

Fig. 3. Entropy budget of the Earth. The symbols are: $\dot{S}_{gen}$, the rate of entropy generation; σ, entropy flux; $\dot{Q}$, the rate of radiation heat transfer; G, radiation flux; and T, temperature.

1.2.8 Absorbtion

Before the subject of absorption, it may be useful to give a brief information about radiation. The existence of radiation was theoretically found in 1864 by physicist J. C. Maxwell. As a result, electric and magnetic fields have been discovered and these moving fields have been called *electromagnetic waves* or *electromagnetic radiation* [15]. Unlike other heat transfer types such as convection and conduction, transfer of energy by radiation does not necessary a physical material to intervene. Since the space acts like a vacuum, the energy of the Sun reach the Earth only by radiation. Radiation is a very fast energy transfer that the Sun can use to conserve its vitality [16].

The radiation emitted by surfaces at an absolute temperature T_s (in K) is given by the Stefan–Boltzmann law [17,18] as: (Eq(1)).

$$\dot{Q}_{emit} = \mathcal{E}\sigma A_s T_s^4 \quad (1)$$

where $\mathcal{E}$ is the emissivity of the surface, σ is the Stefan-Boltzmann constant with a value of 5.67×10^{-8} W/m^2·K^4 and A_s is the surface area. Value of $\mathcal{E}$ is in the range $0\leq \mathcal{E} \leq 1$ and it will have a value of 1 in case the surface is blackbody. Although the Earth is not an excellent blackbody, $\mathcal{E}$ could assumed to be 1 in calculations. Another important radiative property of a surface is absorptivity. Its value is in the range $0 \leq \alpha \leq 1$ similar to emissivity. Values of α is 1 for the blackbody, because the blackbody is a perfect absorber. These two properties of a surface firmly depend on the wavelength of the radiation and the temperature. For opaque (non-transparent) surfaces, the irradiated radiation is reflected back by the surface ($\dot{Q}_{ref}$). The rate at which a surface absorbs radiation is determined from Fig. 4 $\dot{Q}_{incident}$ represents the rate of incident radiation on the surface (Eq(2)).

$$\dot{Q}_{absorbed} = \alpha\dot{Q}_{incident} \quad (2)$$

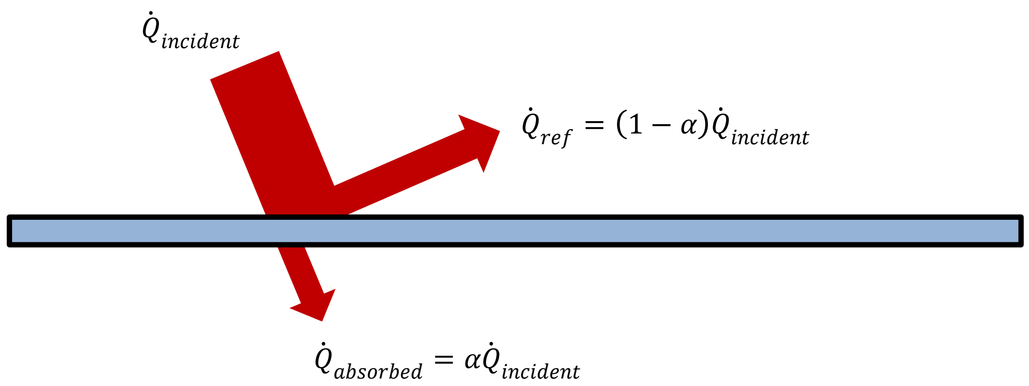

Fig. 4 The absorption of radiation by an opaque surface.

When a surface at the absolute temperature (Ts) is completely covered with a gas such as radiation-conducting air at the absolute temperature *Tsurr* is covered with the other surface, radiation heat transfer between these two surfaces is shown in Fig. 5.

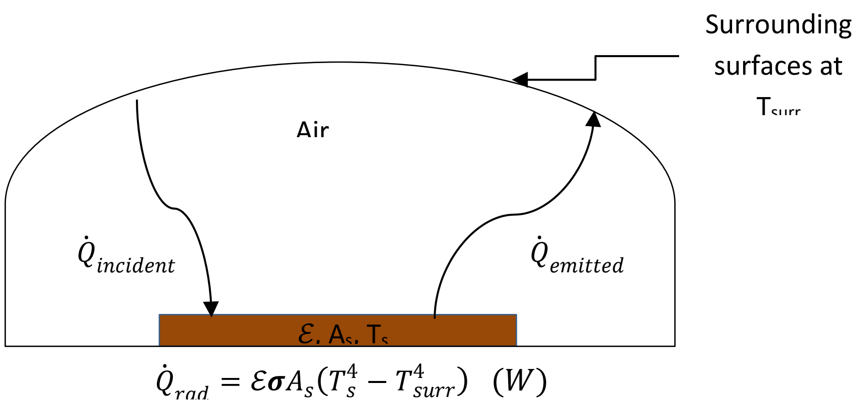

Fig. 5. Radiation heat transfer between a surface and its surrounding.

The direction of heat transfer by conduction and convection occur from high temperature to low temperature. However, for instance, solar radiation reaches to the Earth by passing through air layers colder than surface. Similarly, the surface inside the greenhouse reaches high temperatures by absorbing the incident radiation even though the outer surface of the glass or plastic of the greenhouse is relatively colder.

By Max Planck's photon theory which he worked on in 1900, it was understood that the photon energy was reverse proportional to the wavelength and therefore the short wavelength radiation has larger photon energies [19].

The electromagnetic radiation is called the thermal radiation which is related to the heat transfer emitted in terms of energy transitions of, atoms, molecules, and electrons of a substance [16]. With reference to Fig. 6, the thermal radiation is in the range of 0.1 to 10^2 µm in this spectrum. Therefore, thermal radiation includes all visible and part of the ultraviolet radiation with infrared radiation.

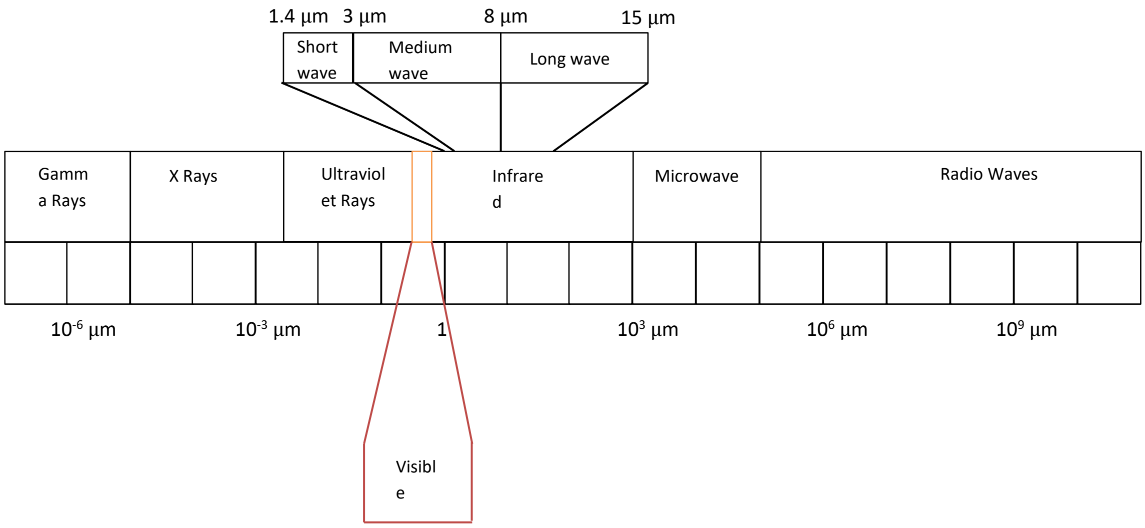

Fig 6. The electromagnetic wave spectrum

About half of the solar radiation is light-shaped (visible light), the remainders are ultraviolet and infrared rays. The ultraviolet radiation is somewhere in the band gap of thermal radiation spectrum (between the wavelengths 0.01 and 0.40 µm) and it also includes some part of the short, medium wavelength and the thermal radiation spectrum as shown in Fig 6. It should be avoided from the ultraviolet rays since most of those are harmful for man and all living organisms. Approximately 12 % the solar radiation is in the ultraviolet range, and if it reaches the Earth's surface directly, it will cause devastating results. Fortunately, the Earth is under protection by the ozone (O_3) layer absorbing most of the ultraviolet radiation [16].

The radiation flux from all directions to any surface is called irradiation G (W/m^2). Surface reflect some part of incoming irridiation and emit radiation, thus the radiation leaving a surface composes of reflected and emitted components, as given in Fig. 7. In order to calculate the radiation heat transfer on the surface, it is necessary to consider the radiation energy sliding away from a surface.

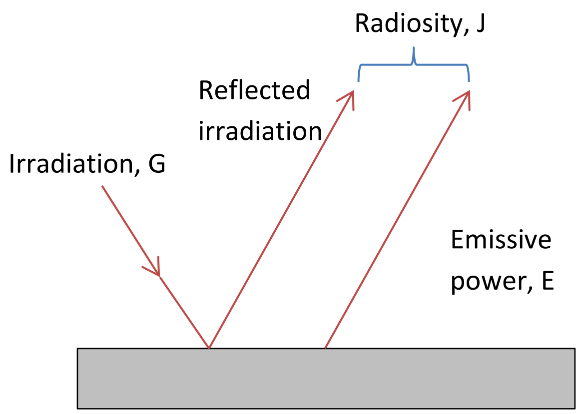

Fig. 7. The three kinds of radiation flux (in W/m^2): emissive power, irradiation, and radiosity.

A part of the radiation coming to the surface is absorbed, a part of it is reflected, and the remaining part, if any, is transmitted as illustrated in Fig. 8, G represents the radiation energy on the surface, and G_{abs} is the absorbed, G_{ref} is the reflected and G_{tr} is the transmitted parts of it. According to the first law of thermodynamics; the sum of the absorbed, reflected and transmitted portions must equal to the incident radiation. That is: $G_{abs} + G_{ref} + G_{tr} = G$.

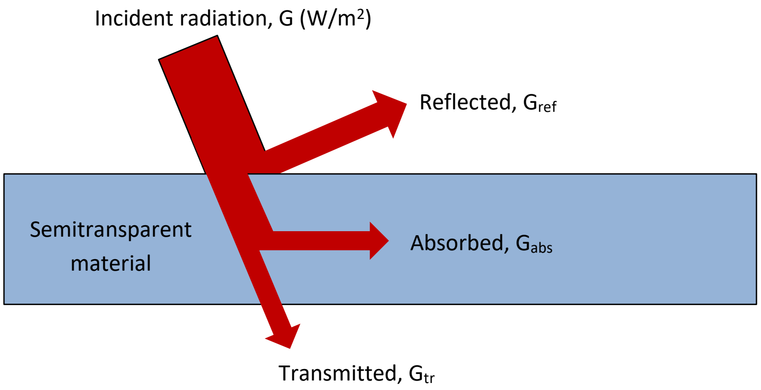

Fig. 8. The absorbed, reflected, and transmitted portions of incident radiation by a semitransparent material.

Glass surrounding volume allows the solar radiation to pass through the interior, but does not allow the infrared radiation to exit from the interior of glass as shown in Fig. 9. This results a temperature rise at the interior of glass.

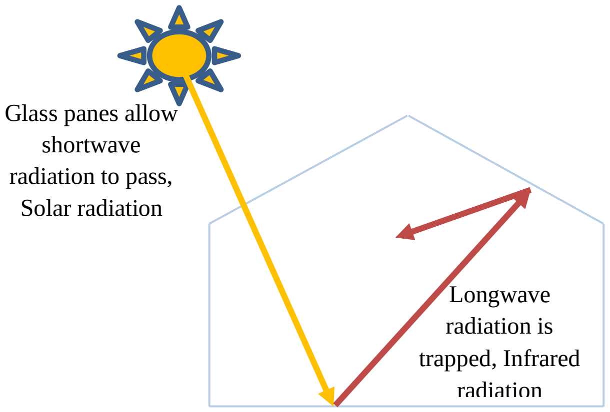

Fig. 9. Greenhouse effect in glass volume.

Beyond the small example given above; this event has a profound effect on the Earth. The surface of the Earth heat by absorbing the solar radiation during the day, and cools down by radiating this energy into the space as infrared radiation at night.

In addition to transmitting the most of solar radiation, the gases such as CH_4, CO_2, ozone and water vapor in the atmosphere absorb the infrared radiation emitted by the surface of the Earth. Therefore, the energy confined to the Earth gradually results in global warming.

Although the temperature at the core of the sun is approximate 40 000 000 K, this temperature drops to 5800 K at the outer region, which causes energy dissipation by radiation. In addition, the sun can be assumed as a blackbody at a temperature of 5780 K. The solar energy that reaches the atmosphere of the Earth is called the total solar irradiance G_s, which is about 1373 W/m^2. The solar radiation lightens due to the effects of scattering and absorption when passing through the atmosphere. Due to the absorption of some gases such as O_2, O_3 (ozone), H_2O, and CO_2 on the Earth's surface, value of the solar energy is about 950 W/m^2. The nitrogen and oxygen molecules scatter radiation at short wavelengths, which vary according to the molecule size.

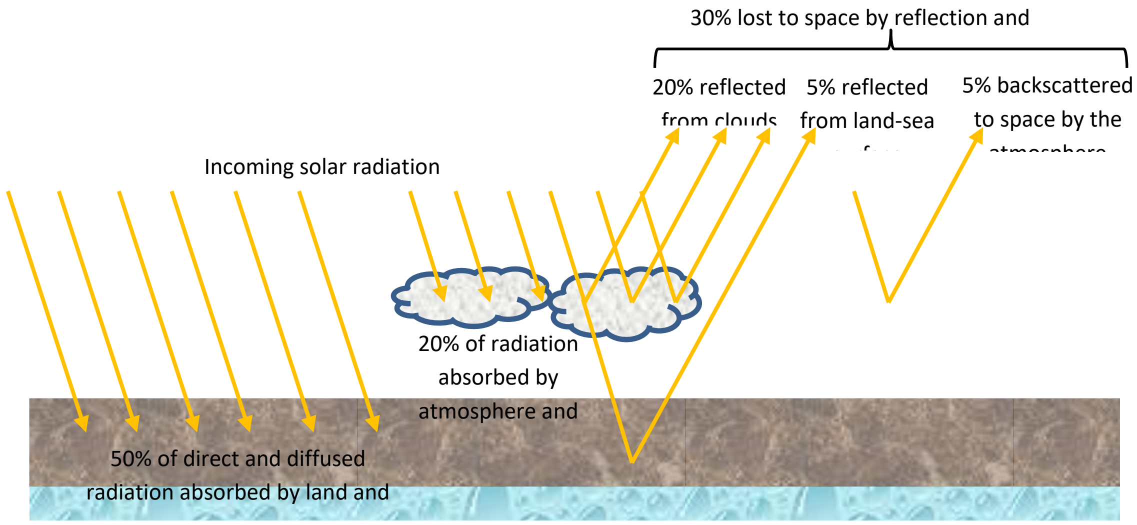

Fig. 10. Distribution of incoming solar radiation [20].

Fig. 10 shows the distribution of incoming solar radiation. Accordingly, 30% of total incoming radiation is reflected to space (5% by land-sea surface, 20% by clouds, and 5% by the atmosphere). In summary, the atmosphere reradiates to space at a rate of about 70% in total with 20% of shortwave radiation absorbed directly from the sun and 50% of longwave infrared radiation absorbed afterwards. The radiation flux at the top of the atmosphere is about to1366 W/m^2. However, due to the specific geometrical structure of the Earth and reflective surfaces, only 235 W/m^2 (67 W/m^2 by air and 168 W/m^2 by land and water) is absorbed.

Referring to Fig. 11, the gases in the atmosphere absorb 452 W/m^2 thermal infrared radiation that emitted by the Earth's surface. 324 W/m^2 of the total enery, which is 519 W/m^2 (67+452), is routed to the Earth's surface and the remainder amount is routed to space. The total energy (492 W/m^2) consists of 168 W/m^2 from sunlight and 324 W/m^2 from atmosphere raises the Earth's surface temperature. These processes and radiation effects provide a balance and warm the Earth's surface so that habitats can sustain their existence. This is known as greenhouse effect as mentioned earlier.

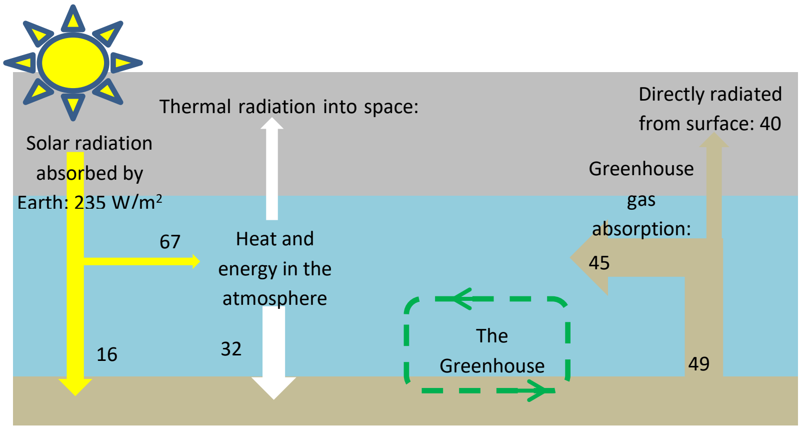

Fig. 11. Greenhouse effect and energy balance [1].

Absorption of solar radiation make the largest contribution to the entropy budget of the Earth due to the temperature difference and large heat flux. To explain a bit more about the irreversibility of absorption, wavelengths of the absorbed solar radiation are larger than the emitted radiation from the Earth, namely the absorbed one has longer wavelength when compared to the emitted one. In addition, the emitted radiation from the Earth's surface leave the Earth system in the form of terrestrial radiation.

1.2.9 Scattering

Irreversibility of the unrestrained expansion of a gas has been mentioned earlier. Meanwhile, scattering would assumed to be the free expansion of photon gas. The solar energy (radiation) falling into the Earth's surface is divided to two different sorts that are called *direct* and *diffuse*. Diffuse solar radiation G_d, that is the scattered radiation, is assumed to reach the Earth's surface uniformly from all directions (Fig 12).

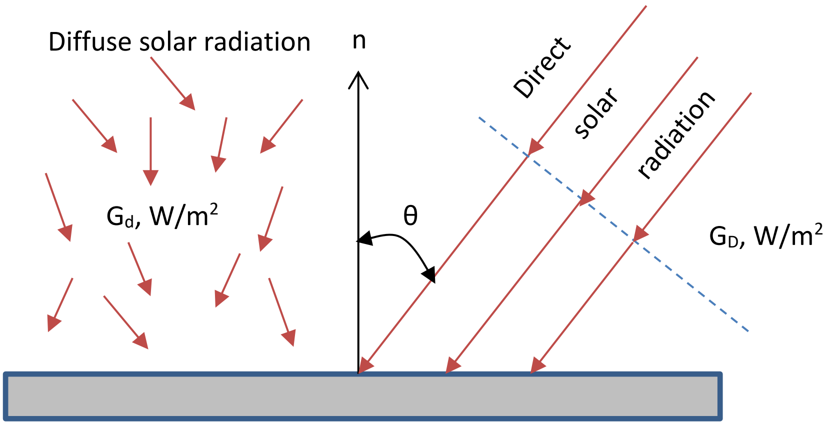

Fig. 12. The direct and diffuse radiation falling into the Earth's surface.

The gas molecules in the atmosphere and the suspended particles *emit radiation* and so absorbing it. CO_2 and H_2O molecules are the main factors of the atmospheric emission. The amount of radiation radiates back to space and the radiation emission from the atmosphere to the Earth's surface are determined by the effective sky temperature (T_{sky}) through the well-known Stefan-Boltzmann law (Eq(3)).

$$G = \sigma T_{sky}^4 \ (W/m^2) \tag{3}$$

To summarize, the irreversibility here results from lack of certain direction of the scattering process.

1.2.10 Thermal Diffusion

Thermal diffusion established in case of a temperature gradient in a medium is a relative motion of a gaseous mixture or solution. The Swiss scientist Charles Soret studied on thermal diffusion in liquids (salt solutions), in 1879, and he found that a flux of salt was generated by a temperature gradient [21]. In addition, thermal diffusion in gases was investigated on the basis of the kinetic theory of gases and was later discovered experimentally in few studies of literature [22,23].

Thermal diffusion on the Earth's surface is the case of some changes in heat storage of the ground that is also called temperature gradient. Variance of solar radiation due to the diurnal and seasonal factors creates unstable cooling and heating resources at the Earth's surface completioning a temperature gradient at the surface. This gradient motives the heat exchange with the ground, in fact it decreases the gradient [12]. The irreversibility here is caused by the fact that the initial variables are forced to change over time.

1.2.11 Dry convection and frictional (large-scale motion) dissipation

The notion of dissipation was first introduced in the field of thermodynamics by William Thompson in 1852. He has classified the irreversible processes in those years as friction, diffusion, heat conduction and the absorption of light. Dissipation is generally the result of irreversible processes that generates entropy at a certain rate.

The frictional dispersion of atmospheric movements constitutes approximately 30 % of the total entropy production of atmospheric circulation in the world [14, 24-25]. The remaining 20 % is the uncertainty of the entropy generation. When the atmosphere is considered as a whole, the hydrological cycle is responsible for almost half of the entropy generation of atmospheric circulation [26-29].

In consideration of the above-mentioned: All irreversible processes compete with each other in terms of their entropy generation since the total irreversible entropy generation by the atmospheric circulation is constrained by the radiative forcing.

A strong atmospheric action causes the friction distribution to be significantly reduced and effectively absorbing the atmosphere. Kinetic energy is a sub-branch of free energy. It is irreversibly converted to heat by friction dispersion. The movement is mostly caused by gradients in radiation cooling and heating events and by pressure and density gradients due to external factors similar to the gravitational force of the Moon [30].

The fact that the Earth is not in the thermodynamic equilibrium is a result of planetary vitality. If the Earth was in thermal equilibrium, the large-scale motion and hence frictional dissipation could not exist [12].

1.2.12 Hydrologic cycle

Air upon an clear water surface ultimately reach saturation by evaporation in the absence of motion. The atmospheric circuit afterwards acts to dehumidify the atmosphere by evaluating air to oversaturation that allows for precipitation and condensation precipitation of water [27,28]. In the absence of precipitation and evaporation, the hydrologic cycle can not exist.

The irreversibility of hydrologic cycle incident arises from the fact that condensed vapour can not be evaporated into oversatured air, and this evaporated water can not be removed from the unsaturated air [12,26].

Although the water vapor in the atmosphere is saturated, it is in thermodynamic equilibrium with the open water surface, the vaporizing superstructure to the super saturation and the dynamics such as the precipitation that removes the moisture from the raised air will destroy the water vapor from the thermodynamic balance [31].

Atmospheric motion is also related to hydrologic cycle: Water vapor passes through the stages of saturation, condensation and precipitation by lifting air masses.

Concentrated water loss to the environment results in general dehumidification and then allows water to evaporate from the surface to the atmosphere. Therefore, the power of the hydrological cycle and its lack of thermodynamic equilibrium are directly related to the strength of the atmospheric movement. When the moisture carried by the atmosphere turns to the oceans after the rivers, it transports sediments and dissolved elements from terrestrial rocks to oceans. There is a close relationship between the hydrological cycle and the geological carbon cycle, and more information can be obtained from the literature [14,32]. Energy conversion chain between different type of gradients and the cycles is progressing in various directions. For example, temperature gradients cause unequal spread of terrestrial radiation and consequently alter radiation gradients. The movement thus carries heat and consumes temperature gradients. The hydrological cycle is effective on the convection of water from vapor and its inverse to heat transfer in the event of a phase change of the water. For more detailed and figurative perspective of the chain and irreversible processes within the Earth, the literature work can be examined [12].

Hydrologic cycle also affects clouds and ice cap which are very important in terms of reflection and scattering of incident solar radiation to space. In addition to the geochemical cycle (especially the carbon cycle), the hydrological cycle changes the atmospheric composition, especially in terms of greenhouse gases consisting of water vapor, clouds and CO_2. These, of course, affect the radiation gradients [32].

If there was a thermodynamic equilibrium everywhere on Earth and also the net rates of precipitation and evaporation were zero, the hydrologic cycle could be absent. In other words, the hydrologic cycle is intimately linked with the energy balance and the redistribution of heat since precipitation and evaporation culminate in large amounts of heat transfer.

1.2.13 Biotic activity and Carbon cycling

The non-equilibrium between atmospheric CO_2 and crust causes volcanic degassing of CO_2, thus this situation causes carbonate deposits to form the geological carbon cycle at the seabed. The irreversibility here is due to the depletion of CO_2 gradients [33].

As for the biotic activity, it strongly influences the CO_2 concentration in the atmosphere and contributes to the overall entropy generation. Photosynthesis benefits from the sunlight to carry out a series of chemical reactions that allow CO_2 to be expelled from the atmosphere, thus it generate free energy in carbohydrate form. When these carbohydrates are inhaled somehow (e.g. by the activity of heterotrophs) the chemical energy is transported into heat. The irreversibility here derives from the transformation of solar radiation into heat.[12]. In addition to this, there is a relation between the greenhouse gases and the pair of the carbon cycle and the biotic activity. Biotic activity affects carbon dioxide (and methane) concentrations in the atmosphere, and therefore the atmospheric greenhouse effect and surface temperature [34].

Atmospheric turbulence interact with weathering: Motion drives the water cycle that cause dissolved rock minerals transport from the land to the ocean. The solute transport is an important part of the geological carbon cycle because it binds with the carbon dioxide (CO_2) to form limestone and supply an amount of the calcium to the ocean, thereby removing CO_2 from the climate system. The difference in the CO_2 concentration in the atmosphere and the mantle causes non-equilibrium in the carbon cycle. This variation culminates in volcanic outgassing. The process driving this non-equilibrium is the generator called mantle convection. Mantle convection maintains the potential gradient between the interior and the atmosphere.

Other generator called photosynthesis supplies the carbohydrates to create organic carbon. Consequently, the two generators directing the carbon cycle are mantle transport and photosynthesis [30].

In brief, these two generators continue gradients in CO_2 concentration and free energy. The various processes such as volcanic outgassing, respiration, precipitation etc. which deplete these gradients to complete the carbon cycle are related the irreversibilities.

Here the following information should be mentioned: The amount of heat that flows under the Earth’s surface is approximately 46 TW, which is tens of thousands of times smaller than the heat absorbed from the sun [35].

1.2.14 Summary of this section

The predominant part of the dissipative procedure is to absorb sunlight at much lower temperatures (around 280 K) compared to the sun's emission temperature (about Tsun = 5760 K). More than 90 % of the planetary entropy generation is due to absorption.

The remainder by dispersing processes associated with scattering of direct sunlight to scattered radiation (ie, expanding the solid angle, see for example [14]), phase transition hydrological cycle occurring at different temperatures, frictional dispersion of the movement, diffusion of heat entering and exiting the soil at different temperatures, solar It consists of reasons such as the carbon cycle which causes the use of photosensitivity [36].

1.3 In General Sense of Entropy, Entropy Balance and Entropy Generation

The word "entropy", was used for the first time by Clausius, and it came to be called the Greek word "tropee" which means "transformation". To describe the "entropy" property passing through a historical path; initiated with Carnot, an engineer, detailed with Kelvin and Clasius. He also inferred an integrating factor connected with the Kelvin temperature. This mathematical inference can be examined in the literature [4].

The inequality of R. J. E. Clausius (1822-1888), one of the pioneer of thermodynamics, is denoted as a mathematical notation as follows: (Eq(4)).

$$\oint \frac{\delta Q}{T} \leq 0 \tag{4}$$

Where "T" is the boundary temperature of the system and "δQ" is the amount of heat entering the system. Clasius's inequality states that the integral on the thermodynamic cycle of the $\delta Q/T$ expression is equal to zero or less than zero. This inequality can be applied to all reversible or irreversible cycles. If there is absence of irreversibility in the system, the cycle performed by the combined system is internally reversible. In this case, the cycle can take place in the reverse direction. When the cycle takes place in the reverse direction, all quantities will remain the same, but the sign will change in opposite way, so for internally reversible cycles: (Eq(5)).

$$\oint \left(\frac{\delta Q}{T}\right)_{\text{int rev}} = 0 \tag{5}$$

Thus, the equality in Clausius inequality is valid for internally or the inequality for irreversible cycles, and totally reversible cycles. To improve a relationship that defines entropy: The integral (Eq. 2) on the cycle of a property such as volume, that is, the net change in the cycle is zero. A magnitude with a zero integral on the cycle is only dependent on the state and is independent of the process path, therefore it is a property. Thus a property of $(\delta Q/T)_{\text{int rev}}$ must be written in the differential form. In 1865, Clausius discovered a new thermodynamic property and gave it the title “entropy”. Entropy is denoted by "S" (kJ/K) and is defined as follows: (Eq(6)).

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \tag{6}$$

If Eq. (3) is integrated between the initial and final states, there may be an entropy change of the system during a process: (Eq(7)).

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \tag{7}$$

The entropy change ΔS between the two states is not dependent on the path during a process, in other words, the entropy change is the same whether the process is reversible or irreversible. Isothermal state change is the state change that the temperature is constant during heat tranfer and this state change is internally reversible. For this reason, the entropy change of a system during an isothermal heat transfer process can be determined by integration in Eq. (8).

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} = \int_1^2 \left(\frac{\delta Q}{T_0}\right)_{\text{int rev}} = \frac{1}{T_0}\int_1^2 (\delta Q)_{\text{int rev}} = \frac{Q}{T_0} \tag{8}$$

where Q is the heat transfer and T_0 is the constant temperature of the system. Eq. (5) is used especially when calculating the entropy changes of the thermal energy reservoirs that absorb or supply heat as desired at the constant temperature. Accordingly, it may not be very accurate to think of the heat transfer process between the sun and the earth as isothermal.

Consider a cycle consisting of two processes, proceed from 1 to 2 and from 2 to 1, and assume that process 1-2 is reversible or irreversible and process 2-1 is internally reversible. Starting from Clasius inequality (Eq. (3)), if the following steps are followed:

$$\int_1^2 \left(\frac{\delta Q}{T}\right) + \int_2^1 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \leq 0 \tag{9}$$

$$\int_1^2 \frac{\delta Q}{T} + S_1 - S_2 \leq 0 \tag{10}$$

$$S_1 - S_2 \geq \int_1^2 \frac{\delta Q}{T} \tag{11}$$

$$dS \geq \frac{\delta Q}{T} \tag{12}$$

Eq. (12) is obtained. Here the equality is for the inwardly reversible process and the inequality is for the irreversible process. T is the thermodynamic boundary (where the differential heat δQ occurs) temperature between the system and the surrounding. The "inequality" state in Eq. (7) implies that the entropy change in a closed system is always greater than the entropy transfer in the case of an irreversible process. In other words, some entropy is produced in an irreversible process, and entropy production is completely related to irreversibility. Here, the irreversible processes in the Earth and the entropy generation that these processes cause should come to minds. The entropy produced during a process is called entropy generation and is indicated by S_{gen}. If the difference between entropy change and entropy transfer for a closed system is equal to the entropy generation: (Eq(13)).

$$\Delta S_{sys} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen} \tag{13}$$

If the universe is considered as a isolated or an closed adiabatic system,that is the heat transfer is zero, Eq. (14) becomes:

$$\Delta S_{\text{isolated (or universe)}} \geq 0 \tag{14}$$

According to this equation, the entropy of an isolated system always increases during a real process. This is the " increase of entropy principle ". If the space is considered as a isolated system, that is, assuming no heat transfer, then entropy change is only due to irreversibility and this effect always increases entropy. An isolated system, like the universe, consists of an infinite number of subsystems. Because entropy is an extensive property, the entropy of the universe equals the sum of entropies of these subsystems. If the Earth and the space are considered as a system and environment respectively and this environment and system are considered as two subsystems of an isolated system, the entropy change in the system and its surroundings is directly equivalent to the entropy generation, because an isolated system does not involve entropy transfer, as shown in Fig. 13.

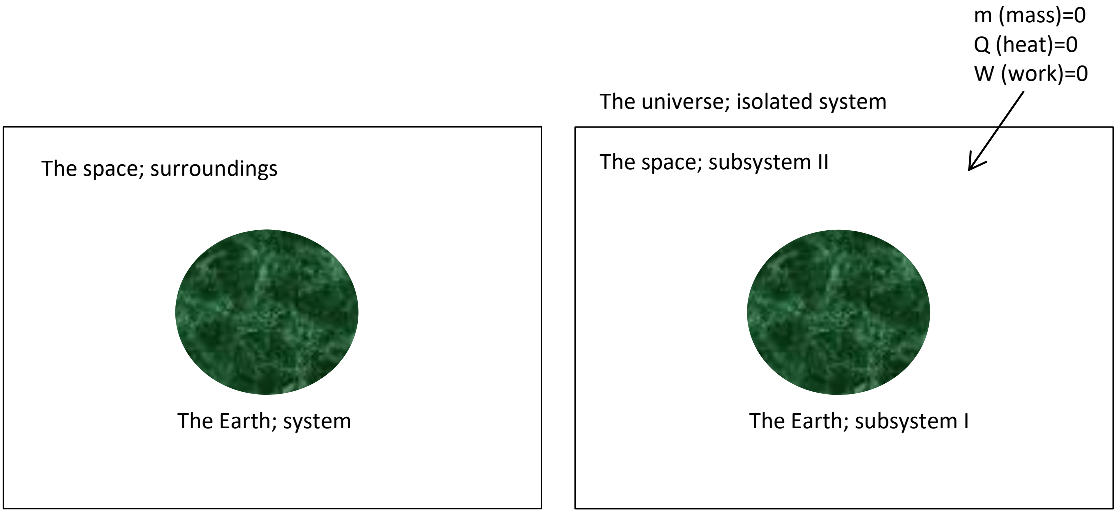

Fig. 13. An isolated system consists of two subsystems

If the increase of entropy principle is applied to the isolated system shown in Fig. 13, the entropy change of the isolated system equals entropy generation:

$$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \geq 0 \qquad (15)$$

The inequality holds for irreversible processes in Eq. (15). The processes in nature are irreversible, so any change that occurs causes the total entropy to increase slightly. From this hypothetical path, it can be said that the entropy of the universe, an isolated system, is constantly increasing. If it is thought in terms of the Earth, entropy transfer with mass between space and the Earth can be neglected since entropy transfer is much larger than heat. Additionally, the Earth is assumed to be a closed system.

In nature, there is a tendency to change until equilibrium is reached. Here the word " equilibrium " states absence of unbalanced potentials (or driving forces) within the system. Because all processes are irreversible, the conservation of entropy can not be mentioned. This is why the entropy of the Earth and of the universe is constantly increasing. When entropy is considered as molecular disorder, it is obvious that the entropy in the gas phase of a substance will be higher than that is in the solid phase. The following conclusion can be drawn: Entropy is high because of the molecular disorder in the atmosphere of the Earth.

In 1877, Ludwig Boltzmann developed a statistical concept to describe disorder by adding together the probabilities of the thermodynamic processes.

$$S = k \ln p \qquad (16)$$

where p is thermodynamic probability and $k=1.3806\times10^{-23}$ J/K is the Boltzmann constant. The higher disorder, the higher value of p. According to Eq. (16), it can be said that: For every state of macroscopic equilibrium, there are a great number of microscopic states in which the system can. The entropy of a system is interested in value of p, which is possible microscopic states of that system.

The heat energy that the Earth receives from the Sun is actually an disorganized form of energy. Therefore, heat transfer increases disorder in the Earth, so an amount of entropy is transferred to Earth. According to the second law of thermodynamics, entropy can be created but not eliminated. When this expression and the increase of the entropy principle are combined, the following expression appears: Eq(17)).

$$S_{in} - S_{out} + S_{gen} = \Delta S_{sys} \tag{17}$$

This equality is often known as entropy balance and can be applied to any system that enduring process. The first two terms in the left side of the equation refer to net entropy transfer by heat (entropy transfer by mass flow is neglected). The term in the right side of the equation refers to entropy change. The entropy transfer out of a system or into the system occurs by two mechanisms, heat transfer and mass flow. However, in this work, the issue of entropy transfer by mass flow is not tackled. Entropy transfer by heat transfer in general form: Eq(18)).

$$S_{heat} = \int_1^2 \frac{\delta Q}{T} \tag{18}$$

The irreversibility mentioned in the previous sections always leads to an increase in the entropy of the system. Entropy production is a measure of entropy created by irreversibility throughout the process. Eq. (12) is expressed in the ratio form (kW / K) as follows: Eq(19)).

$$\dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen} = dS_{sys}/dt \tag{19}$$

When the Earth considered as a closed system, entropy change depends on entropy transfer associated with heat transfer and entropy formation within system boundaries. In its most general form, the entropy balance for the Earth can be expressed as: Eq(20)).

$$\sum \frac{Q}{T} + S_{gen} = \Delta S_{sys} = S_2 - S_1 \tag{20}$$

If this equation is re-expressed for the universe (closed adiabatic or discrete system):

$$S_{gen} = \Delta S_{sys} \tag{21}$$

As the Earth is in a long period of time, a steady state regime can be assumed. Thus, entropy generation of the Earth can be quantified by the net entropy change in an overall entropy budget. It should be noted that entropy transfer is due to heat transfer in this entropy balance. In previous sections, the entropy generation is calculated through the entropy fluxes at the top of the amosphere due to the irreversibilities based on solar radiation. The overall rate of entropy generation (W/K) of the Earth can be determined by re-arranged equation of Eq. (18), as shown below:

$$\dot{S}_{gen} = \frac{\dot{Q}}{T} \tag{22}$$

where $\dot{Q}$ is the radiation energy flux, and T is the temperature. The entropy budget shown in Fig. 3 is based on Eq. (22).

2. CONCLUSION

This study reviews major irreversibilities in the Earth system and the rate of entropy generation due to this irreversible processes. At the beginning of this study, irreversibility, irreversible processes on the Earth, and entropy term in general have been tackled in order to clear perspective. Also, when the entropy budget has been investigated, some assumptions are made on the Earth and the universe in accordance with second law of thermodynamics.

The mass flow between the Earth and the space is neglected and the rate of entropy generation is determined by the solar radiation flux. The reason of neglecting entropy transfer with mass is that the entropy transfer with mass is very small compared to entropy transfer with heat. In this study, the Earth is considered as a closed system and according to this, there are the terms of "entropy transfer with heat" and "entropy generation" in entropy balance equation. The rates of entropy generation, which are caused by irreversible processes on the Earth, is calculated by using entropy balance equation derived for the Earth. Although the subject of this study is related to the entropy generation on the Earth, the entropy of the Universe has been mentioned occasionally. A thermodynamic relationship has been established between Earth, space and Universe, then resultant entropy events are explained. According to this relationship, it would not be wrong to say that the entropy of the Universe is increasing. This situation also coincides with the " increase of entropy principle" which applies to an isolated system. In conclusion, the solar radiation flux combining with the irreversible processes leads to high entropy generation in the atmosphere. However, since there is a limited number of studies on this subject in the literature, the researchers can examine the entropy balance and generation in the Earth in more detail in the future.

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