Hypothesis



# Pre-Biotic Earth and a More Complete Theory of Heat Transformation, Part II – Chemical Dissipative Structures and Networks

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# Pre-Biotic Earth and a More Complete Theory of Heat Transformation, Part II – Chemical Dissipative Structures and Networks

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**Abstract**

The origin of life on prebiotic Earth is one of science's greatest mysteries. Traditional approaches to the search for answers often rely on isolated universe models that fail to account for the open, far-from-equilibrium conditions of natural systems. Such limitations might be hindering progress in understanding the thermodynamic processes that drive the emergence of life. This theoretical study presents the second installment in a series exploring a thermodynamic theory of heat transformation and its role in the development of prebiotic Earth. Building on the foundational concepts introduced in Part I, this work focuses on the dissipation of heat through chemical systems, examining chemical dissipative structures (CDSs) and their ability to store and release energy through endothermic and exothermic reactions. By modeling CDSs as heat engines, the paper investigates the interplay between entropy, order, and complexity, revealing how energy storage and transformation drive the generation of complexity. The analysis extends to the networking of gravitational dissipative structures (GDSs) covered in Part I and CDSs, demonstrating how these networks facilitate the transfer of stored energy and contribute to the development and growth of prebiotic chemosystems. The findings suggest that the dominance of endothermic synthesis reactions in CDSs plays a critical role in the generation of complexity, resilience, and mutualism, ultimately shaping the conditions for the emergence of life. This work provides a novel perspective on the thermodynamic underpinnings of prebiotic evolution, offering insights into the relationship between energy, information, and the development of complex systems.

**Keywords:** dissipative structures; heat engines; thermodynamics; entropy; complexity; order; information; heat quality; prebiotic chemistry; network ecology; sustainability; prebiotic Earth; evolution

## 1. Introduction

This is the second of a series of papers presenting a thermodynamic theory of the development of a pre-biotic Earth by the transformation of heat, hereafter referred to as *heat transformation theory*. In Part I of this paper series [1], the question is raised regarding the sustainability of the development of a last universal common ancestor (LUCA) species based upon a preceding single instantiation of the first universal common ancestor (FUCA) life form referred to as an original first universal common ancestor (OG-FUCA), bringing into question the current "hard steps" theory of the evolution of life on Earth. If life is sustainable today in an ecosystem that enables life to be persistent and resilient, then life must be sustainable when it is first formed. The initial life form or life forms are sustained by a pre-biotic chemosystem. Without such a system, the hard steps proposed by current evolutionary theory are not only improbable, but hard to survive.

What Earth starts with for a growth process is a planet of all of the elements and nuclides of the periodic table collected as a tectonically active planet in a gravity well with the heat of its collapse slowly dissipating to space and the solar insolation of the local Sun pouring down on it. From this point, Earth must stick build the capacity for life. Part I [1] of this series of papers on heat

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transformation theory focuses on the modeling of gravitational dissipative structures (GDSs) as heat engines with conservative forces acting to perform work. The model demonstrates that dissipative structures (DSs) are reversible in the work stages, making the DS as a whole act as a semi-reversible heat engine. A special aspect of GDSs is they have both the conservative force of buoyancy and the conservative force of gravity acting to store potential energy as heat dissipates out of the gravity well. The model also reveals that DSs achieve average values of positive net changes in internal energy, stored potential energy, and non-equilibrium entropy when the DS achieves far-from-equilibrium steady state, revealing that DSs grow to steady state values of stored energy based upon the amount of heat they are dissipating.

Part I of the series also defines the properties of auto-powering capacity (APC) and auto-restoring order (ARO) of a DS and mathematically develops examples for the tropospheric water cycle (TWC) and tropospheric air cycle (TAC) [1] (Section 4.3), revealing that the combination of dissipating heat and the conservative force of gravity results in more power in the form of kinetic mass flow added to the total power throughput of Earth beyond just the solar insolation of the Sun. The power of kinetic mass also carries stored gravitational potential energy that can be passed with the moving material through a network of GDSs spread throughout the lithosphere, hydrosphere, and atmosphere. This results in a massive mixing of water, air, and heavier elements on Earth [1] (Section 4.7).

Part I of the series also mathematically develops additional properties of DSs: specific universal entropies [1] (Equations 29, 37, and 41), complexity yield [1] (Equation 33), specific heat quality outputs [1] (Equations 45 and 49), specific heat quality drops [1] (Equations 46, 50, and 58), and heat transformation effectivity [1] (Equation 53). Two theorems associated with heat transformation effectivity and efficiency of a DS are presented, revealing that DSs perform better at greater local heat sink temperature, producing the same complexity yield with greater heat quality output and no change in efficiency, unlike non-conservative engineered forced convection heat engines that lose efficiency and work output at greater local heat sink temperatures. The efficiency of a DS is coupled to its conservative force field that is not affected by local heat sink temperature. Part I concludes that there is no local negative entropy effect associated with DSs and suggests that the storage of energy using material properties coupled to conservative force fields has an impact on Boltzmann's statistical entropy that is not reflected in Clausius' entropy.

This second paper examines dissipation of heat through chemical systems. Endothermic and exothermic chemical reactions are examined for the effect of the number distribution of elements produces by supernovae on synthesis and decomposition. The Gibbs isolated universe model is evaluated for use in the analysis of chemical reactions occurring in open systems and is compared with an open system model. The chemical dissipative structure (CDS) is modeled using the laws of thermodynamics, and the properties of DSs defined in Part I of this paper series are applied to the CDS. Finally, network ecology theory is applied to GDS and CDS networks to determine network complexity and network heat quality output rate density. The paper concludes on the relationship between entropy, order, and complexity, as well as on the relationship between energy storage and information. These relationships reveal a possible reason why Boltzmann's statistical entropy and Clausius' entropy are not always equal.

## 2. Dissipation of Heat through a Chemical System

Consider a system that is a region of water on Earth within the heat and matter flow of a GDS. This could be in a region of major flow or it could be in a region of minor flow or eddying current. It could be at the sunny surface of a sea in the tropics, a thermal vent in the mid-Atlantic ridge, or in the Gulf Stream flow into the North Atlantic. The matter of the system is an aqueous mixture of undissolved micro- and macro- particulates and dissolved atoms and molecules that have the potential to be chemically reactive and are concentrated in the aqueous solution. Such a body of water is an open system. This example suggests the use of an open system CDS model to study the chemical reactions occurring in the body of water. The following discussion examines models of chemical

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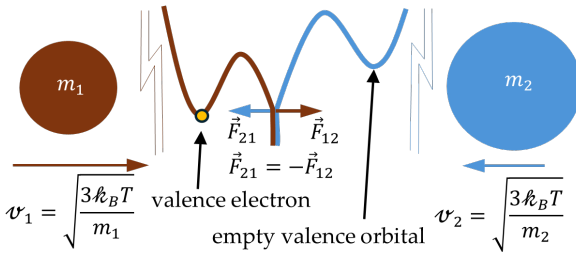
reactions to determine if such a CDS can be modeled in similar fashion to the approach taken above to model GDSs.

The atoms and molecules in solution in the region of water hold the internal energy of heat capacity because of the heat delivered to them directly by the Sun, by GDSs, or by reagents. They dynamically interact with each other by way of their negative-polarity electric fields. In the micro-spaces just outside the orbitals of a group of electrons held by an atom, the negative charge of the group of electrons dominates the generated electric field of the atom over the positive charge of the atomic nucleus. Any two atoms that are not bonded to each other and are kinetically moving toward each other dynamically collide in a Newton's-third-law interaction by way of their electrical fields pushing against each other, Figure 1a. This collision of two electrical force fields of the same polarity is elastic. The force fields are conservative and there is no transverse dissipation dampening that occurs on the atomic level in a collision between two atoms, considering dissipation is a macroscopic phenomenon resulting from matter being comprised of independent microscopic particles.

With the collision of two atoms, valence electrons at the bottom energy plateaus of their lowest possible energy states in their orbitals are pushed up a potential energy well formed between the two atoms with the molecular-kinetic energy of the two atoms pushing toward one another, Figure 1b. This acts as a type of electrical buoyancy of the valence electron, so all of the kinetic energy converts directly into potential energy with no losses. If two atoms have sufficient kinetic energy to buoy the valence electron to the peak of potential energy at the top of the energy well of the interaction of their electric fields, then they achieve activation energy of a chemical reaction, Figure 1c. On a macroscopic scale, when many of these reactions occur, it is the heat that is dissipating through the system of a GDS that is being converted into chemical activation energy.

Upon achieving activation energy, each valence electron of the two atoms involved in the interaction are pushed past the potential energy peak formed by the balance of force between the negatively charged electrons of the atom and the positively charged nucleus and fall into a separate potential energy well of a covalent bond with the positively charged nucleus of the atom that it previously was not bonded with, while staying bonded to its original atom, Figure 1d. This sudden drop in potential energy from the peak of the potential barrier to the bottom of the potential well results in activation energy being converted back into heat dissipating through the aqueous solution, with the valence electron now being shared in the valence electron orbitals of a covalent bond between the atoms, Figure 1e.

If the bottom of the potential energy well of the new bond is at a greater energy level than the bottom of the potential well of the electron orbital that the valence electron inhabited with its source atom, then the bonding reaction is a potential energy storing chemical reaction, with only some of the activation energy converting back to heat, Figure 1e. An example of this is when an atom of lesser atomic number and lesser valence bonds covalently with an atom of greater atomic number and greater valence. This results in one or more electrons being shared covalently, with the electrons

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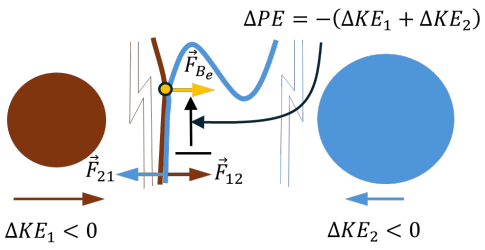


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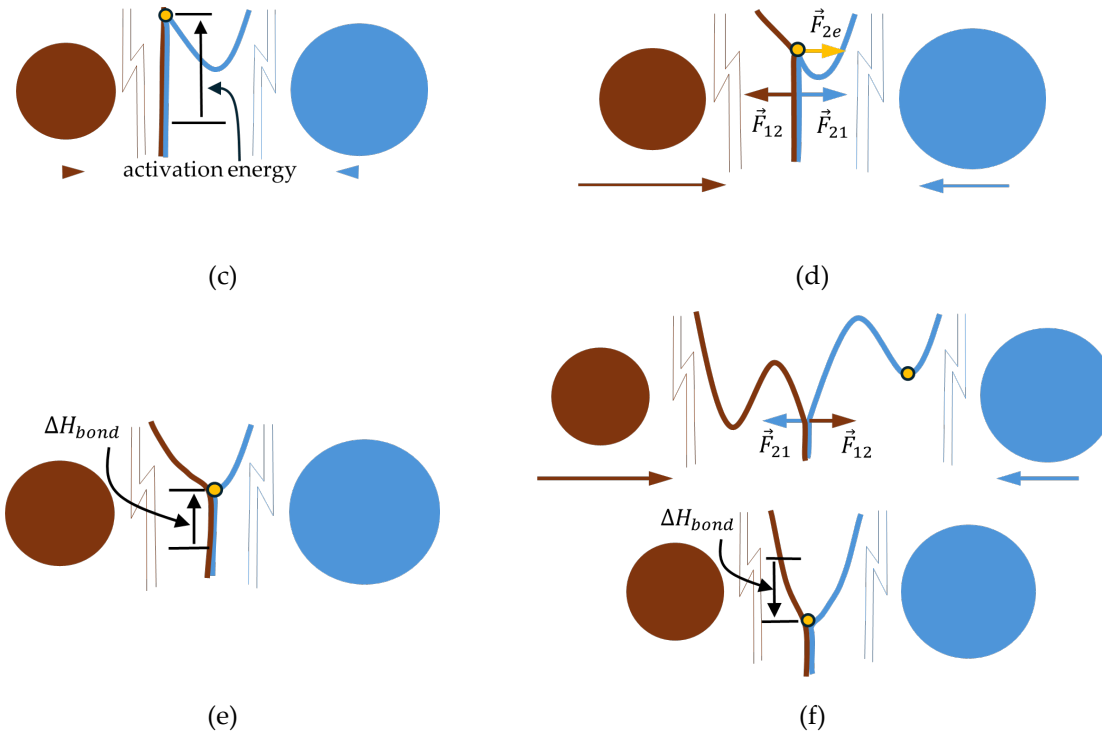


**Figure 1. (a)** Endothermic synthesis. The negative polarity electric fields of two atoms in proximity repel with the force of atom two on atom one being equal and opposite to the force of atom one on atom two in a Newton's-third-law interaction. The velocities of the atoms are based upon their temperature and the Boltzmann constant, $k_B$ , as dictated by the kinetic molecular theory of gases [2]. **(b)** The kinetic energies of the two atoms drive them together. The interaction of the two electric fields drives the valence electron of atom one toward the peak of the electric potential barrier of atom two. The kinetic drive of atom one and atom two driving their negative polarity electric fields against each other creates an electrical force differential pressure on the valence electron toward atom two due to atom one's electric field gradient being greater than atom two. This acts as an electrical buoyant force, $\vec{F}_{B_e}$ , on the valence electron to lift the electron up the hill of the electric potential barrier of atom two. **(c)** The valence electron reaches the peak of the potential barrier of atom two, achieving activation energy by the conversion of kinetic energy of the atoms to electrical potential energy. **(d)** The forces of the atoms on each other flip, resulting in atom one and atom two now pulling on each other by their shared electrical couple to the valence electron. Atom two now has a net electrical force on the valence electron, $\vec{F}_{2e}$ , with no prevailing negative polarity gradient to prevent the valence electron from falling into its valence orbital. This results in the valence electron "rolling down" the side of the potential energy well that is the empty valence orbital. **(e)** The valence electron of atom one is shared by the two atoms, filling the valence orbitals of both atoms in a covalent bond. The change in bond enthalpy, $\Delta H_{bond}$ , is positive. **(f)** Exothermic synthesis. Energy is released as the valence electron falls into a potential energy well at a lower energy level

shifting toward the greater energy states of valence electron orbitals that were previously vacant in the greater-atomic-number greater-valence atom, doing so by absorbing some of the activation energy into the potential energy of the greater electron orbital energy level. If the bottom of the potential well of the new bond is at a lesser energy level than the bottom of the potential well of the electron orbital that the valence electron inhabited with its source atom, then the bonding reaction releases the valence electron potential energy to heat, Figure 1f, with all the activation energy also converting back to heat. An example of this is when an atom of lesser valence that is in a greater period of the periodic table bonds covalently with an atom of greater valence that is in a lesser period table. This results in one or more electrons being shared covalently, with the electrons shifting toward the lesser energy states of valence electron orbitals that are vacant in the greater-valence-lesser period atom. In doing so, the valence electrons also release some potential energy as they "fall" to lesser

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valence electron orbital energy levels. The potential energy of valence electrons in their bonded orbitals is known as bond enthalpy.[1]

The forming and breaking of covalent bonds is a chemical reaction. When a chemical reaction occurs, two or more molecular reactants are driven kinetically together to form one or more new molecular products. The reaction can break previously existing bonds and create new bonds. Note that the forming of a bond that increases bond enthalpy when it forms will release that bond enthalpy when it breaks, and a bond that releases bond enthalpy when it forms will gain back that bond enthalpy when it breaks. A net positive change in bond enthalpy, $\Delta H_{bond}$, because of a chemical reaction is due to the products of the chemical reaction having more bond enthalpy than that of the original reactants. A net negative change in bond enthalpy is a result of the opposite.

### *2.1. General Chemical Reaction Model*

The modeling of the chemical reaction begins with a return to the open-system simple heat transfer model in a conservative force field as developed in [1] (Equation 11). A net positive change in bond enthalpy of the product molecules of the chemical reaction over the reactant molecules is a net positive change in the equilibrium level(s) of the potential energy well(s) within which the valence electron(s) reside(s). For a chemical reaction system, the change in potential energy is defined as the change in bond enthalpy,

$$\Delta U_{PE-sys} \equiv \Delta H_{bond} \,. \tag{1}$$

For a chemical reaction that results from a dissipation of heat that drives reactant molecules together, the molecular-dynamic impulse of the collision results in a molecular level of work that converts the molecular-kinetic energy of the molecules into increasing potential energy up to the activation level of a chemical reaction. Even though this is technically work being performed on a molecular level to buoy valence electrons against the of the periodic repulsive force of the negatively polarized electric field, the impulse of the interaction is already factored into the first law of thermodynamics as the net heat input process property, $\Delta Q_{sys}$. There is no work input in this model and therefore no need for the work input process property, $W_{in}$. Physically what is happening is that molecular-dynamic work is being done to either convert dissipating heat to bond enthalpy or bond enthalpy to dissipating heat,

$$\Delta U_{Q-sys} + \Delta H_{bond} = \Delta Q_{sys} \,. \tag{2}$$

What remains to be analyzed is the $\Delta U_{Q-sys}$ term. In addition to changing bond enthalpy, a change to internal energy results from a change in heat capacity of the products of a chemical reaction relative to the reactants. This converts dissipating heat into a net positive or net negative change in molecular-kinetic energy stored in the 3N degrees of freedom that make up the heat capacity of N bonded atoms of the product molecules of a chemical reaction relative to the reactants. The reaction affects the ability to capture more or less heat as internal energy for the same temperature. The sum of the numbers of atoms of the products of the chemical reaction is exactly the same as the sum of the numbers of atoms of the reactants, so a chemical reaction does not change the number of degrees of freedom. However, some of the degrees of freedom of the atoms in the molecular structures of the

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[1] The electrical-potential wells of a chemical bond are a result of the electrical field of the positively charged nuclei of the atoms of the reacting particles dominating the electrical field in the presence of each's electrons, thus attracting the electrons weakly from one atom to the other to create an ionic bond or attracting electrons more strongly to create a covalent bond. This potential well can be compared to water that is evaporated at sea level and then carried over a mountain where it then rains and collects in a mountain lake. The mountain lake is at a higher altitude than sea level, and so not all of the potential energy that was stored in the gravitational field is released. This is endothermic. It is also possible for water to be evaporated from a mountain lake, and then rained on the plains below, resulting in an exothermic process.

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products can become more or less able to hold molecular-kinetic energy compared to those same atoms in the molecular structures of the reactants. The amount of the change in heat capacity of the products relative to the reactants depends upon several factors that affect the involvement of these degrees of freedom in holding heat, including the molecular structures, the phases, and the temperature of the reactant and product molecules. At standard temperature and pressure, molecules with greater numbers of bonded atoms tend to have lower heat capacities. A chemical reaction tends to result in a negative change in heat capacity when reactant molecules with fewer atoms per individual molecule become one or more product molecules with more atoms per individual molecule, even if the products include a molecule that is comparable in number of atoms to the reactant molecules. This is because molecules with greater numbers of atoms tend to inactivate vibrational-mode degrees of freedom of some of the atoms. However, this is case specific.

This heat absorption or release associated with the change in heat capacity of the products of a chemical reaction relative to the reactants is different than the heat absorption or release of a substance as determined by its change in temperature. This heat absorption or release is not a result of a change in temperature but is a result of an increase or decrease in the capacity of the degrees of freedom of the products of the reaction to hold more or less heat for the same temperature relative to the reactants. Thus, even though the temperature does not change, the products absorb more or less heat present in the environment at the same temperature. This is key to understanding how dissipating heat through an aqueous solution that results in a chemical reaction that changes the average heat capacity can result in extra heat being absorbed into or released from internal energy when there is no change to the temperature gradient that is driving the dissipating heat. The change of the internal energy of heat capacity as a result of a change in heat capacity is put in terms of a change in system entropy (Equation 6 of [1]) with any change in system termpature equalizing by heat transfer, $\Delta Q_{sys}$. This results in the energy balance,

$$\Delta H_{bond} + T_{avg}\Delta S_{sys} = \Delta Q_{sys} . \quad (3)$$

This reveals that a heat flow process can result in two forms of stored energy resulting from a chemical reaction, the first being a result of a net change in bond enthalpies and the second being a result of a net change in heat capacities. Compared to the change in bond enthalpy of products relative to the reactants, change in the internal energy of heat capacity of the products compared to the reactants tends to be as much as one or two magnitudes lesser of an effect in chemical reactions occurring near standard temperature and pressure.

When the contributions to the change in the internal energy of bond enthalpy are summed with the change in the internal energy of heat capacity, the sum is generally called a change in enthalpy of the system,

$$\Delta H_{sys} \equiv \Delta U_{sys} \equiv \Delta H_{bond} + T_{avg}\Delta S_{sys} . \quad (4)$$

Combining Equation 4 with Equation 3 results in first law of thermodynamics for isochoric chemical reactions now involving a change in system enthalpy,

$$\Delta H_{sys} = \Delta Q_{sys} . \quad (5)$$

As noted above, the change in internal energy of heat capacity resulting from an increase in the number of bonded atoms tends to be negative. The increase in total bond enthalpy of the products of the reaction as a result of having more bonded atoms tends to dominate over the decrease in total internal energy of heat capacity of the products, making most such reactions endothermic.

### *2.2. The Isolated Universe Model of Chemical Reactions and Gibbs Free Energy*

A separate model to consider is that of the universe as an isolated system developed by Josiah Gibbs in 1873 [3]. This model contains an aqueous solution of the molecular reactants, reagents, catalysts, and cofactors of some chemical reaction with the solution at some temperature. The water with chemical reactants is isolated from all heat exchange, work exchange, and material exchange

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with anything outside, effectively making it an isolated universe unto itself that is treated as an ideal near-equilibrium universe. The question to be answered is whether the chemical reaction will occur spontaneously. A spontaneous chemical reaction is one that occurs between time zero when the "universe in a bottle" is created and some indefinite time in the future without assistance from outside of the universe.

Consider the entropy balance of the change in entropy of the isolated universe being a sum of the change in universal entropy as the reactants become the products (subscript *prds*) of the reaction, $\Delta S_{prds}$, and the change in universal entropy as the surroundings made up of the water of the solution either release heat to the chemical products or dissipate from the chemical products, $\Delta S_{water}$, with the chemical products plus the water making up the entire universe in a near equilibrium condition,

$$\Delta S_{uni} = \Delta S_{prds} + \Delta S_{water} . \tag{6}$$

Considering that the entire solution starts at the same temperature, either a generation of heat or an absorption of heat resulting from the reaction of the chemicals must transfer into or out of the water, $Q_{water}$, in accordance with the second law of thermodynamics, bringing all constituents of the universe to a new equilibrium temperature, $T_{sol}$. This means that the water is either a heat source or a heat sink. With such a heat transfer, applying the definition of entropy (Equation 5 of [1]) to the change in entropy of the water results in,

$$\Delta S_{uni} = \Delta S_{prds} + \frac{Q_{water}}{T_{sol}} . \tag{7}$$

The chemical products in the model either generate heat that transfers to the heat sink of the water or absorb heat that transfers from the heat source of the water, $Q_{prds}$, upon the reaction occurring. This means that we can treat the chemicals involved in the reaction as an open system within the isolated universe of the water. The heat is the sum of the net difference of bond enthalpies and internal energies of heat capacities between the products and reactants as shown in the general chemical reaction model of Equation 4 and Equation 5, the resulting heat going to or coming from covalent bonds and degrees of freedom of chemical products as they change from being reactants. Applying Equation 4 to this model, the change in enthalpy of the products over the reactants is put in terms of the change in bond enthalpies of the products over the reactants and the change in internal energies of the heat capacities of the products,

$$\Delta H_{prds} = \Delta H_{bond-prds} + T_{sol}\Delta S_{prds} . \tag{8}$$

Equation 5 is a model for an open system in which the reactant molecules involved in the chemical reaction are considered to be a system separate from the water they are in. When considering a fixed quantity of reactant molecules as a system and the heat that is generated and passes between the system and the surrounding water as a result of reactant molecules undergoing chemical reactions until equilibrium is reached, then Equation 5 can be used for this isolated universe model to reveal,

$$\Delta H_{prds} = Q_{prds} . \tag{9}$$

As noted above, as this heat goes to or comes from the chemicals, it comes from or goes to the water,

$$Q_{water} = -Q_{prds} . \tag{10}$$

Substituting Equation 9 and Equation 10 into Equation 7 results in the change in entropy of the universe in terms of the change in enthalpy,

$$\Delta S_{uni} = \Delta S_{prds} - \frac{\Delta H_{prds}}{T_{sol}} . \tag{11}$$

This theoretical change in enthalpy of the open chemical system in the isolated universe can be determined empirically using the difference between the sum of the enthalpies of formation of the

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products and the sum of enthalpies of formation of the reactants that are determined experimentally. The difference is defined to be the number of moles, $n$, involved in the chemical reaction multiplied by the enthalpy of the reaction or reaction enthalpy, $\Delta H^{o}$,

$$\Delta H_{prds} = \sum n\Delta H_f^o(products) - \sum n\Delta H_f^o(reactants) \equiv n\Delta H^{o}\,, \tag{12}$$

determined empirically in units of energy per mole.[2]

From here forward, all equations are converted into *per mole* quantities (*per mole* is symbolized by superscript o), using the term *enthalpy of the reaction* or *reaction enthalpy*. Though change in system enthalpy and reaction enthalpy are defined by two different models, they are both the sum of the net difference between the bond enthalpies of the products and reactants and net difference between the internal energies of heat capacities of the products and reactants, with reaction enthalpy and the associated change in bond enthalpy per mole and change in internal energy of heat capacity per mole determined on a per mole basis.

Converting Equation 11 to per-mole terms, the Gibbs free energy [3] is defined as the product of the negative of the temperature of the solution and the change in entropy of the universe,

$$\Delta G^{\circ} \equiv -T_{sol}\Delta S_{uni}^{o} = \Delta H^{\circ} - T_{sol}\Delta S_{prds}^{o}\,. \tag{13}$$

Tests of the model confirm that the Gibbs free energy of such a reaction must be negative for the change in entropy of the isolated universe to be greater than zero. The second law of thermodynamics is applied to changes in entropy of an isolated universe between equilibrium states requires and reveals that the change in entropy of the universe must be greater than zero. Therefore, the Gibbs free energy must be negative for the reaction to be able to occur at some indefinite time period following the initial creation of the solution, i.e., spontaneously.

Examine the change in entropy of the universe more closely by substituting Equation 8 into Equation 11. The net difference in internal energies of the heat capacities cancels out of the equation for the change in entropy of the universe,

$$\Delta S_{uni}^{o} = \Delta S_{prds}^{o} - \frac{\left(\Delta H_{bond-prds}^{o} + T_{sol}\Delta S_{prds}^{o}\right)}{T_{sol}} = -\frac{\Delta H_{bond-prds}^{o}}{T_{sol}}\,. \tag{14}$$

The change in entropy of the universe as a result of transitioning between chemical equilibrium states must be greater than or equal to zero for any process involving the dissipation of heat that does not involve work or heat process from outside of the universe. Applying this to Equation 14 results in the negative of the net difference in bond enthalpies per mole between the products and reactants of the chemical reaction divided by the temperature of the solution being greater than or equal to zero. This provides a solution that the net difference in bond enthalpies per mole must be zero or negative for the chemical reaction to occur spontaneously only due to heat dissipation to equilibrium,

$$\Delta S_{uni}^{o} = -\frac{\Delta H_{bond-prds}^{o}}{T_{sol}} \geq 0 \Rightarrow \Delta H_{bond-prds}^{o} \leq 0\,. \tag{15}$$

A net zero difference in bond enthalpies per mole is not of concern in this analysis, because there is no net release or storage of energy in the covalent bonds. A net negative difference in bond enthalpies per mole only can mean that a spontaneous chemical reaction results in a net release of energy from covalent bonds. Applying Equation 9 to Equation 13 verifies that a net release of covalent bond energy (i.e., a negative change in bond enthalpy per mole) is indeed a negative Gibbs free energy,

$$\Delta G^{\circ} = \Delta H_{bond-prds}^{o} + T_{sol}\Delta S_{prds}^{o} - T_{sol}\Delta S_{prds}^{o} = \Delta H_{bond-prds}^{o}\,. \tag{16}$$

The isolated universe model does not allow work and heat processes to occur across the boundary of the universe. This meets with the definition of the real universe, i.e., the universe is

[2] Values of enthalpies of formation are determined experimentally by empirical measure. This enables reaction enthalpies to be calculated.

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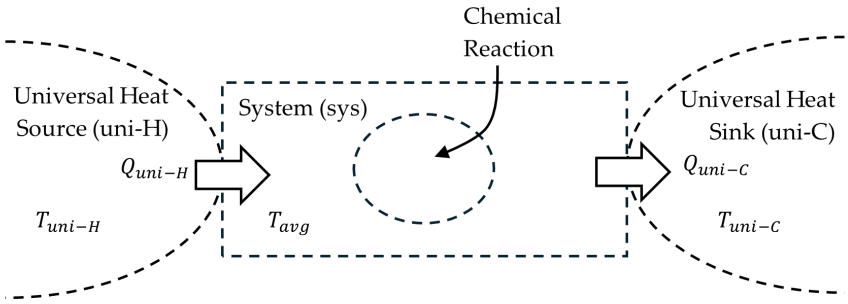
everything and therefore there is nothing outside of the universe with which it can react. However, unlike the isolated universe model discussed here, the real universe is filled with sources of macroscopic work and heat other than a single fixed set of chemicals associated with a single chemical reaction. The isolated universe model is used to analyze controlled chemical reactions in the lab or on the chemical manufacturing process. To consider how other sources of work and heat inside the universe can affect a chemical reaction, expand the scale of this isolated universe model to be our actual universe. Now put stars in it that are generating high temperature heat from the release of fusion energy and put gravity wells in it formed by the coalescence of matter. Heat from stars radiating onto planets of matter in gravity wells result in the macroscopic work of GDSs discussed earlier, resulting in massive mixing of material as heat dissipates across the planet. Focus in on any particular collection of an aqueous solution of water and chemicals of some defined boundary and note the material and heat flowing into and out of that boundary driven by GDSs. This is an open system within the isolated universe into and out of which is flowing heat, water, and numerous elements, molecules, ionized salts, and particles of minerals. The chemical reactions are not isolated from external heat and work sources.

This reveals the challenge with using Gibbs free energy to evaluate whether a chemical reaction can occur in nature. The Gibbs free energy equation does not consider work and heat processes occurring within the universe outside of the chemical system. It only considers heat dissipation as the chemical system transitions from equilibrium to equilibrium as a result of spontaneous chemical reactions (reactions without external heat or work to activate them). It does not allow the consideration of open, far-from-equilibrium chemical systems within the universe. When considering chemical reactions occurring in nature, say in an open body of water, they are occurring in an open system in which external work interactions and external heat exchanges are not only possible, but normal.

### *2.3. Open System Chemical Reaction Model*

To model the open system of a naturally occurring chemical reaction within the heat dissipation of a GDS, consider a batch of reactants, reagents, catalysts, and cofactors associated with a single chemical reaction equation. This model effectively starts with the isolated universe model, but opens the isolated universe of the controlled laboratory to a surrounding real universe that provides uncontrolled heat inputs and outputs, Figure 2a. Heat dissipates into the reactants from an effectively

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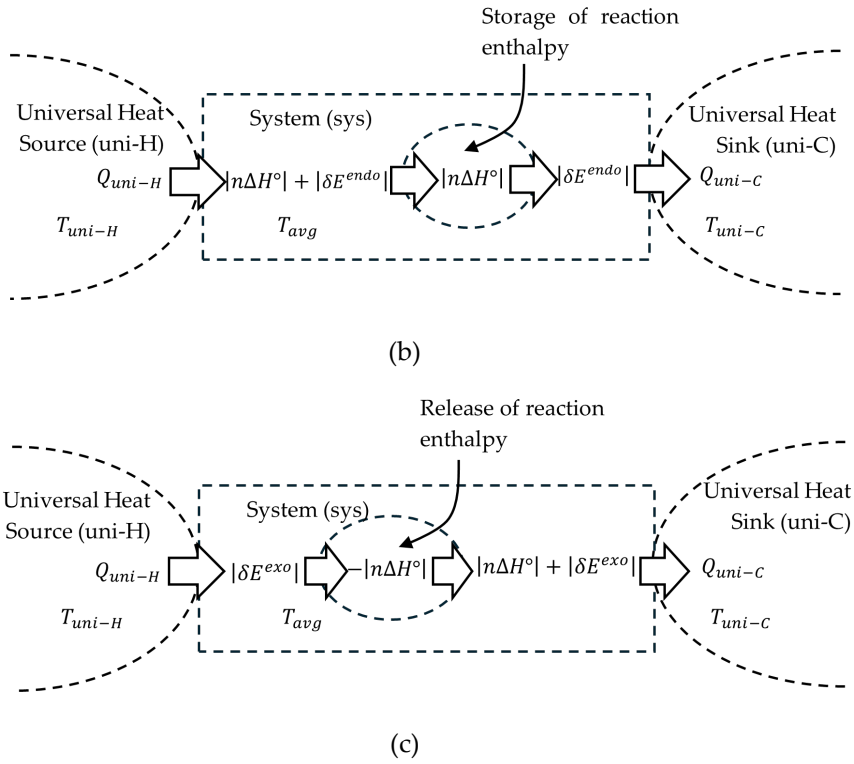


**Figure 2. (a)** Open system chemical reaction model. **(b)** Open system endothermic chemical reaction model. Heat input provides enough internal energy for it to equal or exceed the activation energy of the endothermic chemical reaction and provide sufficient available energy for storage of reaction enthalpy. Heat output to the universal heat sink is the remaining internal energy of the system following the chemical reaction and the storage of reaction enthalpy. **(c)** Open system exothermic chemical reaction model. Heat input provides enough internal energy for it to equal or exceed the activation energy of the exothermic chemical reaction. Heat output to the universal heat sink is original activation energy plus the released reaction enthalpy.

unlimited heat source, activating the reactants and resulting in ongoing spontaneous chemical reactions of the batch. There are two possible results regarding reaction enthalpy in such a system mathematically modeled by Equation 4 and Equation 5.

The first result of heat dissipation through an open chemical system is shown in Figure 2b. When there is a net positive change of the sum of the changes in bond enthalpies and changes in the isothermal internal energies of heat capacity of the products of the reaction relative to the reactants of the reaction, this means there is net positive reaction enthalpy. For there to be enough energy to make this chemical reaction happen, the heat input must be equal to the reaction enthalpy plus some additional amount of energy per mole, $\delta E^{endo}$, needed to achieve activation energy (also in units of energy per mole) for the chemical reaction. Such a chemical reaction is endothermic, capturing some of the dissipating heat in the storage of energy that cannot now dissipate to the heat sink. The portion of the activation energy that is released, $\delta E^{endo}$, as the products of the reaction form is excess heat that dissipates into the heat sink. The change in universal entropy,

$$\Delta S_{uni} = \left(\frac{|\delta E^{endo}|}{T_{uni-C}}\right) - \left(\frac{|n\Delta H°| + |\delta E^{endo}|}{T_{uni-H}}\right) > 0\,, \tag{17}$$

is positive because $T_{uni-H} \gg T_{uni-C}$, making the second term of Equation 17 much smaller than the first term. Therefore, the endothermic chemical reaction is spontaneous in an open system with sufficient heat input.

The second possible result is an exothermic reaction in which there is a net negative change of the sum of the change in bond enthalpy and the change in the isothermal internal energy of heat capacity of the products of the reaction relative to the reactants of the reaction, Figure 2c. This is a

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negative reaction enthalpy. This is a result of the net positive conversion of stored energy into dissipating heat. For there to be enough energy to make this chemical reaction happen, the heat input, $\delta E^{exo}$, must be equal to the activation energy for the chemical reaction. The heat of the activation energy plus the enthalpy of the exothermic chemical reaction that are both released upon the formation of the products of the reaction then dissipates to the heat sink. The change in universal entropy,

$$\Delta S_{uni} = \left(\frac{|n\Delta H°| + |\delta E^{exo}|}{T_{unic}}\right) - \left(\frac{|\delta E^{exo}|}{T_{uni-H}}\right) > 0\,, \tag{18}$$

is positive again because $T_{uni-H} \gg T_{uni-C}$, making the second term of Equation 18 much smaller than the first term. Therefore, the exothermic chemical reaction is also spontaneous in an open system with sufficient heat input.

Neither the endothermic nor the exothermic reactions are limited in their ability to occur spontaneously in nature. This differs from the conclusion that is reached when the isolated universe model with Gibbs free energy is applied to try to explain naturally occurring chemistry on Earth, especially in the literature studying pre-biotic chemistry [4–6]. Table 1 shows for the isolated universe model that only one of the three possible cases of endothermic reactions is spontaneous and two of the three possible cases of exothermic reactions are spontaneous. For the open system chemical reaction model, Table 1 shows that all chemical reactions occur spontaneously with sufficient heat input, regardless of what happens in an isolated universe model. The question for an open system chemical reaction is not whether the chemical reaction is spontaneous, because they are all spontaneous with the right heat input conditions. As exhibited in Figure 2b and Figure 2c, the endothermic reaction has a net storage of energy, whereas the exothermic reaction has a net release of energy, both resulting in a positive change in universal entropy. The storage of energy indicates a generation of complexity. The question for an open system chemical reaction is whether it generates complexity.

**Table 1.** Isolated Universe Model vs. Open System Chemical Reaction Model.

| Isolated Universe Model | | | Chemical Reaction Parameters | | | | | Open System Chemical Reaction Model | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Conditions | Results [1] | $\Delta S_{univ} > 0$ | $\Delta H°$ | $T\Delta S°$ | $\Delta G°$ | $\Delta H°_{bond}$ | Type [2] | $\Delta S_{univ} > 0$ | Results [1] | Conditions |
| Mathematically Undefined | | | + | – | – | – | undef | Mathematically Undefined | | |
| All $T_{sol}$ | NonSp | | + | – | + | + | Endo | ✓ | Sp | $Q_H = n\Delta H° + \delta E^{endo} = nE_a$ |
| High $T_{sol}$ | Sp | ✓ | + | + | – | – | Endo | ✓ | Sp | $Q_H = n\Delta H° + \delta E^{endo} = nE_a$ |
| Low $T_{sol}$ | NonSp | | + | + | + | + | Endo | ✓ | Sp | $Q_H = n\Delta H° + \delta E^{endo} = nE_a$ |
| Low $T_{sol}$ | Sp | ✓ | – | – | – | – | Exo | ✓ | Sp | $Q_H = \delta E^{exo} = nE_a$ |
| High $T_{sol}$ | NonSp | | – | – | + | + | Exo | ✓ | Sp | $Q_H = \delta E^{exo} = nE_a$ |
| All $T_{sol}$ | Sp | ✓ | – | + | – | – | Exo | ✓ | Sp | $Q_H = \delta E^{exo} = nE_a$ |
| Mathematically Undefined | | | – | + | + | + | undef | Mathematically Undefined | | |

1. NonSp = Non-spontaneous, Sp = Spontaneous.
2. Endo = Endothermic, Exo = Exothermic, undef = mathematically undefined.

If the two systems of Figure 2b and Figure 2c are put together in a cycle in which the exothermic chemical reaction is half of the cycle and the endothermic chemical reaction that is the reverse of the exothermic chemical reaction is the other half of the cycle, the cycle takes on the form of a DS, with the same type of functional involvement of a conservative force in energy storing and energy releasing and the same fundamental thermodynamics as a GDS. If the exothermic and endothermic

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reactions are both the forward and reverse directions of a single chemical reaction, then we know that one must be a synthesis and the other must be a decomposition, with the chemical products of the first half of the cycle being the chemical reactants of the second half of the cycle and the products of the second half of the cycle being the reactants of the first half of the cycle. In the universe of all chemical reactions, both synthesis and decomposition reactions exist that store energy and release energy. Considering that all such reactions can occur spontaneously in nature, the two questions to be answered are regarding whether either the synthesis or the decomposition dominates the leading of CDS cycles and regarding whether an exothermic reaction or endothermic reaction dominates the leading of CDSs.

To answer the first question, consider a primordial collection of atoms in a mixture of an ionic plasma and a dust cloud floating in a nebula of older and newly forming stars following the first ever supernova of an original star of the universe that has occurred in the nebula. The mixture of ionic plasma and dust contains a mixture of all of the elements with half-lives that are long enough for the elements to be found in nature. The moment in time is just before the first ever formation of a molecule by a chemical reaction between two atoms. This first chemical reaction is a synthesis. It is not a decomposition chemical reaction, because there is no molecule yet to decompose. Another way to look at this is to analyze the progression of the newly born universe through the formation of elementary particles, followed by atoms, followed by molecules. In the case of the early universe, chemical synthesis must precede chemical decomposition in pre-biotic progression. Both of these analyses suggest that the dominant natural CDS cycles start with synthesis and end with decomposition.

To answer the second question of whether the leading reaction is endothermic or exothermic, consider the production ratio in the lifecycle of a star of the atomic elements on the periodic table. In general, the trend is for the production ratio of lesser-valence atoms to greater-valence atoms of the same or greater period is much greater than the production ratio of lesser-valence atoms to greater-valence atoms of a lesser period [7–11]. It is the latter set of permutations of two atoms that have the lesser production ratio that synthesize while decreasing storage of bond enthalpy. Higher-energy-orbital-valence electrons shift toward vacant lower-energy-valence shells in the formation of the covalent bond of a lesser-valence atom with a greater-valence atom in a lesser period, thus releasing bond enthalpy to heat in the formation of a covalent bond. Therefore, the former set of permutations of two atoms that have greater production ratio of lesser-valence atoms to greater-valence atoms of the same or greater period results in covalent bonds between lesser-valence and greater-valence atoms that synthesize while increasing storage of bond enthalpy. This suggests that bonding reactions that dominate because of greater production ratios of the set in stars (greater set abundance in nature) and increase storage of bond enthalpy dominate the heat dissipation pathways of the GDSs of the solar system and Earth. Recall earlier with the derivation of Equation 5 that synthesis tends to decrease the total internal energy of heat capacity of the products of the reaction compared to the reactants. However, the increase in storage of bond enthalpy dominates, resulting in the dominating synthesis reactions being endothermic.

It is noteworthy that any molecules that do synthesize exothermically will either decompose endothermically back into smaller molecules or they will exothermically grow large enough to be involved in an endothermic reaction that synthesizes a larger molecule. The latter pathway adds to the dominance of endothermic synthesis in being the majority of CDSs in nature. Thus, even exothermic synthesis that can occur with the chemical reaction that generates the smallest of molecules eventually leads to endothermic synthesis as these smaller molecules bond to make larger molecules.

The result is that the CDSs that dominate nature and therefore lead the majority of cycles are endothermic synthesis reactions. The dominating CDS has an endothermic synthesis reaction at stage 2 and the reverse reaction of exothermic decomposition at stage 4. This means that the dominating CDSs have a net storage of energy at stage 2, resulting in complexity being generated by the majority of CDSs occurring in nature. This aligns with the function of GDSs in their generation of complexity.

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Nature is dominated by gravitational and CDSs that increase complexity. The next step is to analyze the CDS that increases complexity using the same method as used above for the GDS.

*2.4. CDS Model of a Leading Endothermic Auto-Synthesis*

Appendix A provides an analysis of the CDS of a leading endothermic auto-synthesis that is depicted in Figure A1. In this model, an ongoing flux of heat and matter into and out of the system drives the chemo-dynamics. The term auto-synthesis is used here to describe a spontaneous chemical reaction that results in a net increase in molecular bonds. Heat input at stage 1 is a result of excess differential forces between the molecules of a heat source and the molecules involved in the reaction. Heat, reactants, reagents, catalysts, and cofactors come together in water and undergo a chemical reaction that results in a chemical synthesis that stores energy. The molecules involved in the reaction bring internal energy of heat capacity with them because of heat input directly from the Sun, from GDSs, or from the stored energy of reagents,

$$Q_H^{S1} = Q_H^{sun} + Q_H^{gds} + Q_H^{rgnt} \rightarrow \Delta U_Q^{S1} . \quad (19)$$

Heat is driven from the heat input at stage 1 through to the stage 3 heat exhaust by a temperature gradient of a gravitational dissipation structure. This heat dissipating down the temperature gradient acts to drive any two atoms of interacting molecules up the conservative electrical potential barriers of each's electrical fields at stage 2 (also Equation A4),

$$\Delta H_{sys}^{S2} = |Q_H^{S1}| - |Q_C^{S3}| . \quad (20)$$

The result is that the valence electrons of one atom are buoyed up the electrical field barrier of the other atom, Figure 1. The buoy-action of the negative polarity electrical fields on the valence electrons is a result of the internal energy of the atoms exhibited on the molecular scale as kinetic energy. This buoying effect on valence electrons forms the basis of the CDS. Considering a chemical reaction involves two molecules, multiple pairs of atoms could be interacting in this way, with the net effect being endothermic.

The endothermic reaction involves two or more reactants that are driven by the molecular-kinetic energy measured by their temperatures, with the assistance of possible reagents that provide additional sources of heat from energy they have stored at activated levels. The energy of reagents helps drive reactants together if heat being dissipated through the system to the reactants is not great enough to drive the interacting atoms of the reactants to activation energy level, the top of the electrical-potential barrier of the atom receiving the valence electrons. Catalysts assist in lowering these barriers, thus reducing activation energy needed for a reaction. Cofactors can also assist in any number of specific ways but generally help guide and redirect the momentum of molecules and their atoms toward chemical bonding orientation and configuration using electrodynamics. During stage 2, the result is a positive reaction enthalpy (also Equation A10),

$$\Delta H_{sys}^{S2} = \left|n\overrightarrow{\Delta H^{\circ}}\right| . \quad (21)$$

Figure 3 shows that the internal energy generated by the heat sources achieves activation energy of the reactants to produce an endothermic chemical reaction at stage 2, resulting in a reaction enthalpy of net stored energy that is a net sum of the differences of bond enthalpies and internal energies of heat capacity of the products over the reactant in the transition from reactants to products. What remains is an internal energy of the chemical system comprised of the amount of activation energy that is not stored as reaction enthalpy. The remaining internal energy is output immediately following the chemical reaction as heat to the heat sink at stage 3 (also Equation A13),

$$|Q_C^{S3}| = |\delta E^{endo}| . \quad (22)$$

The CDS heat engine cycle completes at stage 4 with an auto-decomposition that is the ARO decay process. The term auto-decomposition is used here to describe a spontaneous chemical reaction

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that results in a net decrease in molecular bonds. Auto-decomposition is exothermic, releasing reaction enthalpy stored in stage 2 (also Equation A18),

$$\Delta H_{sys}^{S4} = |Q_H^{S4}| - |Q_C^{S4}| . \quad (23)$$

The chemical products of stage 2 build up and experience further heat input at stage 4 from the same sources as the stage 1 heat input,

$$Q_H^{S4} = Q_H^{sun} + Q_H^{gds} + Q_H^{rgnt} \rightarrow \Delta U_Q^{S4\text{init}} . \quad (24)$$

The imbalance in chemical product concentrations on the product side of the stage 2 ongoing reactions that are driven by an ongoing influx of heat and reactants to stage 2 result in the reverse exothermic auto-decomposition reaction becoming imbalanced on its reactant side (it being the product side of the forward endothermic auto-synthesis reaction. This imbalance resulting from the far-from-equilibrium state of the CDS drives the reverse action to start and increase in reaction rate until it reaches a steady state with the stage 2 forward reaction. In Figure 4, activation energy is achieved of the reverse, exothermic chemical reaction of the endothermic chemical reaction that

$$\left|\Delta U_Q^{S4\text{init}}\right| \xrightarrow{achieves\ activation\ energy} |nE_a| \xrightarrow{releases\ reaction\ enthalpy} n\overleftarrow{\Delta H^\circ} = -\mathrm{n}\overrightarrow{\Delta H^\circ}$$

$$\xrightarrow{and\ returns\ activation\ energy} |\delta E^{exo}| \xrightarrow{to\ internal\ energy} \left|\Delta U_Q^{S4\text{inter}}\right| = \left|n\overrightarrow{\Delta H^\circ}\right| + |\delta E^{exo}|$$

**Figure 4.** Exothermic auto-decomposition chemical reaction. Initial internal energy at stage 4, $\left|\Delta U_Q^{S4\text{init}}\right|$, is a result of heat input at stage 4 and enables interacting molecules to achieve activation energy, $|nE_a|$, for the chemical reaction. A negative reaction enthalpy, $-\left|n\overleftarrow{\Delta H^\circ}\right|$, results a positive contribution of energy release to internal energy, $\left|n\overrightarrow{\Delta H^\circ}\right|$, with the return of the additional energy that is required to achieve activation energy, $|\delta E^{exo}|$, is released back into an interim change in internal energy for stage 4, $\left|\Delta U_Q^{S4\text{inter}}\right|$.

occurs at stage 2. This results in a release of the reaction enthalpy that was stored at stage 2. The term auto-decomposition is used here to describe an ongoing chemical reaction that is perpetuated by ongoing heat input and the inevitability of entropy as the trend of matter to fall to the lowest energy states of conservative fields. Auto-decomposition is exothermic, releasing the reaction enthalpy that is stored in stage 2.

The auto-decomposition releases the energy that was stored as a net positive combination of bond enthalpy and isothermal internal energy in stage 2. Each valence electron of the covalent bond that is being broken in the decomposition reaction is pushed back up to the top of the potential well of the covalent bond by an activation energy level of heat input that is needed to start the decomposition process. The electron then falls from the activated energy level downhill into the potential well orbital of the nucleus of the atom that provided the electron to the covalent bond and out of bond of the atom with which it was shared or into a new covalent bond with another reactant of the decomposition. The net result of all broken bonds and possibly new bonds is a net release of reaction enthalpy equal and opposite to the reaction enthalpy previously stored at stage 2. This release of stored energy becomes heat that is exhausted from the system at stage 4.

The result of the stage 4 auto-decomposition chemical reaction is a heat output of both the activation energy and the released reaction enthalpy (also Equation A27),

$$|Q_C^{S4}| = \left|n\overrightarrow{\Delta H^\circ}\right| + |\delta E^{exo}| . \quad (25)$$

Stage 4 closes the cycle of the CDS. The products of the auto-decomposition chemical reaction at stage 4 are now available to cycle again through stage 1 with the introduction of more heat and more

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material and on to stage 2 to be reactants for a potentially growing auto-synthesis. Thus, though the system is open to both heat and material moving in and out of the system, the cycle is closed. The net result is that the change in non-equilibrium entropy of the DS for a single cycle is zero and the change in equilibrium entropy of the universe for a single cycle is positive.

*2.5. APC and ARO of a CDS*

For the APC and ARO of a CDS, power per unit volume is used rather than the power per unit area calculations of APC and ARO for GDSs. Just as APC and ARO are done in terms of power per unit area for GDSs because empirical data that is used is in terms of power fluxes, the APC and ARO for CDSs are done in terms of power per unit volume due to standard approaches to empirically determining chemical reaction rates. Consider the steady state net in-flow at stage 1 of heat, reactants, reagents, catalysts, and cofactors for an auto-synthetic endothermic chemical reaction occurring at stage 2 of the CDS. For purposes of our mathematical model, consider a CDS with a single step chemical reaction,

$$\mathrm{a}_1\mathrm{A}_1 + \mathrm{a}_2\mathrm{A}_2 + \cdots + \mathrm{a}_{X-3}\mathrm{A}_{X-3} \rightleftarrows \mathrm{b}_1\mathrm{B}_1 + \mathrm{b}_2\mathrm{B}_2 + \cdots + \mathrm{b}_Y\mathrm{B}_{Y-3}\,, \tag{26}$$

for which the forward reaction is the endothermic auto-synthesis and the reverse reaction is the exothermic auto-decomposition, in which $\mathrm{a}_x$ for $x = 1$ to $X-3$ and $\mathrm{b}_y$ for $y = 1$ to $Y-3$ are coefficients of the reaction, $\mathrm{A}_x$ are reactant molecules, and $\mathrm{B}_y$ are products molecules. Also, consider $\mathrm{a}_{X-2}$ and $\mathrm{A}_{X-2}$ for a reagent molecule, $\mathrm{a}_{X-1}$ and $\mathrm{A}_{X-1}$ for a catalyst molecule, and $\mathrm{a}_X$ and $\mathrm{A}_X$ for a cofactor molecule required for the forward reaction, as well as $\mathrm{b}_{Y-2}$ and $\mathrm{B}_{Y-2}$ for a reagent molecule, $\mathrm{b}_{Y-1}$ and $\mathrm{B}_{Y-1}$ for a catalyst molecule, and $\mathrm{b}_Y$ and $\mathrm{B}_Y$ for a cofactor molecule required for the reverse reaction

A mass balance,

$$\Delta F_{A_{x1}} - \int_0^V \nu_{endo-x1} dV = \frac{dC_{A_{x1}}}{dt}\,, \tag{27}$$

is used to determine the maximum steady state reaction rate density of the auto-synthetic endothermic chemical reaction, $\nu_{endo-x1}$, based upon the least available molecule x1. The reaction rate density is measured as the number of chemical reactions per unit volume per unit time. $\Delta F_{A_{x1}}$ is the net feed rate of batches of coefficient quantity $\mathrm{a}_{x1}$ per second of the least available $A_{x1}$ reactant, reagent, catalysts, or cofactor needed for the reaction. $\frac{dC_{A_{x1}}}{dt}$ is the net collection rate of batches of coefficient quantity $\mathrm{a}_{x1}$ per second of the least available molecule $A_{x1}$ within the volume (the concentration of which is $C_{A_{x1}}$ divided by the product of Avogadro's number and the volume).

To calculate the APC for steady state, Equation 27 is solved for some unknown positive collection rate of $\mathrm{A}_{x1}$ where $\mathrm{A}_{x1}$ could be any of the molecules $\mathrm{A}_1$ through $\mathrm{A}_X$. Assuming the chemical reaction is occurring at a consistent average rate when calculated across the volume of the CDS at steady state, then the integral can be simplified to the product of the chemical reaction rate and the volume of the CDS, leading to

$$\nu_{endo-x1} = \frac{\Delta F_{A_{x1}} - \frac{dC_{A_{x1}}}{dt}}{V}\,. \tag{28}$$

If we eliminate the collection rate from the equation by defining a CDS as only including those molecules engaged in the reaction, the result is the inequality of

$$\nu_{endo-x1} \leq \frac{\Delta F_{A_{x1}}}{V}\,. \tag{29}$$

that provides a maximum reaction rate based upon the worst case inflow of required molecules. This is a maximum reaction rate, considering sufficient heat flow rate must be available to support the reaction rate. The maximum reaction rate also is not necessarily a result of all minimum available molecules being involved in immediate reactions even if sufficient heat is available, but is determined

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empirically based upon the conditions of the solution, including system factors including but not necessarily limited to pressure, temperature, volume of the open system, the presence of cofactors, and mixing intensity.

A series of inequalities are determined based upon the next lowest available molecule required for the reaction. Considering all of the molecules that are required for the reaction in order of availability leads to

$$\nu_{endo-x1} \leq \frac{\Delta F_{A_{x1}}}{V} \leq \frac{\Delta F_{A_{x2}}}{V} \leq \cdots \leq \frac{\Delta F_{A_{xn}}}{V}. \tag{30}$$

This equation reveals that the reaction rate is limited by the next least available molecule required for the endothermic auto-synthetic reaction whenever the previous least available molecule is no longer the least available.

Finally, consider the heat that is available to provide the activation energy for the auto-synthetic endothermic reaction. For this example of a CDS at steady state, heat flow rate into the volume of the CDS provides a minimum of energy to drive the multiple chemical reactions based upon the least available molecule required for the reaction. Considering $\Delta F_{A_{x1}}$ represents a maximum number of chemical reactions per second based upon the inequality of Equation 29, the minimum heat flow rate per unit volume that must be available for use by the CDS to drive a reaction rate based on the least available molecule is calculated by dividing $\Delta F_{A_{x1}}$ by Avogadro's number to obtain the number of mole-batches per second consumed in chemical reactions based upon the least available molecule, $A_{x1}$, and then multiplying that by the activation energy (in units of energy per mole) divided by the volume of the CDS,

$$\frac{\dot{Q}}{V} \geq \frac{\Delta F_{A_{x1}}}{N_A} \cdot \frac{E_a}{V}. \tag{31}$$

Solving Equation 31 for $\frac{\Delta F_{A_{x1}}}{V}$ and merging it with Equation 29 results in a maximum reaction rate in number of reactions per second,

$$\nu_{endo-x1} \leq \frac{\Delta F_{A_{x1}}}{V} \leq \frac{\dot{Q} \cdot N_A}{E_a \cdot V}. \tag{32}$$

The APC of the CDS now becomes the heat rate flow into the CDS per unit volume that produces the maximum reaction rate at steady state,

$$\mathbb{T}_{cds}^{APC} = \frac{\dot{Q}}{V} = \frac{\nu_{endo-x1}}{N_A} \cdot E_a. \tag{33}$$

Based upon the CDS model of a leading endothermic auto-synthesis, Figure A1, the heat inflow must provide a minimum amount of energy to achieve the endothermic activation energy, as described by the model,

$$\mathbb{T}_{cds}^{APC} = \frac{\nu_{endo-x1}}{N_A} \cdot E_a^{endo} \tag{34}$$

ARO is developed with similar logic based upon the reverse auto-decomposition reaction of Figure A1., but with the idea previously presented for GDSs that it is associated with the heat associated with the release of stored energy. The released heat of exothermic auto-decomposition chemical reaction, $E_r^{exo}$, is the released reaction enthalpy plus the exothermic activation energy, $\left|\overrightarrow{\Delta H^{\circ}}\right| + |E_a^{exo}|$, resulting from local heat input of $Q_H^{exo}$ to the molecules that make up the CDS in order to achieve the activation energy for the reverse reaction. The exothermic chemical reaction rate, $\nu_{exo-y1}$, is based upon the least available molecule, $B_{y1}$, and is also determined empirically based upon the unique conditions of the open system for endothermic auto-decomposition. This results in the ARO of the CDS model of a leading endothermic auto-synthesis,

$$\mathbb{T}_{cds}^{ARO} = \frac{\nu_{exo-y1}}{N_A} \cdot E_r^{exo} \text{ where } E_r^{exo} = \left|\overrightarrow{\Delta H^{\circ}}\right| + |E_a^{exo}|. \tag{35}$$

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Once steady state is achieved, the reaction rate of the stage 4 reaction is equal to the reaction rate of the stage 2 reaction, resulting in the ratio of the APC to the ARO being the ratio of the endothermic reaction activation energy to the exothermic reaction release energy.

*2.6. Intensive State Properties of the CDS*

Specific universal entropies, complexity yield, specific heat quality drops, specific heat quality outputs, and heat transformation effectivity are defined for the CDS using the same approach as for the GDS. For these equations, just as for APC and ARO, the activation energies of the endothermic and exothermic chemical reactions are used. Activation energies are in units of energy per mole. For the properties that are divided by mass, a kilogram molar mass of the reaction is used instead. When dividing activation energy by kilogram molar mass of the reaction, the unit of moles cancels in the numerator and denominator, leaving kilograms in the denominator.

The kilogram molar mass of the reaction term is determined by summing the products of the coefficients and the kilogram molar masses for the reactant molecules $i = 1$ to $X - 3$ on the left-hand side or product molecules $j = 1$ to $Y - 3$ on the right-hand side of Equation 26. These are all molecules that are utilized by the CDS in the actual storage of reaction enthalpy. The sum is calculated using

$$\sum M = \sum_{x=1}^{X-3} a_x M(A_x) = \sum_{y=1}^{Y-3} b_y M(B_y)\,, \tag{36}$$

where $M(A_x)$ or $M(B_y)$ is the kilogram molar mass (in kilograms per mole) of $A_i$ or $B_j$ with coefficients $a_i$ and $b_j$ from Equation 26 providing the reaction multiplier to get the total kilograms per mole of each molecule. The result is the kilograms per mole of the reaction. This expression is abbreviated as $\sum M$ for a single CDS. The following equations are developed using the general forms of the equations defined in Part I of this paper series [1] (Section 4) and the Figure A1 model of the CDS.

Applying Equation 29 of [1] for specific maximum universal entropy, the total heat input $Q_{loc-H}^{Tot} = Q_H^{S1} + Q_H^{S4} = \left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{endo}| + |\delta E^{exo}| = nE_a^{endo} + nE_a^{exo}$ results in

$$\Delta s_{max}^{CDS} = \left(\frac{E_a^{endo} + E_a^{exo}}{\sum M}\right)\left(\frac{1}{T_{uni-C}} - \frac{1}{T_{uni-H}}\right). \tag{37}$$

Applying Equation 37 of [1] for specific conditional universal entropy, the heat input,

$$Q_{loc-H}^{S1\to 2} = \left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{endo}| = nE_a^{endo}\,, \tag{38}$$

and heat output,

$$Q_{loc-C}^{S3} = |\delta E^{endo}| = nE_a^{endo} - \left|n\overrightarrow{\Delta H^{\circ}}\right|\,, \tag{39}$$

results in

$$\Delta s_{con}^{CDS} = \frac{1}{\sum M}\left(\frac{E_a^{endo} - \left|\overrightarrow{\Delta H^{\circ}}\right|}{T_{uni-C}} - \frac{E_a^{endo}}{T_{uni-H}}\right). \tag{40}$$

Applying Equation 41 of [1] for specific mutual universal entropy results in

$$\Delta s_{mut}^{CDS} = \frac{1}{\sum M}\left[\frac{E_a^{exo} + \left|\overrightarrow{\Delta H^{\circ}}\right|}{T_{uni-C}} - \frac{E_a^{exo}}{T_{uni-H}}\right]. \tag{41}$$

Applying Equation 33 of [1] for the complexity yield results in

$$\Delta u_{Cx}^{CDS} = \left|\overrightarrow{\Delta H^{\circ}}\right|\,. \tag{42}$$

Applying Equation 45 of [1] for specific conditional heat quality output results in

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$$\sigma_{con}^{CDS} = \left(\frac{E_a^{endo} - \left|\overrightarrow{\Delta H^{\circ}}\right|}{\sum M}\right)\left(\frac{1}{T_{uni-C}} - \frac{1}{T_{loc-C}}\right). \tag{43}$$

Applying Equation 46 of [1] for specific conditional heat quality drop results in

$$\Delta\sigma_{con}^{CDS} = \frac{1}{\sum M}\left(\frac{E_a^{endo} - \left|\overrightarrow{\Delta H^{\circ}}\right|}{T_{loc-C}} - \frac{E_a^{endo}}{T_{loc-H}}\right). \tag{44}$$

Applying Equation 49 of [1] for specific mutual heat quality output results in

$$\sigma_{mut}^{DS} = \left(\frac{E_a^{exo} + \left|\overrightarrow{\Delta H^{\circ}}\right|}{\sum M}\right)\left(\frac{1}{T_{uni-C}} - \frac{1}{T_{loc-C}}\right). \tag{45}$$

Applying Equation 50 of [1] for specific mutual heat quality drop results in

$$\Delta\sigma_{mut}^{DS} = \frac{1}{\sum M}\left(\frac{E_a^{exo} + \left|\overrightarrow{\Delta H^{\circ}}\right|}{T_{loc-C}} - \frac{E_a^{exo}}{T_{loc-H}}\right). \tag{46}$$

Applying Equation 58 of [1] for specific maximum heat quality drop results in

$$\Delta\sigma_{max}^{DS} = \left(\frac{E_a^{endo} + E_a^{exo}}{\sum M}\right)\left(\frac{1}{T_{loc-C}} - \frac{1}{T_{loc-H}}\right). \tag{47}$$

For heat transformation effectivity, use Equation 53 of [1] as used for GDSs, but use the assumption that CDSs are highly localized unlike GDSs. Based on this, the assumption is that the local heat source temperature is approximately equal to the local heat sink temperature. With this assumption, the heat transformation effectivity for a CDS is approximately equal to the local heat sink temperature. Theorem 1 of the heat transformation theory provided in [1] applies,

$$\mathcal{T}_{eff}^{CDS} \equiv \frac{1}{\sum M}\cdot\frac{\Delta u_{Cx}^{CDS}}{\Delta\sigma_{mut}^{CDS}} \cong \frac{\left|\overrightarrow{\Delta H^{\circ}}\right|}{\sum M} \Big/ \frac{1}{\sum M}\left(\frac{E_a^{exo} + \left|\overrightarrow{\Delta H^{\circ}}\right|}{T_{loc-C}} - \frac{E_a^{exo}}{T_{loc-C}}\right) = T_{loc-C}\,. \tag{48}$$

*2.7. Transient Growth of CDSs*

CDSs are steady-state-seeking in a far-from-equilibrium state just as GDSs. This steady-state-seeking function shifts the properties of the DS to drive toward total heat output coming into equality with total heat input as the DS asymptotically approaches a maximum APC based upon the available heat and available reactants, reagents, catalysts, and cofactors that are specifically involved in the chemical reaction of the CDS and constitute the heat transfer medium.

The logical assumption is that there is a starting point of each DS, and that it goes through a process of growth of its APC and ARO until it reaches a steady state level. Growth of the TWC is assumed to be a result of more and more solar insolation being utilized in the evaporation of water. For a CDS, when there are the right concentrations of the right chemicals and the right environmental conditions needed to perform an endothermic auto-synthesis reaction, the cycle is initiated. Growth of APC occurs as the influx of matter and heat driven by GDSs provide the molecules and activation energies for ongoing auto-synthesis, increasing the reaction rate and resulting in an increasing storage of the energy of endothermic reaction enthalpy.

The first ever exothermic auto-decomposition chemical reaction to occur on Earth can only occur as a reverse of an endothermic auto-synthesis. This is a result of the products from the endothermic auto-synthesis being at the right concentrations with the right conditions and an ongoing heat input. The reaction rate of the exothermic auto-decomposition increases but initially lags behind the endothermic auto-synthesis reaction rate increases. The exothermic auto-decomposition reaction rate continues to increase until it catches up with the endothermic auto-synthesis reaction rate when total heat output of the CDS comes into equality with total heat input. This is when steady state is achieved. It is important to note that this is not an equilibrium state at which point forward and reverse reactions are occurring randomly at the same low rates. This is a far-from-equilibrium state at which point forward and reverse reactions are driven by available heat and ongoing replenishments of

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reactants, reagents, catalysts, and cofactors for both the forward and reverse reactions. At this point, the CDS could be closed to all new inputs except heat, and it would continue to cycle with its existing material levels due to the forward and reverse reactions providing the reactants, reagents, catalysts, and cofactors for each other, assuming the heat input from outside of the system continues to be available at the right level of quantity and quality.

CDSs in which the stage 4 exothermic auto-decomposition chemical reactions initiate at the lowest reaction rates compared to the attained reaction rate levels that their stage 2 endothermic auto-synthesis counterpart chemical reactions build up in volume and stored energy at a greater rate in the form of increasing quantities of stage 2 product molecules. In addition, if such a CDS has high rates of stage 2 endothermic auto-synthesis, then they are likely to recapture the stage 4 products of the reverse exothermic auto-decomposition reactions into stage 1 and stage 2 with the specific mutual heat quality output released by the reverse reactions recaptured at the same level of specific heat quality as the original input heat. This can happen even as an ongoing quantity of new molecules and new heat are supplied by the GDSs that are feeding the CDS, engaging even more reactants, reagents, catalysts, and cofactors in the forward reaction at stage 2. This combination of high endothermic auto-synthesis reaction rate and low initial exothermic auto-decomposition reaction rate exponentially builds up stored energy over the initial growth period of the CDS. However, for any CDS that has either or both of these conditions, the tendency will be to grow the population of endothermic auto-synthesized product molecules. On the other hand, any leading endothermic auto-synthesis CDS in which the stage 4 reverse chemical reaction happens just as quickly than the stage 2 forward reaction will never grow and would likely be broken up by the massive mixing of local GDSs. This analysis differentiates the types of endothermic auto-synthesis chemical reactions that are likely to dominate Earth.

The storage of energy makes CDSs that lead with endothermic auto-synthesis both mutualistic and resilient. In times of low heat availability, the greater release of the stored energy of the stage 4 exothermic auto-decomposition can be utilized by stage 1 and stage 2 of the cycle to dampen the decline of the DS. This makes it resilient. The greater exothermic heat release of the stored energy can also be utilized by other collocated leading endothermic auto-synthesis CDSs during times of low heat availability. This makes leading endothermic auto-synthesis mutualistic, supporting an ecosystem of CDSs.

The combined effect of the resilience and mutualism of the leading endothermic auto-synthesis CDSs can be better understood by contrasting it with the leading exothermic auto-synthesis CDS. Such a CDS must later use its ARO to endothermically auto-decompose. If the stage 4 reverse reaction is as fast as the stage 2 forward reaction, then the CDS will never grow and would likely be broken up by the massive mixing of local GDSs, the same as for leading endothermic auto-synthesis CDSs. The stage 4 endothermic auto-decomposition requires greater heat at greater specific heat quality levels compared to lesser heat at lesser heat quality levels to exothermically auto-synthesize. If the stage 4 endothermic auto-decomposition reverse reaction has a lesser reaction rate than the stage 2 exothermic auto-synthesis forward reaction that releases a lot of heat, then much of the stage 2 heat release will be lost to downstream flow or to local leading endothermic auto-synthesis CDSs before the stage 4 reverse reaction can take advantage of it and use it.

This means that in times of low heat availability, the reverse endothermic auto-decomposition declines at a greater rate than the forward exothermic auto-synthesis reaction. In addition, when endothermic auto decomposition does occur, it consumes even more of the less-available, higher quality heat, stealing it from being available for the stage 2 exothermic auto-synthesis of its own cycle. These two circumstances create a compounded effect of loss of both heat and material feedback support from the ARO end of endothermic auto-decomposition to buffer the loss of heat availability and the decline of exothermic auto-synthesis. This makes the leading exothermic auto-synthesis CDS less resilient to times of low heat availability. As a result, neighboring leading exothermic auto-synthesis CDSs are also antagonistic to each other in times of low heat availability. In contrast, resilient and mutualistic leading endothermic auto-synthesis CDSs are in a better position to utilize

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the heat and specific heat quality released at stage 2 of leading exothermic auto-synthesis CDSs. In times of low heat availability, leading endothermic auto-synthesis CDSs win the competition of survival of the fittest. The progressive results of ongoing rounds of heat availability and heat scarcity results in a net accumulation of endothermic synthetic CDSs in excess of exothermic synthetic CDSs.

This discussion of the growth of CDSs and the relative lack of resilience and mutualism of an leading exothermic auto-synthesis CDS support the conclusion arrived at previously that the vast majority of exothermic reactions occur as stage 4 auto-decomposition reactions that follow stage 2 endothermic auto-synthesis reactions. Relatively few CDSs are an exothermic auto-synthesis followed by an endothermic auto-decomposition. This reveals that the trend of a universe that is dissipating heat to the grand equilibrium heat sink of space is to synthesize larger and larger molecules while storing more and more energy as reaction enthalpy.

There is a question of multiplicity and ergodicity to determine how likely it is for all of the right chemicals to come together with sufficient heat at the right temperature and quality in the right concentrations and at the right pressures and volumes to result in an endothermic auto-synthesis that initiates and grows a CDS. This is covered in Part III of this paper series.

Up to this point, the assumption has been that the endothermic auto-synthesis and exothermic auto-decomposition of a CDS each occur with a single step chemical reaction. However, it is theoretically possible for either or both of stage 2 and stage 4 to occur with a multi-step-chemical-reaction process. If the number of stage 4 chemical reaction process steps are the exact reversal of the stage 2 chemical reaction process steps, then these are effectively a networked series if DS of single chemical steps, requiring a model of a network of Figure A1 structures. However, if the stage 4 reverse chemical reaction process steps are not the exact reversal of the stage 4 chemical reaction process steps, the analysis is a little more complicated.

Consider a stage 4 decay portion of the cycle that is a series of reactions that results in the eventual decomposition to the reactants of the stage 2 endothermic auto-synthesis reaction. The reverse series of reactions at stage 4 will have the equal but opposite total change in reaction enthalpy as the forward reaction occurring at stage 2. However, the more chemical process steps it takes at stage 4 to decay the products of stage 2 back into the reactants of stage 2, the greater the total quantity of $Q_H^{exo}$, it now being a sum of the heat needed to achieve activation energy at each chemical reaction step of the reverse chemical process.[3] As noted in the discussion of Figure A1, the total of both $|Q_{in}|$ and $|Q_{out}|$ increase by the same amount to achieve steady state. The result is that total mutual universal entropy and total maximum universal entropy are both greater by the same amount. Inefficient chemical processes that require more steps to achieve the same end products, whether in the forward direction at stage 2 or the reverse direction at stage 4 produce greater amounts of universal entropy. This is simply saying that it requires greater amounts of heat to accomplish the same growth in complexity. The greater quantity of heat is not used to produce more complexity, nor can it now or ever be used to produce complexity at that level of heat quality in the universe. This is an outcome of the second law of thermodynamics.

## 3. Networks and Complexity

### *3.1. CDS Networks*

Part I of this paper series [1] (Section 4.7) provides a qualitative discussion of the networking of GDSs. The networking of CDSs occurs in similar fashion by transferring matter that holds stored energy. CDSs network together by the transfer of the product molecules of a chemical reaction of a CDS to be reactant molecules of one or more other CDSs. This networking generally occurs by the

[3] Even if there are one or more endothermic syntheses involved with the stage 4 exothermic auto-decomposition chemical process, the products of those syntheses will eventually have to go through a reversal by way of exothermic decomposition that releases the stored energy. The result is additional amounts of $Q_H^{endo}$ included in the sum of utilized heat at stage 4.

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product molecules of stage 2 of a CDS being passed on to be stage 2 reactants of other CDSs, as well as the product molecules of stage 4 of a CDS being passed on to be stage 4 reactants of other CDSs. The reason for this is because of the way in which chemical processes involving multiple chemical reaction steps use products of the previous step as reactants of the next step, whether the process is a series of syntheses, a series of decompositions, or a combination. When two CDSs are linked by stage 2 and stage 4, at least one product of the upstream CDS stage 2 reaction is a reactant of the downstream CDS stage 2 reaction, as well as a product of the downstream CDS stage 4 reaction and a reactant of its own stage 4 (Figure 5).

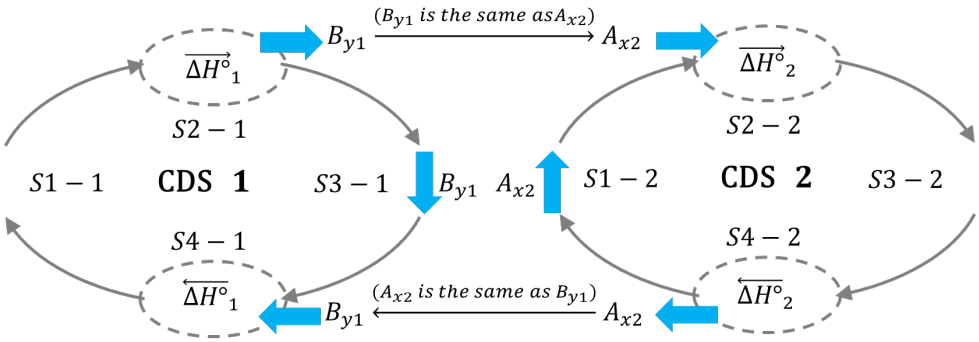


**Figure 5.** The stage 2 chemical reaction of CDS 1 is $\sum_{x=1}^{X-3} a_{x1}A_{x1} \rightarrow \sum_{y=1}^{Y-3} b_{y1}B_{y1}$ and the stage 4 chemical reaction of CDS 1 is $\sum_{y=1}^{Y-3} b_{y1}B_{y1} \rightarrow \sum_{x=1}^{X-3} a_{x1}A_{x1}$. The stage 2 chemical reaction of CDS 2 is $\sum_{x=1}^{X-3} a_{x2}A_{x2} \rightarrow \sum_{y=1}^{Y-3} b_{y2}B_{y2}$ and the stage 4 chemical reaction of CDS 1 is $\sum_{y=1}^{Y-3} b_{y2}B_{y2} \rightarrow \sum_{x=1}^{X-3} a_{x2}A_{x2}$. Product molecule $B_{y1}$ of stage 2 of CDS 1 is reactant molecule $A_{x2}$ of stage 2 of CDS 2. This means that stage 2 of CDS 2 can utilize $B_{y1}$ molecules being produced by stage 2 of CDS 1, allowing these two CDSs to network as a downstream flow. Considering the stage 4 chemical reactions are the reverse of the stage 2 chemical reactions, this networking works in the opposite (upstream) direction from stage 4 of CDS 2 to stage 4 of CDS 1. $B_{y1}$ and $A_{x2}$ can also be recycled to the reverse stage within their respective CDSs to be utilized as reactant molecules.

There are a few possible combinations of networking that result from this type of network configuration. First, any leading exothermic auto-synthesis CDSs of simple molecules that occur early in the chemosystem are likely to pass their stage 2 products to stage 2 of leading endothermic auto-synthesis CDSs.[4] Second, the products of a stage 2 auto-synthesis of a CDS can either immediately be cycled to its stage 4 auto-decomposition or they can be passed downstream to a sequence of stages 2 of one ore more CDSs before eventually being cycled to a stage 4 auto-decomposition. It can then make its way back to the stage 4 of the starting CDS through the stages 4 of auto-decompositions of the same CDSs it passed through by way of stages 2, except in reverse. It is also noteworthy that the products of a stage 4 can be cycled to the stage 2 of the same CDS. With this type of network connectivity, the atoms that make up molecules can continue to cycle down and up a network indefinitely as heat continues to dissipate through the network. Finally, because chemical reactions always have two or more products, these products can be passed to up to as CDSs as there are products (or perhaps more if multiple CDSs in the same network use the same reactants).

There are some special cases of CDS networking to consider. Stage 2 products and stage 4 products can be used as reagents, catalysts, and cofactors of any stage 2 or stage 4 reaction of any CDS in a local CDS network. It is also possible for a stage 2 product of a CDS to be used as a catalyst

[4] The complexity yield of a CDS is based upon the endothermic stage, just as for a GDS. For CDSs, though the model developed in this paper is that of a leading endothermic auto-synthesis CDS based upon it being the most common form of CDS according to heat transformation theory, it is possible for the production of a leading exothermic auto-decomposition CDS. In such a case, the endothermic stage that the complexity yield is based on is stage 4.

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of its own stage 2 reaction. This is known as autocatalysis. It is also theoretically possible for stage 2 products of a DS to be passed to stage 4 reactions of a different CDS rather than cycling to its own stage 4 (and vice versa for stage 4 to stage 2) when any two or more CDSs within the local network have a stage 2 product molecule that is the same, and therefore indistinguishable in its product source.

All of the variety of possible network configurations reveals the extent of observable complexity. The complexity is quantifiable in the stored energy in the form of enthalpy of formation that is passed in the flows between networked CDSs. In general, for both GDSs and CDSs, *complexity* is defined as a property of a network of DSs measured in units of energy per mole that is the additive transfer of stored energy between DSs of the network. Just as GDSs pass stored energy in the form of gravitational potential energy per mole from one GDS to the next, CDSs pass molecular enthalpy of formation in units of energy per mole from one CDS to the next. The previously discussed complexity yield of the GDS and CDS represents how the GDS increases the potential energy of a mole of material between radial distances from the center of Earth or how the CDS increases the sum of the enthalpies of formation of the product molecules over the reactant molecules for a mole of product molecules.

### *3.2. The Complexity of GDS to CDS Networking*

The first function of GDSs mentioned at the end of Section 4.7 of [1] is their material delivery. GDSs capture and displace molecules over great distance in their upward kinetic flow driven by buoyancy in stage 2 and in their kinetic flow driven by the release of gravitational energy. Along with the kinetic energy, GDSs provide a second function of heat delivery. The GDSs provide internal energy to CDSs by the heat they carry. Thus, GDSs network with CDSs by providing the conditions for CDS creation within their flows. The molecules involved in the chemical reactions of CDSs also have stored gravitational potential energy from as a result of their engagement in GDSs. This is one of two reasons for using potential energy per mole for complexity yield and complexity, rather than the per unit mass calculation of specific maximum universal entropy. It enables heat transformation theory to add complexities of GDSs to complexities of CDSs. Potential energy per mole is additive, and the sum of complexities being passed between DSs of a network has physical meaning. Any given mole of a DS has received an amount of real potential energy per mole based upon the total amount of potential energy contributed to or taken from that mole of molecules as a result of the complexity yield of every DS it passes through.

The second reason for using energy stored per unit mole is because it can be either linearly or exponentially scalable depending upon the type of DS the heat transferring medium passes through. GDSs are scaled linearly in complexity, stored potential energy being transferred from one GDS to the next resulting in linear growth of stored energy per mole proportional to the distance from the center of Earth. If a water-based GDS is passing stored energy to an air-based GDS, then it is just a matter of simple stoichiometry to figure out the complexity conversion from moles of water to moles of air, or vice versa. For CDSs, scaling up complexities added to a network complexity in a series of auto-synthesis reactions or scaling down complexities added to a network complexity in a series of auto-decompositions is exponential based upon the respective increasing or decreasing of enthalpies of formation. The larger that auto-synthesis product molecules get, the greater the enthalpy of formation (energy per mole), and therefore a greater complexity than a smaller molecule. Using enthalpy of formation of molecules being passed between CDSs as a measure of complexity exponentially scales the quantitative complexity to match the qualitatively observable complexity in the chemical world of nature. This scaling results in asymmetries that exhibit in nature as emergent properties of networks of CDSs, quantified as a complexity ascendency, and resilience properties of networks of CDSs, quantified as complexity reserve.

### *3.3. Ecological Network Theory*

Ulanowicz and Norden [12] provide the earliest reference to a complete mathematical model that can be used to determine network properties of DSs for heat transformation theory. The work is

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based on earlier work that started with Shannon [13] who developed a statistical entropy of information networks that is based on microstates with non-equivalent probabilities and that becomes the Boltzmann statistical mechanics entropy [14] when all probabilities are made equal. Next, Odum [15] recognized the existence of a multiplicity of pathways of resource interchange between the species of an ecosystem that promotes homeostasis against ecosystem disruptions. MacArthur [16] then recognized that these interchanges formed a network, and that the fraction of the total flow of energy in the network going through each connection between species could be used in the Shannon-Weiner index to calculate a diversity of flows. Rutledge, Basore, and Mulholland [17] put MacArthur's ideas in terms of conditional probabilities by multiplying the MacArthur fractional probability that a unit of energy flows from species $i$ to species $j$ when species $j$ consumes species $i$ by the probability that a unit of energy is flowing to species $i$ as a result of everything that species $i$ eats. This allowed Rutledge to define statistical entropy, average mutual information, and conditional entropy of an ecosystem food chain as if it were an information network.

Finally, Ulanowicz, Hirata, and Norden [18–20,12,21] further developed Rutledge's network of a closed ecosystem food chain network to an open system that includes inputs of species consuming things outside of the food chain and exports of species being eaten by things outside of the food chain in the statistical calculations, normalized the calculations to make them symmetrical to energy flow reversal, and added to the statistical calculations energy losses through heat dissipation resulting from cellular respiration of life and the decay resulting from death and defecation. The purpose of the latter adds an asymmetry that distinguishes the irreversibility of entropy. The result is four equations [12] (Equations 10 through 13) that are a set of network properties for the inputs, internal transfers, and outputs of food energy to a food network, as well as dissipations expressed as losses of energy from the food chain resulting from respiration (of herbivores, carnivores, and decomposers) and simple chemical decomposition of carcasses and feces. In these equations, $i = 0$ are the inputs, $i = 1\ to\ \mathbb{N}$ and $j = 1\ to\ \mathbb{N}$ are the internal food chain connections, $j = \mathbb{N} + 1$ are the exports, and $j = \mathbb{N} + 2$ are the heat dissipations, and $T_{ij}$ are energy-based values of the flows between any two nodes. Ulanowicz [22–28] further develops the ecosystem applications of these statistics, and frequently changes the name and symbol conventions of these equations. However, the form of these equations have not changed for 35 years.

### *3.4. Network Analysis of Formation Enthalpy Transfers*

Heat transformation theory applies these equations to pre-biotic networks of GDSs and CDSs. However, a network of pre-biotic DSs is different from a food network. Rather than food value flows, DSs have stored energy flows. In addition, unlike food networks, the stored energy can flow backwards (from downstream to upstream) to the very same node that performed an upstream flow. Finally, stored energy flows can occur from exports, $i = \mathbb{N} + 1$, back to internal network nodes, $j = 1\ to\ \mathbb{N}$, and from internal network nodes, $i = 1\ to\ \mathbb{N}$, back to imports, $j = 0$.[5]

Consider a network of CDSs that transfer stored energy between themselves in the form of the enthalpies of formation of molecular products of chemical reactions. The analysis of such a network using the statistical tools discussed above for food networks provides a direction in calculating a network complexity, considering complexity yield of a CDS, Equation 42, involves reaction enthalpy that is made up of differences in molecular enthalpies of formation, Equation 12. Figure 5 and Figure 6 represent a simple network of two CDS nodes with an import from upstream outside of the network and an export to downstream outside of the network. The downstream flows (moving to the right in the simplified version provided in Figure 6) of stored energy are:

[5] Ulanowicz and Norden used the terms inputs and exports for food value flows. Heat transformation theory uses the terms imports rather than inputs to inputs for stored energy flows into a network from upstream and outside of a network. The terms inputs and outputs are used to describe heat flows.

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1. Stage 2 products of CDSs $i = 1\ to\ \mathbb{N}$ that are upstream and internal to the network ($CDS\ 1$ in Figure 6), to become the stage 2 reactants of CDSs $j = 1\ to\ \mathbb{N}$ that are downstream and internal to the network ($CDS\ 2$ in Figure 6),
2. Imports:

a. Of stage 2 products of multiple CDSs all accounted as $i = 0$ that are upstream and outside of the network ($i = 0$ Imports in Figure 6), to become the stage 2 reactants of CDSs $j = 1\ to\ \mathbb{N}$ that are downstream and internal to the network ($CDS\ 1$ in Figure 6) and

b. Of reagents, catalysts, and cofactors used in stage 2 reactions of CDSs inside the network and

3. Exports:

a. Of stage 2 products of CDSs $i = 1\ to\ \mathbb{N}$ that are upstream and internal to the network ($CDS\ 2$ in Figure 6), to become the stage 2 reactants of CDSs all accounted as $j = \mathbb{N}+1$ that are downstream and outside of the network ($j = 3$ Exports in Figure 6).

b. Of reagents, catalysts, and cofactors used in stage 2 reactions of CDSs outside of the network, and

c. Of molecules that are not used by any CDSs outside the network.

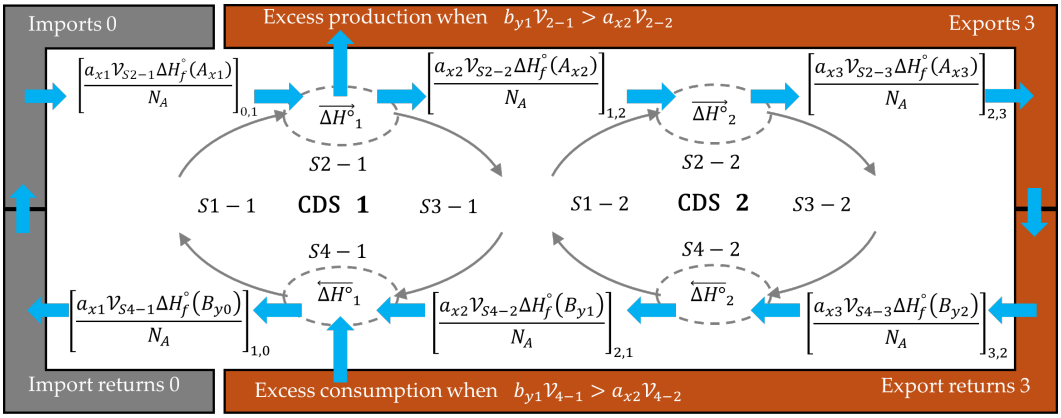


**Figure 6.** A simple network of two chemical dissipative structure (CDS) nodes. $CDS\ 1$ imports a flow of molecules with their formation enthalpies from outside of the network. $CDS\ 1$ stage 2 reaction generates product molecules, at least one of which is passed as flow with its formation enthalpy to $CDS\ 2$. Excess production of any molecules are passed as exported flows outside the network. Stage 2 production molecules of $CDS\ 2$ are all passed as export flows. Export returns reenter the network to stage 4 of $CDS\ 2$ to undergo decomposition. The one or more stage 4 products of $CDS\ 2$, which are the same as the stage 2 products of $CDS\ 1$ that are passed to stage 2 of $CDS\ 2$, are passed to stage 4 of $CDS\ 1$. Export returns are alo passed from outside the network to stage 4 of $CDS\ 1$, allowing for a complete set of reactants for the decomposition reaction of stage 4 of $CDS\ 1$. Stage4 products of $CDS\ 1$ are passed as import returns to outside of the network. Some quantities of products of stage 2 and stage 4 reactions can pass immediately within the same CDS to be used as reactants without ever entering a flow that takes it away from the CDS.

Molecules produced by CDSs in the network that are used as reagents, catalysts, and cofactors of any other CDS inside or outside of the network are considered to be exports. Such molecules are also treated as imports when used as a reagent, catalyst, or cofactor of a CDS in the network, whether a separate CDS or the same CDS undergoing autocatalysis. Their availability and concentration can affect the reaction rate of a chemical reaction of a CDS in the network, though they do not contribute to the complexity yield of the CDS.

The downstream flows, $i$ to $j$, are a result of enthalpies of formation, $\Delta H_f^\circ(A_{xj})$ of molecules, $A_{xj}$ (Equation 26) of all stage 2 chemical reactions of internal nodes of the network ($j = 1\ to\ \mathbb{N}$ individual CDSs, with $x = 1\ to\ X_j - 3$ being reactants and $X_j - 2$, $Y_i - 1$, and $X_j$ being reagents, catalysts, and cofactors) and all export destinations ($j = \mathbb{N} + 1$ in a network summation, with $x = 1\ to\ X_{\mathbb{N}+1}$ going to various external export destination CDSs, and not just one CDS). Each flow is in

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terms of units of enthalpy transfer rate per unit volume, multiplying the enthalpy of formation of the molecule to the downstream CDS, $\Delta H_f^{\circ}(A_{xj})$, by the fractional number of moles of that molecule consumed per stage 2 chemical reaction of the downstream CDS, $\frac{a_{xj}}{N_A}$, and by the reaction rate per unit volume of the stage 2 chemical reaction of the downstream CDS, $\mathcal{V}_{S2-j}$ for $j = 1\ to\ \mathbb{N}+1$ ($j = \mathbb{N}+1$ being various external export destination CDSs, and not just one CDS).

$$\left[\frac{a_{xj}\mathcal{V}_{S2-j}\Delta H_f^{\circ}(A_{xj})}{N_A}\right]_{i,j}, \text{for which } i \neq j. \tag{49}$$

The flow is based on the chemical reaction coefficient of the molecule, $a_{xj}$, and the chemical reaction rate per unit volume of $CDS\ j$ stage 2 because CDS $j$ stage 2 is assumed to take an inflow rate of any molecule $B_{yi}$ only as it has APC to consume it in its own stage 2 chemical reaction. Any excess production of $B_{yi}$ by the upstream CDS $i$ stage 2 for $i = 0\ to\ \mathbb{N}$ goes to $j = \mathbb{N}+1$ as an export destination of excess production.

The upstream flows (moving to the left in Figure 6) of stored energy resulting from stage 4 reactions that are the reverse of stage 2 reactions are:

1. Stage 4 products of CDSs $i' = 1\ to\ \mathbb{N}$ that are downstream and internal to the network ($CDS\ 2$ in Figure 6), to become the stage 4 reactants of CDSs $j' = 1\ to\ \mathbb{N}$ that are upstream and internal to the network ($CDS\ 2$ in Figure 6),
2. Export returns:

a. Of stage 4 products from CDSs all accounted as $i' = \mathbb{N}+1$ that are downstream and outside of the network ($i' = 3$ Export Returns in Figure 6), to become the stage 4 reactants of CDSs $j' = 1\ to\ \mathbb{N}$ that are upstream and internal to the network ($CDS\ 2$ in Figure 6),

b. Of reagents, catalysts, and cofactors used outside of the network and ultimately being drawn back to become export-returns to stage 4 reactions in the network, and

c. Of molecules that are not used by any other CDSs outside the network and ultimately being drawn back to become export-returns to stage 4 reactions in the network,

and

3. Import returns:

a. Of stage 4 products of CDSs $i' = 1\ to\ \mathbb{N}$ that are downstream and internal to the network ($CDS\ 1$ in Figure 6), to become import-returns as the stage 4 reactants of CDSs $j' = 0$ that are upstream and outside of the network ($j' = 0$ Import Returns in Figure 6), and

b. Of reagents, catalysts, and cofactors used inside of the network and ultimately being drawn back to become import-returns to stage 4 reactions outside of the network.

The reverse stage 4 reaction of a given CDS produces products that are the same as the reactants it uses in stage 2. Once available upon undergoing a stage 4 auto-decomposition reaction, those molecules can reengage in stage 2 reactions of the same CDS, or they can return to the upstream CDSs from which they came to be used as reactants of the stage 4 auto-decomposition in the upstream CDSs.

The upstream flows, $i'$ to $j'$, are a result of enthalpies of formation, $\Delta H_f^{\circ}(B_{yj'})$ of molecules, $B_{yj'}$ (Equation 26), of the upstream stage 4 chemical reactions of all internal nodes of the network ($j' = 1\ to\ \mathbb{N}$ individual CDSs, with $y = 1\ to\ Y_{j'} - 3$ being reactants and $Y_{j'} - 2$, $Y_{j'} - 1$, and $Y_{j'}$ being reagents, catalysts, and cofactors) and import-returns ($j' = 0$ in a network summation, with $y = 1\ to\ Y_0$ going to various external CDSs, and not just one CDS). Each flow is in terms of units of enthalpy transfer rate per unit volume, multiplying the enthalpy of formation of the molecule from the upstream CDS, $\Delta H_f^{\circ}(B_{yj'})$, by the fractional number of moles of that molecule produced per stage 4 chemical reaction of the downstream CDS, $\frac{a_{xi'}}{N_A}$, and the reaction rate per unit volume of the stage 4 chemical reaction of the downstream CDS, $\mathcal{V}_{S4-i'}$ for $i' = 1\ to\ \mathbb{N}+1$ ($i' = \mathbb{N}+1$ being various external export return CDSs, and not just one CDS).

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$$\left[\frac{a_{xi'}\mathcal{V}_{S4-i'}\Delta H_f^{\circ}\left(B_{yj'}\right)}{N_A}\right]_{i',j'}, \text{for which } i=j', j=i' \text{ and } i'\neq j'. \tag{50}$$

The flow is based on the chemical reaction coefficient of the molecule, $a_{xi'}$, and the chemical reaction rate per unit volume of $CDS\ i'$ stage 4 because CDS $j'$ stage 4 is assumed to take an inflow rate of any molecule $B_{yj'}$ only as $CDS\ i'$ stage 4 has APC to produce it. Any excess consumption needs of $B_{yj'}$ by the upstream CDS $j'$ stage 4 for $j'=0\ to\ \mathbb{N}$ comes from $i'=\mathbb{N}+1$ as an export return of previous excess production of the $CDS\ i$ stage 2.

Both the stage 2 reaction rate per unit volume of the upstream $CDS\ i$ ($CDS$ 1 in Figure 6) and the stage 4 reaction rate per unit volume of the downstream $CDS\ i'$ ($CDS$ 2 in Figure 6) are feeding the same local concentration of molecules $A_{xj}=B_{yj'}$ ($A_{x1}=B_{y0}$, $A_{x2}=B_{y1}$, and $A_{x3}=B_{y2}$ in Figure 6). Both the stage 2 reaction rate per unit volume of the downstream $CDS\ j$ ($CDS$ 2 in Figure 6) and the stage 4 reaction rate per unit volume of the upstream $CDS\ j'$ ($CDS$ 1 in Figure 6) are pulling from that same local concentration of molecule $A_{xj}=B_{yj'}$ ($A_{x2}$ and $B_{y1}$ are the same molecule in Figure 6). These molecular concentration pools are part of the determining factor for the reaction rates per unit volume of all of the chemical reactions in the network. When all the CDSs of the network along with their imports and exports are growing these molecular concentrations toward a quasi-steady state of asymptotically approaching a maximum, the following conditions result (using Figure 6 as a simplified example):

1. Considering that $B_{y1}$ and $A_{x2}$ are the same molecule, therefore,

$$\Delta H_f^{\circ}\left(B_{y1}\right)=\Delta H_f^{\circ}(A_{x2}). \tag{51}$$

The enthalpy transfer rate density flow associated with $B_{y1}$ from $CDS$ 1 stage 2 chemical reaction to be used as $A_{x2}$ in $CDS$ 2 stage 2 chemical reaction is established by the enthalpy consumption rate density of $CDS$ 2 stage 2,

$$T_{1,2}^{\Delta H}=\frac{a_{x2}\mathcal{V}_{2-2}\Delta H_f^{\circ}(A_{x2})}{N_A}, \tag{52}$$

either because the $CDS$ 1 stage 2 is producing $B_{y1}$ at the same or lesser rate than what $CDS$ 2 stage 2 is able to consume $A_{x2}$ as the network asymptotically approaches steady state, $b_{y1}\mathcal{V}_{2-1}\approx a_{x2}\mathcal{V}_{2-2}$, or because any excess production of $CDS$ 1 stage 2, $b_{y1}\mathcal{V}_{2-1}>a_{x2}\mathcal{V}_{2-2}$, is accounted as going to exports, $j=3$, rather than to $CDS$ 2 stage 2 that does not have the other necessary resources in the right proportions to consume it. Based on this, the network tends to be limited at flows between CDSs where synthesis consumption of a molecule is occurring at a lower rate than synthesis production the molecule.

2. The enthalpy transfer rate density flow of a given molecule from $CDS$ 2 stage 4 chemical reaction to $CDS$ 1 stage 4 chemical reaction is equal to the enthalpy production rate density of $CDS$ 2 stage 4,

$$T_{2,1}^{\Delta H}=\frac{a_{x2}\mathcal{V}_{4-2}\Delta H_f^{\circ}\left(B_{y1}\right)}{N_A}, \tag{53}$$

either because $CDS$ 1 stage 4 is consuming $B_{y1}$ at the same rate that $CDS$ 2 stage 4 can produce $A_{x2}$ as the network asymptotically approaches steady state, $b_{y1}\mathcal{V}_{4-1}\approx a_{x2}\mathcal{V}_{4-2}$, or because any excess consumption of $CDS$ 1 stage 4, $b_{y1}\mathcal{V}_{4-1}>a_{x2}\mathcal{V}_{4-2}$, is accounted as coming from export returns, $j=3$. Based on this, the network tends to be limited at flows between CDSs where decomposition production of a molecule is occurring at a lower rate than decomposition consumption the molecule.

3. True steady state is a result of each CDS stage 2 reaction rate per unit volume being equal to its stage 4 reaction rate per unit volume. CDS networks never quite reach true steady state, but asymptotically approach it. This asymptotic approach results in a CDS stage 2 reaction rate per unit volume that is somewhat greater than its stage 4 reaction rate per unit volume,

$$\mathcal{V}_{S2-1}>\mathcal{V}_{S4-1} \text{ and } \mathcal{V}_{S2-2}>\mathcal{V}_{S4-2}. \tag{54}$$

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For a given CDS, the enthalpy per reaction of intake flow for stage 2 is the same as the enthalpy per reaction of the output flow for stage 4,

$$\left[\frac{a_{x1}\Delta H_f^\circ(A_{x1})}{N_A}\right]_{0,1} = \left[\frac{a_{x1}\Delta H_f^\circ(B_{y0})}{N_A}\right]_{1,0} \text{ and} \quad (55)$$

$$\left[\frac{a_{x2}\Delta H_f^\circ(A_{x2})}{N_A}\right]_{1,2} = \left[\frac{a_{x2}\Delta H_f^\circ(B_{y1})}{N_A}\right]_{2,1},$$

because $A_{x2} = B_{y1}$ and $A_{x1} = B_{y0}$. This means that the enthalpy transfer rate density upstream and downstream flows between any two CDSs have an asymmetry,

$$\left[\frac{a_{x1}\mathcal{V}_{S2-1}\Delta H_f^\circ(A_{x1})}{N_A}\right]_{0,1} > \left[\frac{a_{x1}\mathcal{V}_{S4-1}\Delta H_f^\circ(B_{y0})}{N_A}\right]_{1,0} \text{ and} \quad (56)$$

$$\left[\frac{a_{x2}\mathcal{V}_{S2-2}\Delta H_f^\circ(A_{x2})}{N_A}\right]_{1,2} > \left[\frac{a_{x2}\mathcal{V}_{S4-2}\Delta H_f^\circ(B_{y1})}{N_A}\right]_{2,1}.$$

4. The reaction rate of a CDS stage 2 endothermic auto-synthesis is the same for both its intake from an upstream CDS and its output to a downstream CDS, because intake and output are a result of the same stage 2 chemical reaction. However, the enthalpies of formation tend to be greater in the output than they are in the intake. This means that the enthalpy consumption rate density and enthalpy production rate density of a CDS stage 2 has an asymmetry. The same applies to the CDS stage 4, but with the enthalpies of formation being lesser for the production from stage 4 than for the consumption of stage 4.

5. The net effect is that the concentration pool of each molecule is at a growth rate that is asymptotically approaching a maximum. The production rates of each of the stages 2 and stages 4 of all the CDSs in the network that produce the same shared molecule and the consumption rates of the stages 2 and stages 4 of all the CDSs in the network that consume the same shared molecule, combined, establish the growth rate that is asymptotically approaching a maximum

Asymmetries of growing flows through the CDSs of a network that are asymptotically approaching maximums are certain to be a source of growth, as is evident with asymmetries that drive variance throughout theories of physics. Asymmetries of flows are also present in GDSs, though not as impactful on network complexity. Asymmetric growth in a GDS network is linear, because complexity yields are linear as stored gravitational potential energy per mole changes linearly. The linear asymmetries of stored gravitational potential energy transfers of GDSs have their impact on the mixing of materials, referred to in Section 4.7 of [1] as massive mixing, which can lead to increased probabilities of CDSs forming. It is then with the exponential asymmetries of CDSs where theoretical support for observed growth in evolution is likely to be found. This is explored in Part III of this paper series.

### *3.5. CDS Network Enthalpy Transfer Rate Density and Complexity*

*Flow complexity* associated with each flow into a DS is equal to the amount of stored energy per mole that is being carried by the material flow into the DS. For CDSs, the *flow complexity* of a stream of a given molecule, $B_{yi}$, to a $CDS\ j$ is defined as the enthalpy of formation for the molecule being transferred,

$$\mathcal{u}_{Cx}(B_{yi})_{i,j,y} = \Delta H_f^\circ(B_{yi}). \quad (57)$$

Any passage of molecule $B_{yi}$ to any CDS that uses it in a chemical reaction has this amount of complexity associated with it.

The *network complexity* of a network of CDSs is defined as the sum of all of the flow complexities of the network. For this reason, heat transformation uses a simple approach of summing all of the flow complexities (Equation 57) of a network to obtain *network complexity*,

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$$u_{Cx} \equiv \mathrm{TST}^{Cx} = \sum_{i,j=0}^{\mathbb{N}+1} \sum_{y=1}^{Y_i} u_{Cx}\left(B_{yi}\right)_{i,j,y}, \tag{58}$$

based on the equation for total system throughput utilized by Ulanowicz and Norden [12].

The flow complexity of any given stream of a product molecule between two CDSs does not have the same magnitude of impact as any other flow complexity of any other streaming product molecule between any two other CDSs, even though the simple sum of flow complexities suggests it does. The asymmetries of enthalpy transfer rate density flows are a complete picture of the impact of the complexity. To differentiate on level of impact of the flow complexities in the context of these enthalpy transfer rate density flows, calculate the *enthalpy transfer rate density flow* and the *total system throughflow of enthalpy transfer rate density*.

There are separate terms for stage 2 and stage 4 *enthalpy transfer rate density flows*,

$$T^{\Delta H}_{S2(i,j,xi)} = \left[\frac{a_{xj}\mathcal{V}_{S2-j}\Delta H_f^{\circ}\left(A_{xj}\right)}{N_A}\right]_{i,j} \text{ and} \tag{59}$$

$$T^{\Delta H}_{S4(i',j',xi')} = \left[\frac{a_{xi'}\mathcal{V}_{S4-i'}\Delta H_f^{\circ}\left(A_{xi'}\right)}{N_A}\right]_{i',j'}.$$

Note that for the stage 4 flows, $B_{yj'}$ is replaced with $A_{xi'}$ as a convention, considering they are the same molecule. By this convention, it is more obvious that stage 2 flows and stage 4 flows are both constrained by the downstream CDS of two networked CDSs.

For so the sum of *total system throughflow of enthalpy transfer rate density* is the sum of stage 2 and stage 4 summations,

$$TST^{\Delta H} = \sum_{S2(i=0)}^{\mathbb{N}} \sum_{S2(j=1)}^{\mathbb{N}+1} \sum_{x=1}^{X_j} \left[\frac{a_{xj}\mathcal{V}_{S2-j}\Delta H_f^{\circ}\left(A_{xj}\right)}{N_A}\right]_{i,j} + \sum_{S4(i'=1)}^{\mathbb{N}+1} \sum_{S4(j'=0)}^{\mathbb{N}} \sum_{x=1}^{X_{i'}} \left[\frac{a_{xi'}\mathcal{V}_{S4-i'}\Delta H_f^{\circ}\left(A_{xi'}\right)}{N_A}\right]_{i',j'}. \tag{60}$$

In this summation, many of the terms are zero due to most stage 2 reactions only involving two or three reactants resulting in two or three products, with most of these molecules only being produced by one CDS stage 2 and consumed by one other CDS stage 2. The terms for $i = j$ and $i' = j'$ are also zero due to autocatalysis being treated as an export followed by an import.

Incorporate these to the network model described above of [12] (Equations 10 through 12). Merging these three sets of equations in the context of Abramson [29] joint entropy results in a *joint entropy of enthalpy transfer rate density*,

$$H_{\Delta H} = -\sum_{i=0}^{\mathbb{N}} \sum_{j=1}^{\mathbb{N}+1} \sum_{x=1}^{X_i} \frac{T^{\Delta H}_{S2(i,j,x)}}{TST^{\Delta H}} \ln\left(\frac{T^{\Delta H}_{S2(i,j,x)}}{TST^{\Delta H}}\right) - \sum_{i'=1}^{\mathbb{N}+1} \sum_{j'=0}^{\mathbb{N}} \sum_{x=1}^{X_{i'}} \frac{T^{\Delta H}_{S4(i',j',x)}}{TST^{\Delta H}} \ln\left(\frac{T^{\Delta H}_{S4(i',j',x)}}{TST^{\Delta H}}\right), \tag{61}$$

an *average mutual information of enthalpy transfer rate density*,

$$I_{\Delta H} = \sum_{i=0}^{\mathbb{N}} \sum_{j=1}^{\mathbb{N}+1} \sum_{x=1}^{X_i} \left[\frac{T^{\Delta H}_{S2(i,j,x)}}{TST^{\Delta H}} \ln\left(\frac{T^{\Delta H}_{S2(i,j,x)} TST^{\Delta H}}{\sum_{j=1}^{\mathbb{N}+1} T^{\Delta H}_{S2(i,j,x)} \cdot \sum_{i=0}^{\mathbb{N}} T^{\Delta H}_{S2(i,j,x)}}\right)\right] + \sum_{i'=1}^{\mathbb{N}+1} \sum_{j'=0}^{\mathbb{N}} \sum_{x=1}^{X_{i'}} \frac{T^{\Delta H}_{S4(i',j',x)}}{TST^{\Delta H}} \ln\left(\frac{T^{\Delta H}_{S4(i',j',x)} TST^{\Delta H}}{\sum_{j'=0}^{\mathbb{N}} T^{\Delta H}_{S4(i',j',x)} \cdot \sum_{i'=1}^{\mathbb{N}+1} T^{\Delta H}_{S4(i',j',x)}}\right), \tag{62}$$

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and a *conditional entropy of enthalpy transfer rate density*

$$\Phi_{\Delta H} = \sum_{i=0}^{\mathbb{N}} \sum_{j=1}^{\mathbb{N}+1} \sum_{x=1}^{X_i} \left[ \frac{T_{S2(i,j,x)}^{\Delta H}}{TST^{\Delta H}} \ln \left( \frac{\left(T_{S2(i,j,x)}^{\Delta H}\right)^2}{\sum_{j=1}^{\mathbb{N}+1} T_{S2(i,j,x)}^{\Delta H} \cdot \sum_{i=0}^{\mathbb{N}} T_{S2(i,j,x)}^{\Delta H}} \right) \right] + \sum_{i'=1}^{\mathbb{N}+1} \sum_{j'=0}^{\mathbb{N}} \sum_{x=1}^{X_{i'}} \left[ \frac{T_{S4(i',j',x)}^{\Delta H}}{TST^{\Delta H}} \ln \left( \frac{\left(T_{S4(i',j',x)}^{\Delta H}\right)^2}{\sum_{j'=0}^{\mathbb{N}} T_{S4(i',j',x)}^{\Delta H} \cdot \sum_{i'=1}^{\mathbb{N}+1} T_{S4(i',j',x)}^{\Delta H}} \right) \right]. \quad (63)$$

It is noteworthy that most of the Equation 57 terms in a three-dimensional matrix defined by $i = 0\ to\ \mathbb{N}+1$, $j = 0\ to\ \mathbb{N}+1$, and x= $1\ to\ X_i$ are zero, considering that not all CDSs in the network provide all or even some of their product molecules as reactants to all other CDSs in the network.

Equations 61 through 63 are not thermodynamic entropy values in the sense of Clausius' heat theory [30–32]. They are information entropy values in the sense of Shannon's information theory [13]: probabilistic weighting factors associated with the microstates of an information network. The value of each equation for any network of any type of flow is always between 0.0 and 1.0, with the joint entropy always being equal to 1.0, and the sum of the average mutual information with the conditional entropy always being equal to 1.0. Considering the principle that information is stored energy and that loss of information is the release of stored energy that results in a generation of thermodynamic entropy, these equations can be used to determine network properties of heat transformation theory that are related to thermodynamic entropy. The way to apply each equation is to multiply it by a total system throughflow directly related to the flows.

In the case of heat transformation theory, the results of the use of Equations 61 through 63 could each be multiplied by the total system throughflow of enthalpy transfer rate density (Equation 60) to obtain *enthalpy transfer rate density capacity*,

$$C_{\Delta H} \equiv TST^{\Delta H} \cdot H_{\Delta H} = TST^{\Delta H}, \quad (64)$$

*enthalpy transfer rate density ascendancy*,

$$A_{\Delta H} \equiv TST^{\Delta H} \cdot I_{\Delta H}, \quad (65)$$

and *enthalpy transfer rate density reserve*,

$$R_{\Delta H} \equiv TST^{\Delta H} \cdot \Phi_{\Delta H}. \quad (66)$$

Even though Equation 61 is always equal to 1.0 because it is normalized, to be complete, enthalpy transfer rate density capacity (Equation 64) is defined as the total system throughflow of enthalpy transfer rate density (Equation 60). The purpose of these network properties is to characterize the phenomena of the division of energy flows.

The enthalpy transfer rate density ascendancy (Equation 65) is defined by multiplying Equation 60 by Equation 62. This network property is a statistical weighted average of the enthalpy transfer rate density flows (Equation 59) that accounts for approximately 40% of the total system throughflow of enthalpy transfer rate density. Ulanowicz [26] shows that this relates to the observable number of major trophic levels of a food chain, major species being those of largest population size or greatest population impact. Applied here, it represents an observable number of major CDSs connected in series that dominate a CDS network by taking up 40% of the power throughflow. This number of CDSs ranges statistically between 1.0 and 4.5.

The enthalpy transfer rate density reserve (Equation 66) is defined by multiplying Equation 60 by Equation 63. This network property is a statistical weighted average of the enthalpy transfer rate density flows (Equation 59) that accounts for approximately 60% of the total system throughflow of enthalpy transfer rate density. Ulanowicz [26] shows that this relates to the observable connectivity of a food chain, statistically ranging between 1 and 3, being the less major but still relevant network

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connections into and out of the central, major food chain. Applied here, it represents an observable number of lesser but still high volume supportive side connections in parallel with the central main CDS chain, which side connections take up approximately 60% of the total system throughflow. These side connections in total effect include all of the minor network connections of a broad chemical reaction network of minor CDSs of lesser chemical reaction chains, no matter how minimal the enthalpy transfer rate density flows. These side connections also include:

1. The imports of all reagents, catalysts, and cofactors that support chemical reactions in the network but don't otherwise react within the network, resulting in their auto-decomposing to reverse-import flows,
2. The exports of molecules produced by the network that are used outside of the network as reagents, catalysts, and cofactors, thus ultimately auto-decomposing and reentering the network as a reverse-exports, and
3. The export of molecules that are not used by any other CDSs within or outside the network for any purpose, thus ultimately auto-decomposing and reentering the network as reverse-exports.

The term *reserve* as used by Ulanowicz [24] and Irons and Irons [33] is in preference to the term *overhead* used in [12,34] to bring attention to the fact that it does not include the overhead irreversibility of heat dissipation terms of $j = \mathbb{N} + 2$. As defined previously, these properties only include stored energy flow, and not heat dissipation flow.

These properties are empirically demonstrated for food chains in the ecosystems of today [26]. Food chain flows are the result of consumed biological tissues. Such biological tissues are the result of a statistical production of stored energy as biological tissue that follows from the ten percent law [35] that says that only 10% of the stored energy of consumed biological tissue becomes biological tissue of the consumer. Following this ten percent law out to four trophic levels with a connectivity of up to three results in approximately 40% of the energy being utilized for biological tissue production in the major central food chain and associated side connections, being subdivided between a small number of species, each species accounting for greater than average biological tissue production. Approximately 60% of the energy is outside of the major central food chain and its side connections and is subdivided between a relatively large number of species, resulting in these species individually producing lesser amounts of biological tissue than average. This result aligns with empirically measured ascendancy and reserve performances of real ecosystem food networks [26].

Considering that biological processes that break down and utilize consumed biological tissue are chemical processes, it is expected that networks of CDSs follow the same ten percent law:

1. There can be up to four major CDSs in a chemical reaction series with a connectivity of up to three lesser but substantial side connections to each chemical reaction supporting them. The enthalpy transfer rate density ascendancy comes out to around 40% of the enthalpy transfer rate density capacity. It is calculated using average mutual information of enthalpy transfer rate density. This aligns with heat transformation theory regarding the energy storage of complexity yield and the specific mutual universal entropy resulting from the release of stored energy. This reveals a connection between stored energy and information. See Conclusions Section 4.2. The CDSs that make up the ascendency of a network are on the order of ten in number and each individually are above the weighted average of auto-powering capacity, taking in and putting out relatively great amounts of enthalpy transfer rate density flow.
2. The enthalpy transfer rate density reserve comes out to around 60% of the enthalpy transfer rate density capacity. It is calculated using conditional entropy of enthalpy transfer rate density. This aligns with heat transformation theory regarding the specific conditional universal entropy resulting from the immediate release of heat that is not used for energy storage by the ascendancy. This heat goes to an opportunistic homeostasis of CDSs that are perhaps one or two orders of magnitude greater in number than the CDSs making up the ascendency and that each individually are below the weighted average of auto-powering capacity taking in and putting out relatively little enthalpy transfer rate density flow. These are called a reserve because they provide a competitive redundancy of CDSs in the ascendency if ascendent CDSs fail.

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The results of Equations 61 through 63 are also multiplied by the network complexity (Equation 58) to obtain three additional network properties related complexity. *Complexity ascendancy* is defined as the network complexity multiplied by the average mutual information of enthalpy transfer rate density flow,

$$A_{Cx} \equiv \mathcal{u}_{Cx} \cdot I_{\Delta H} . \tag{67}$$

The average mutual information of enthalpy transfer rate density flow is for portion of a network of CDSs that is made up of major CDSs. Multiplying it by the network complexity provides a statistical measure of the complexity of the major portion of the network of CDSs. The purpose of this property is to characterize the phenomenon of the growth of complexity on Earth. Growth of complexity would not happen without a minority of CDSs taking up a plurality of the stored energy throughflow, thus resulting in the competitive success of the minority of CDSs over the majority of CDSs. This results in a minority of CDSs dominating the chemical ecosystem. By observation, this can account for the observed phenomena of only four nucleotides dominating eukaryotic RNA and four nucleotides dominating eukaryotic DNA. Molecules build on elements, molecular processes build on molecules, and life is built on molecular processes. Each of these is an observable exponential increase in complexity, in the common use of the term, with a severe narrowing down of dominant molecular species.

*Complexity reserve* is defined as the network complexity multiplied by the conditional entropy of enthalpy transfer rate density flow,

$$R_{Cx} \equiv \mathcal{u}_{Cx} \cdot \Phi_{\Delta H} . \tag{68}$$

The conditional entropy of enthalpy transfer rate density flow is for the portion of a network of CDSs that is made up of minor CDSs. Multiplying it by the network complexity provides a statistical measure of the complexity of the minor CDSs of the network. The purpose of this property is to characterize the phenomenon of all the other molecules visible in nature that have either reserve roles of competitive redundancy, minor roles, or seemingly no role, such as the remnant of noncanonical nucleotides that exist within eukaryotic cells but are not a part of the RNA and DNA structure. This could also account for the many proteinoids formed outside of cells, as well as the non-ribosomal peptide synthetases, non-ribosomal protein factors, and nonproteinogenic amino acids within cells. They form much of the organic biomass in nature (i.e., approximately 60% according to this theory).

Together, *complexity ascendancy* and *complexity reserve* add up to be *complexity capacity*, defined as the network complexity (Equation 58),

$$C_{Cx} \equiv \mathcal{u}_{Cx} \cdot H_{\Delta H} = \sum_{i,j=0}^{\mathbb{N}+1} \sum_{y=1}^{Y_i} \mathcal{u}_{Cx}\left(B_{yi}\right)_{i,j,y} , \tag{69}$$

considering that joint entropy of enthalpy transfer rate density flow is equal to 1.0. The complexity of the major and minor molecules that evolve make up the total complexity.

### *3.6. Network Analysis of Heat Quality Output*

As a result of the function of GDS heat delivery to CDSs, CDSs subsequently output heat for GDSs to carry away. This leads to another network property that aids in understanding the performance of a network of CDSs, the heat quality output rate density. Such a value provides information on how much heat quality remains to be used by CDS networks that are downstream. The conditional heat quality output rate density and the mutual heat quality output rate density are particularly easy to calculate because of the forms of the equations for specific conditional heat quality output (Equation 43) and specific mutual heat quality output (Equation 45).

The network properties for these heat quality output rate densities are calculated by similar fashion to the network properties for enthalpy transfer rate densities, but with just the $j = \mathbb{N} + 2$ term for dissipations for dissipations are used, per Equation 13 of [12]. Heat output rate densities are

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used in conjunction with Equation 43 and Equation 45 to obtain the heat quality output rate densities for single CDSs. Figure 7 provides a simplified example of the heat output rate densities.

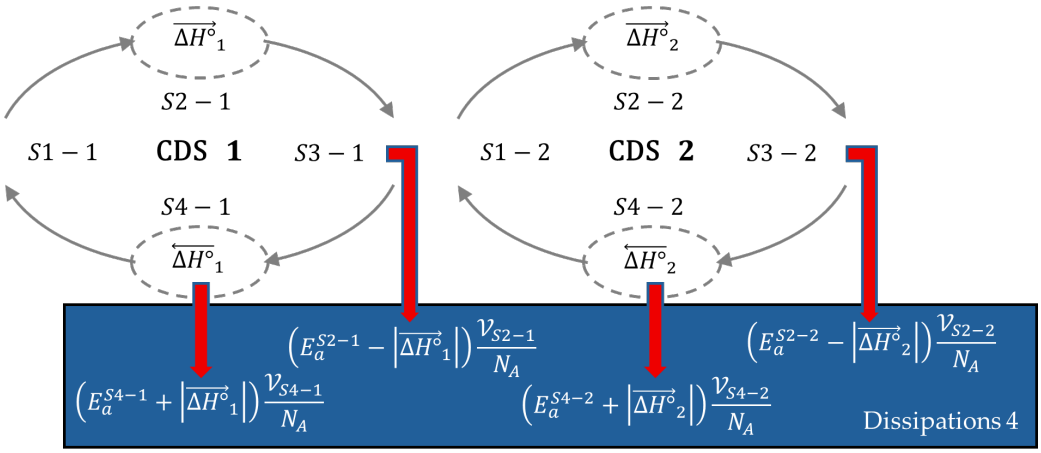


**Figure 7.** Heat outputs of a simple network of two CDS nodes. Heat outputs from stage 3 and stage 4 of CDSs are treated as dissipations for the purpose of calculating network properties of heat quality output rate density.

Based on this approach, the *conditional heat quality output rate density* for $CDS\ i$ of a network is

$$\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2} = \left(E_a^{endo} - \left|\overrightarrow{\Delta H^\circ}\right|\right)_{i,\mathbb{N}+2} \cdot \frac{\mathcal{V}_{2-i}}{N_A} \cdot \left(\frac{1}{T_{uni-C}} - \frac{1}{(T_{loc-C})_{3-i}}\right) \tag{70}$$

and the *mutual heat quality output rate density* is

$$\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2} = \left(E_a^{exo} + \left|\overrightarrow{\Delta H^\circ}\right|\right)_{i,\mathbb{N}+2} \cdot \frac{\mathcal{V}_{4-i}}{N_A} \cdot \left(\frac{1}{T_{uni-C}} - \frac{1}{(T_{loc-C})_{4-i}}\right). \tag{71}$$

Based on Equation 70, the network properties follow for conditional heat quality output rate density using Equation 13 of [12]. Rather than start with the joint entropy, average mutual information, and conditional entropy equations and then multiplying each by the total system throughflow to get the capacity, ascendency, and reserve, the following equations are presented as the expanded version of the latter, showing how the total system throughflow simply cancels out of the denominators to obtain capacity, ascendency and reserve. The *total system throughflow of conditional heat quality output rate density* is,

$$TST^{\Sigma\text{con}} = \sum_{i=1}^{\mathbb{N}} \left[\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2}\right], \tag{72}$$

the *conditional heat quality output rate density capacity* is,

$$C_{\Sigma\text{con}} = -\sum_{i=1}^{\mathbb{N}} \left[\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot \ln\left(\frac{\frac{\dot{\Sigma}_{con}^{CDS}}{V}}{TST^{\Sigma\text{con}}}\right)\right], \tag{73}$$

the *conditional heat quality output rate density ascendency* is,

$$A_{\Sigma\text{con}} = \sum_{i=1}^{\mathbb{N}} \left[\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot ln\left(\frac{\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot TST^{\Sigma\text{con}}}{\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot \sum_{i=1}^{\mathbb{N}}\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2}}\right)\right], \tag{74}$$

and the *conditional heat quality output rate density reserve* is,

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$$R_{\Sigma\text{con}} = -\sum_{i=1}^{\mathbb{N}}\left[\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot ln\left(\frac{\left(\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2}\right)^2}{\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot \sum_{i=1}^{\mathbb{N}}\left(\frac{\dot{\Sigma}_{con}^{CDS}}{V}\right)_{i,\mathbb{N}+2}}\right)\right]. \quad (75)$$

Network properties for mutual heat quality output rate density are similar. The *total system throughflow of mutual heat quality output rate density* is,

$$TST^{\Sigma\text{mut}} = \sum_{i=1}^{\mathbb{N}}\left[\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2}\right], \quad (76)$$

the *mutual heat quality output rate density capacity* is,

$$C_{\Sigma\text{mut}} = -\sum_{i=1}^{\mathbb{N}}\left[\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot \ln\left(\frac{\frac{\dot{\Sigma}_{mut}^{CDS}}{V}}{TST^{\Sigma\text{mut}}}\right)\right], \quad (77)$$

the *mutual heat quality output rate density ascendency* is,

$$A_{\Sigma\text{mut}} = \sum_{i=1}^{\mathbb{N}}\left[\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot ln\left(\frac{\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot TST^{\Sigma\text{mut}}}{\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot \sum_{i=1}^{\mathbb{N}}\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2}}\right)\right], \quad (78)$$

and the *mutual heat quality output rate density reserve* is,

$$R_{\Sigma\text{mut}} = -\sum_{i=1}^{\mathbb{N}}\left[\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot ln\left(\frac{\left(\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2}\right)^2}{\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2} \cdot \sum_{i=1}^{\mathbb{N}}\left(\frac{\dot{\Sigma}_{mut}^{CDS}}{V}\right)_{i,\mathbb{N}+2}}\right)\right]. \quad (79)$$

Network properties for *maximum heat quality output rate density* can easily be calculated if the local heat sinks of all of the CDSs in the network, $(T_{loc-C})_{3-i}$ and $(T_{loc-C})_{4-i}$ are the same heat sink. This can be the case for a network of CDSs that are all within the same GDS heat flow. CDS networks grow within heat flows of GDSs. As a result, the local heat sink temperatures for all of the stages 3 and stages 4 of the CDSs in a network can be the same. Based on this, maximum heat quality output rate density total system throughflow, capacity, ascendency and reserve are calculated using the following *maximum heat quality output rate density*,

$$\left(\frac{\dot{\Sigma}_{max}^{CDS}}{V}\right)_{i,\mathbb{N}+2} = (E_a^{endo} + E_a^{exo})_{i,\mathbb{N}+2} \cdot \frac{\mathcal{V}_{2-i}}{N_A} \cdot \left(\frac{1}{T_{uni-C}} - \frac{1}{T_{loc-C}}\right). \quad (80)$$

This is simply a result of setting $(T_{loc-C})_{3-i}$ and $(T_{loc-C})_{4-i}$ equal to $T_{loc-C}$ and then adding the conditional and mutual heat quality output rate densities. Also as a result of CDS networks growing within convective heat flows that are a result of differential pressures and differential temperatures over great distances, the local heat source temperature and local heat sink temperature tend to be the same temperature. This prevents a loss of heat quality that would be caused by large temperature drops. As a result, the specific maximum heat quality drop of Equation 47 is zero. Networks of CDSs within GDS flows have the potential for utilizing heat without depleting the heat quality. A locality in which many CDSs are networked together could result in a large network complexity with no loss of heat quality as a direct result of the CDSs. The potential impact of recycled heat on prebiotic growth of complex molecules demonstrates that heat quality drop and heat quality output are better measures of DS performance than universal entropy.

## 4. Conclusions

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This paper has explored the thermodynamic principles that govern the formation and function of CDSs and their networks, emphasizing their role in driving complexity on pre-biotic Earth. As heat and stored energy flows through GDSs to engage CDSs, it transforms matter and generates order, creating the conditions necessary for the emergence of complex systems. The terms *complexity* and *order* and how they are related to entropy are defined in numerous ways in the existing literature. These various attempts at definition frequently lack thermodynamic modeling to provide a basis of the offered definition on the laws of thermodynamics The results of modeling in heat transformation theory reveal a relationship between entropy, order, and complexity that enable clarification in the definition of these terms. This clarification also leads to an understanding of the nature of information. The following are the conclusions that could be drawn from Part I [1] and Part II of heat transformation theory.

### *4.1. Entropy, Order, and Complexity*

The element of DSs that has not been adequately addressed in the existing research to-date is in the understanding of ARO as the release of stored energy and the associated matter that stores the energy that closes a heat engine cycle. The literature often calls this releasable energy the *available free energy* or the *work energy* [36,37], fitting descriptively with the function of ARO. Without this decay, new incoming heat for use by the APC of the DS runs out of local material to sustain the complexity yield property of the DS because all the locally available material that can be used by the DS is already engaged in a high-level potential energy storage state. The DS literally stops working (i.e., stops yielding complexity) when it runs out of input material at stage 1.

This is difficult to picture for a DS such as the TWC, because one can't imagine gravity failing to return all of the water of Earth from the top of the troposphere back to surface level. However, if the DS is a brain cell that has achieved full growth and stops moving energy through it because all of the material that can move the energy from stage 1 to stage 3 is locked in place at stage 3 at its maximum stored energy state, then the end effect is that the brain stops the emergent property function of thinking provided by an entire brain of brain cells. Because decay does occur (e.g., the water does fall again as precipitation, and molecules of ATP in a brain cell are broken down to release energy and function), the material releases its potential energy as it returns to its original order at stage 1 that is at a lower-level potential energy state. Dissipation away from the DS occurs following stage 4 heat output. Specific mutual heat quality output is lower because of the specific mutual heat quality drop. The dissipating heat passes on to other DSs that can use the heat at the lower specific heat quality. New heat at the higher necessary specific heat quality level comes through to the local heat source of the DS. This incoming greater specific heat quality reengages the newly-decayed material in stage 2 energy storage and back to the higher-level potential energy state at stage 3.

The heat transformation theory uses the term *order* to differentiate the degree to which material is captured in DSs. Order manifests at greater levels as ions, atoms, and molecules come under greater constraint because of being more tightly captured in conservative force fields generated by properties of collections of matter. Recall that conservative force fields do not generate entropy in the process of kinetic energy converting to potential energy and potential energy converting back to kinetic energy. Material is less orderly when subject to lesser conservative force magnitudes or expanded to greater volumes at further distances from the center of a conservative force field, which tend to go together.

A map of the galactic filaments of the universe has visible order, though hydrogen gas atoms floating in a filament in inter-galactic space outside of the major influence of any one galaxy and having never undergone fusion in a star are less orderly than carbonic acid captured in an ocean current on Earth. The carbonic acid is part of multiple GDSs that move water and air to bring carbon dioxide and dihydrogen oxide (i.e., water) together into a CDS that produces carbonic acid, with all DSs together forming part of the carbon cycle. In addition, the carbon, hydrogen, and oxygen atoms are all nuclear DSs unto themselves. They are created by the generation and dissipation of levels of heat greater than the primary fusion of hydrogen that begins to burn out followed by the star's GDS collapse. The result is the fusion by both leading exothermic synthesis and leading endothermic

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synthesis of all atoms that are heavier than helium-4. The scattered heavy elements then collect into a protoplanetary disk around a newly forming star and collapse into planets, like Earth, that now have carbon, hydrogen, oxygen, and all of the other long-lived isotopes of elements. That is a lot of DSs networked together and therefore a lot of order provided by many conservative force fields that lead to carbonic acid in an ocean stream on a planet.[6]

Using this definition of order, it is apparent that it is not the opposite of entropy. In the early universe shortly following the big bang when high temperature hydrogen forms, this is considered to be a state of low universal entropy due to the high temperature. It is also low order due to the gravitational force not yet exerting major influence. Hydrogen atoms are not yet captured by gravity into star formations. Compare this to the hydrogen that is floating in a filament between old galaxies. The only two differences are that there are galaxies exerting enough net gravitational force to pull the loose hydrogen into filaments and the hydrogen is at a much lower temperature due to heat dissipation that has occurred since the first formation of hydrogen. This means that the loose hydrogen is under a little more order in universal filaments than upon initial formation following the big bang, and the low temperature hydrogen in the universal filaments is at a much greater universal entropy level than the hot hydrogen freshly formed near the beginning of the universe. Order and entropy are independent. Order is a result of conservative forces and conservative forces do not generate entropy in the conservative conversion of energy. Entropy is associated with heat dissipation, which is independent of conservative force fields.

Defined in this way, order is a result of conservative force fields generated by properties of matter, entropy is a result of heat dissipation from high equilibrium temperatures to low equilibrium temperatures, and complexity is a result of the combination of order and entropy in a DS. Complexity is a property that results from the function of the complexity yield of the DS. Complexity yield functions by two methods. The first method is by the APC of heat dissipation out of a lower point in the potential energy well of a conservative force field using material convection that increases potential energy storage. The second method is by ARO driven by heat dissipation that releases the stored potential energy and matter back to a lower potential energy state in the conservative force field. Both APC and ARO are needed to complete the entire cycle of material that maintains the complexity yield of a DS and generates complexity.

### *4.2. Stored Energy and Information*

A distinction made by heat transformation theory is that information and energy stored as enthalpies of formation in molecules are the same thing. There have been many attempts in ecological thermodynamics to understand the nature of information, leading to many varied explanations of it in thermodynamic terms [38–55]. As a result, there is lack of coherence regarding the relationship between Boltzmann statistical entropy [14] and Shannon entropy [13]. Consider the bits of a computer storage that are either on or off and are the informational value of 1 or 0. These bits are controlled by an electrical conservative force field that establishes voltage potential wells that can store energy or release energy depending upon the state of a micro-transistor that controls the bit. Once energy is released and the bit is cleared, the memory of what value that bit had no longer exists. The energy has dissipated as heat.

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[6] Primary fusion in a star is an interesting case. It is a network of nuclear dissipative structures that starts with a leading endothermic synthesis strong force dissipative structure that fuses two ionized hydrogen-1 atoms (two protons) into hydrogen-2, followed by a leading exothermic decomposition weak force dissipative structure that converts one of the protons into a neutron, followed by a leading exothermic synthesis strong force dissipative structure that fuses hydrogen-2 and another proton into helium-3, followed by a leading exothermic synthesis reaction that fuses two helium-3 atoms releasing two protons, and ending with two protons in the fused atom exothermically converting to neutrons to result in helium-4.

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The analogy of Maxwell's Demon is useful. When Maxwell's Demon opens and closes a trap door a chamber filled with particles that can be treated as the universe and an empty chamber to capture one particular particle in the previously empty chamber, information is created. It is now known by the Demon that one particle is in one specific chamber. That is the information. This information is matched by an increase in the particle's inertial potential to leave the chamber if the trap door is ever opened, as measured by the pressure the moving particle imparts on the walls of the chamber. When Maxwell's Demon opens and closes the trap door to release the particle, this releases the inertial potential of that particle to leave the chamber and enter the chamber with all of the other particles, the universe. Until such time as the demon recaptures that particle or any other particular in the empty chamber, no particle's position is fixed and therefore is not differentiable and is just part of the noise level of particles in the universe going wherever their inertia takes them. Until a particle is again differentiated from all the other particles by constraining its inertial potential to that chamber, it cannot be used as a form of differentiable information.

Heat transformation theory identifies the constraining of inertia in a limited volume by Maxwell's Demon to be a form of energy storage just as potential energy and appears to reduce entropy according to Boltzmann statistical entropy. As matter stores potential energy, the result is that inertia of matter is constrained, similar to an inertial particle being trapped in a chamber by a closing door, except that it is the conservative force field that is doing the constraining. This creates information and then releases it as energy the same way a Szilárd's engine creates information, as demonstrated by Toyabe et al. [56]. This is complexity yield that is a result of the creation of inertial constraint. In this case, the inertial constraint is provided by volume restricting barriers rather than phase-space restricting conservative forces. A dissipating particle is trapped in a chamber, giving it inertial potential to leave the chamber, and preventing the particle from generating universal entropy. When the trap door is opened, the particle is free to leave, increasing universal entropy by allowing it to expand into a greater volume of space. This is why Boltzmann statistical entropy and Shannon information entropy take the same form when Shannon information entropy is modified to give all states of information an equal probability.

When reaction enthalpy is stored because of an endothermic auto-synthesis chemical reaction, the information that is stored is the limiting of the position and velocity of the newly bonded atoms to their bonds. The release of the bonding of individual atoms from a molecule returns them to have access to more states of position and velocity, resulting in mutual universal entropy. The nature of stored potential energy and constrained particle inertia is informational. This is why the equations developed from Shannon information theory can be used to calculate thermodynamic properties of state of a network of DSs. The network properties of enthalpy transfer rate density and complexity derived by heat transformation theory from Shannon entropy are not new properties in addition to the thermodynamic properties, but are Boltzmann microstates associated with the constraint of stored energy to network flows.

This relates to order and entropy being independent properties. Reduction in order is a release of stored energy/constrained inertia that subsequently could dissipate as heat to entropy. The released energy/unconstrained inertia does not automatically become universal entropy until it dissipates to the universal heat sink. DSs can recycle heat quality and transform heat to stored energy, delaying its progress to the universal heat sink. Thus, order and entropy vary independently.

This also suggests a relationship between Clausius' entropy and Boltzmann's statistical entropy. Because order and entropy are independent properties in that a reduction in order does not necessarily result in an increase in entropy, this could explain why Clausius' entropy and Boltzmann's entropy do not always agree [57]. Whereas Clausius entropy is a measure of the conditional entropy of heat losing its quality as a result of dropping to a lower temperature, Boltzmann statistical entropy relates to mutual entropy that results from the release of stored/constrained energy held by the material properties of matter, allowing the matter to gain access to more microstates in phase space upon the releasing of the stored energy/constrained inertia.

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When situation results in loss of order followed immediately by increase in entropy, then Clausius' entropy and Boltzmann's statistical entropy agree.

*4.3. Chemosystem Formation*

What has yet to be shown is that the massive mixing of GDSs makes the formation of CDSs probable by achieving multiplicity of microstates and ergodicity of mixing. Researchers are trying to figure out the series of chemical reactions by which the building block of life — precursor molecules, amino acids, and nucleotides — could be generated in nature without the kind of human intervention that occurs in a lab, with some success. Even then, there are more amino acids and nucleotides found in nature and developed artificially in the lab than the canonical amino acids and nucleotides that are utilized in Eukaryote RNA and DNA. So, there is an additional question of how and why canonical amino acids and nucleotides are determined during the development of the chemosystem. Finally, the question remains regarding how canonical amino acids and nucleotides organize into long chains in organized structural systems that lead to life. The objectives of the remaining papers in this series are to answer these questions.

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## Abbreviations

The following abbreviations are used in this manuscript:

| | |
|---|---|
| APC | Auto-powering capacity |
| ARO | Auto-restoring order |
| atmlev | Atmospheric leveling |
| C | Heat sink |
| CDS | Chemical dissipative structure |
| CMBR | Cosmic microwave background radiation |
| Cx | Complexity |
| con | Conditional |
| DNA | Deoxyribonucleic acid |
| DS | Dissipative structure |
| FUCA | First universal common ancestor |
| G | Gravity |
| GDS | Gravitational Dissipative structure |
| H | Heat source |
| in | Input |
| L | Lift |
| loc-H | Local heat source |
| loc-C | Local heat sink |
| LUCA | Last universal common ancestor |
| max | Maximum |
| med | Heat carrying medium of a dissipative structure |
| mut | Mutual |
| NC | Natural convection |
| out | Output |
| OG-FUCA | The original individual of the first universal common ancestor |
| PE | Potential energy |
| precip | Precipitation |

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| | |
|---|---|
| Q | Internal energy of heat capacity (when used as a subscript) |
| S1 | Stage 1 |
| S2 | Stage 2 |
| S3 | Stage 3 |
| S4 | Stage 4 |
| Sys | System |
| TAC | Tropospheric air cycle |
| tac | Tropospheric air cycle |
| tropau | Tropopause |
| trosph | Troposphere |
| TWC and twc | Tropospheric water cycle |
| uni | Universal |
| uni-H | Universal heat source |
| uni-C | Universal heat sink |
| wu | Warm up |
| wv | Water vapor |

## Appendix A. The Leading Endothermic Auto-Synthesis CDS Model

Figure A1 is a heat engine model of the leading endothermic auto-synthesis chemical reaction as a CDS. The following is a physical and mathematical analysis of the model.

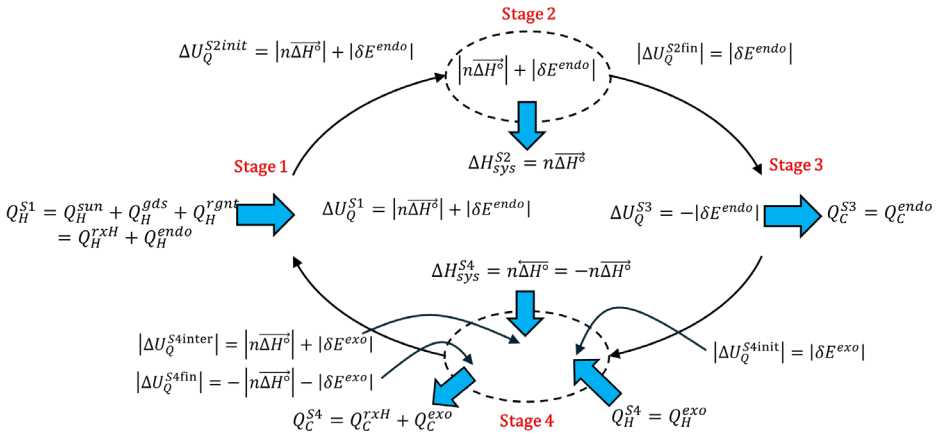


**Figure A1.** The leading endothermic auto-synthesis chemical dissipative structure (CDS) model. At stage 1, chemical reactants absorb heat from heat sources as internal energy. At stage 2, molecular kinetic energy drives reactant molecules together, along with any reagents, catalysts, and cofactors, resulting in an endothermic chemical reaction that stores reaction enthalpy and returns the heat required to achieve activation energy. At stage 3, the remaining heat is exhausted to the heat sink. At stage 4, the chemical products of the stage 2 reaction now become reactants of the exothermic auto-decomposition reaction that is the reverse of the stage 2 reaction. They absorb heat from heat sources as internal energy. Molecular kinetic energy drives reactant molecules together, along with any reagents, catalysts, and cofactors, resulting in an exothermic chemical reaction that releases reaction enthalpy and returns the heat required to achieve activation energy. The released reaction enthalpy and the internal energy required for activation are exhausted to the heat sink. The chemical products of the stage 4 reaction are available again to become reactants of the endothermic auto-synthesis reaction of the CDS.

### *Appendix A.1. Analysis of Stages 1 through 3*

Start with applying the first law of thermodynamics and the work-energy theorem from Equation 5 to the system for stages 1 through 3,

$$\Delta H_{sys}^{S1\to3} = \Delta Q_{sys}^{S1\to3}\,. \tag{A1}$$

There is one change in the state property of system enthalpy at stage 2,

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$$\Delta H_{sys}^{S1\to3} = \Delta H_{sys}^{S2}\,. \tag{A2}$$

The process property of net heat exchange of the system is the difference in heat input from the heat source at stage 1 and heat output to the heat sink at stage 3,

$$\Delta Q^{S1\to3} = |Q_H^{S1}| - |Q_C^{S3}|\,. \tag{A3}$$

Substitute Equation A2 and Equation A3 into Equation A1 to obtain the energy balance for stages 1 through 3 (also Equation 20),

$$\Delta H_{sys}^{S2} = |Q_H^{S1}| - |Q_C^{S3}|\,. \tag{A4}$$

Note that the transient internal energy of temperature change, $\Delta U_Q$, is used in this analysis to track excess heat through the process.

At stage 1, heat comes from the Sun, GDSs, and reagents,

$$Q_H^{S1} = Q_H^{sun} + Q_H^{gds} + Q_H^{rgnt}\,, \tag{A5}$$

heating the chemical reactants with a transient increase in internal energy, $\Delta U_Q^{S1}$, exhibited on the microscopic scale as average molecular-kinetic energy. The heat input is sufficient to provide for the storage of reaction enthalpy of the endothermic reaction in units of energy per mole, $\overrightarrow{\Delta H^{\circ}}$, plus an additional amount of energy needed to achieve activation energy of the endothermic reaction, $\delta E^{endo}$. Multiplying reaction enthalpy by the number of moles that are reacting, $n$, and adding to $\delta E^{endo}$ enables a determination of the total required heat input to achieve the necessary increase in transient internal energy,

$$|Q_H^{S1}| = \left|\Delta U_Q^{S1}\right| = \left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{endo}|\,, \tag{A6}$$

to achieve the activation energy at stage 2. Molecular kinetic energy drives pairs of molecules together and achieves activation energy,

$$\left|\Delta U_Q^{S1}\right| \xrightarrow{molecular\ \Delta KE} \left|\Delta U_Q^{S2\text{init}}\right| = |nE_a^{endo}|\,, \tag{A7}$$

(again, in units of energy per mole) for the endothermic chemical reaction of $n$ moles of reactants. An endothermic chemical reaction uses some of the transient internal energy to convert some activation energy into stored reaction enthalpy,

$$\Delta H_{sys}^{S2} = \left|n\overrightarrow{\Delta H^{\circ}}\right|\,, \tag{A10}$$

a combination of an increase in bond enthalpy and a usually relatively lesser decrease in the internal energy of heat capacity due to a reduction in heat capacity of the products relative to the reactants (see Section 2.1),

$$n\overrightarrow{\Delta H^{\circ}} = n\overrightarrow{T\Delta S^{\circ}} + n\overrightarrow{\Delta H_{bond}^{o}}\,, \tag{A8}$$

returning remaining activation energy to the transient internal energy of chemical products,

$$\left|\Delta U_Q^{S2\text{fin}}\right| = |\delta E^{endo}|\,. \tag{A9}$$

At stage 3, excess transient internal energy becomes heat output,

$$\Delta U_Q^{S3} = -\left|\Delta U_Q^{S2\text{fin}}\right| = -|\delta E^{endo}| = -|Q_C^{S3}|\,, \tag{A11}$$

such that the total change in internal energy of the system for stages 1 through 3 is zero,

$$\Delta U_Q^{S1\to3} = \left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{endo}| - \left|n\overrightarrow{\Delta H^{\circ}}\right| - |\delta E^{endo}| = 0\,, \tag{A12}$$

and heat output at stage 3 is the excess heat remaining following the endothermic reaction (also Equation 22),

$$|Q_C^{S3}| = |\delta E^{endo}| = \left|Q_C^{endo}\right|\,. \tag{A13}$$

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The energy balance of Equation A4 for stages 1 through 3 is shown to be in balance by substituting Equation A6, Equation A10, and Equation A13 into Equation A4,

$$\left|n\overrightarrow{\Delta H^{\circ}}\right| = \left|n\overrightarrow{\Delta H^{\circ}}\right| + \left|\delta E^{endo}\right| - \left|\delta E^{endo}\right| . \tag{A14}$$

The heat input for stages 1 through 3 is,,

$$\left|Q_{in}^{S1\to 3}\right| = \left|n\overrightarrow{\Delta H^{\circ}}\right| + \left|\delta E^{endo}\right| , \tag{A15}$$

and the heat output for stages 1 through 3 is,

$$\left|Q_{out}^{S1\to 3}\right| = \left|\delta E^{endo}\right| . \tag{A16}$$

*Appendix A.2. Analysis of Stage 4*

Start with applying the first law of thermodynamics and the work-energy theorem from Equation 5 to the system for stage 4,

$$\Delta H_{sys}^{S4} = \Delta Q_{sys}^{S4} . \tag{A17}$$

The net heat exchange is due to a heat input and heat output at stage 4 (also Equation 23),

$$\Delta Q_{sys}^{S4} = \left|Q_{H}^{S4}\right| - \left|Q_{C}^{S4}\right| . \tag{A18}$$

Substitute Equation A18 into Equation A17 for the energy balance:

$$\Delta H_{sys}^{S4} = \left|Q_{H}^{S4}\right| - \left|Q_{C}^{S4}\right| . \tag{A19}$$

Initially at stage 4, heat becomes an initial change in transient internal energy of the chemical reactants of the exothermic auto-decomposition reaction that is the reverse of the endothermic auto-synthesis reaction of stage 2 and provides an amount of energy, $\delta E^{exo}$, needed to achieve activation energy of the exothermic reaction,

$$\left|Q_{in}^{S4}\right| = \left|Q_{H}^{S4}\right| = \left|\Delta U_{Q}^{S4\text{init}}\right| = \left|\delta E^{exo}\right| . \tag{A20}$$

The molecular kinetic energy of internal energy drives pairs of molecules together and overcomes the activation energy for an exothermic chemical reaction,

$$\left|\Delta U_{Q}^{S4init}\right| = \left|nE_{a}^{exo}\right| . \tag{A21}$$

An exothermic chemical reaction, the reverse of the endothermic chemical reaction of stage 2, releases previously stored reaction enthalpy,

$$\overleftarrow{\Delta H^{\circ}} = -\overrightarrow{\Delta H^{\circ}} , \tag{A22}$$

and the initial energy needed to achieve activation energy, $\delta E^{exo}$. This results in a localized increase in transient internal energy,

$$\left|\Delta U_{Q}^{S4\text{inter}}\right| = \left|n\overrightarrow{\Delta H^{\circ}}\right| + \left|\delta E^{exo}\right| , \tag{A23}$$

and a change in system enthalpy,

$$\Delta H_{sys}^{S2} = -\left|n\overrightarrow{\Delta H^{\circ}}\right| . \tag{A24}$$

The localized increase in transient internal energy becomes heat output,

$$\Delta U_{Q}^{S4\text{fin}} = -\left|\Delta U_{Q}^{S4\text{inter}}\right| = -\left|n\overrightarrow{\Delta H^{\circ}}\right| - \left|\delta E^{exo}\right| = -\left|Q_{C}^{S4}\right| , \tag{A25}$$

such that the total change in transient internal energy of the system for stage 4 is zero,

$$\Delta U_{Q}^{S4} = 0 , \tag{A26}$$

and heat output at stage 4 is the heat associated with released reaction enthalpy and the original heat input required to achieve the activation energy of the exothermic reaction (also Equation 25),

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$$|Q_{out}^{S4}| = |Q_C^{S4}| = \left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{exo}| = |Q_C^{rxH}| + |Q_C^{exo}|\,. \tag{A27}$$

The energy balance of Equation A19 for stage 4 is shown to be in balance by substituting Equation A19, Equation A24, and Equation A13 into Equation A19,

$$-\left|n\overrightarrow{\Delta H^{\circ}}\right| = |\delta E^{exo}| - \left(\left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{exo}|\right). \tag{A28}$$

*Appendix A.3. Results of Heat Dissipations of Stages 1 through 4*

The first result is revealed by comparing total heat input to total heat output. Sum Equation A15 and Equation A19 to determine the total heat input for stages 1 through 4:

$$\left|Q_{in}^{S1\to4}\right| = \left(\left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{endo}|\right) + |\delta E^{exo}|\ . \tag{A29}$$

Sum Equation A16 and Equation A27 to determine the total heat output for stages 1 through 4:

$$|Q_{out}^{S1\to4}| = |\delta E^{endo}| + \left(\left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{exo}|\right). \tag{A30}$$

Compare Equation A29 and Equation A30,

$$\left|Q_{in}^{S1\to4}\right| = |Q_{out}^{S1\to4}| = \left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{endo}| + |\delta E^{exo}|\,, \tag{A31}$$

to reveal that total heat input equals total heat output.

The second result is revealed by comparing the difference of heat input and heat output of stages 1 through 3 to the difference of heat input and heat output of stage 4. The difference for stages 1 through 3 is

$$\left|Q_{in}^{S1\to3}\right| - |Q_{out}^{S1\to3}| = \left(\left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{endo}|\right) - |\delta E^{endo}| = \left|n\overrightarrow{\Delta H^{\circ}}\right|. \tag{A32}$$

This is the amount of energy that is stored during stage 2. The difference for stage 4 is

$$\left|Q_{in}^{S4}\right| - |Q_{out}^{S4}| = |\delta E^{exo}| - \left(\left|n\overrightarrow{\Delta H^{\circ}}\right| + |\delta E^{exo}|\right) = -\left|n\overrightarrow{\Delta H^{\circ}}\right|. \tag{A33}$$

This is the amount of stored energy that is released at stage 4. The result is that the stored energy at stage 2 is equal and opposite to the released energy at stage 4, the same as for the TWC GDS as shown in Equation A38 of [1]. This reveals that stage 2 and stage 4 of the leading endothermic auto-synthesis CDS are reversible. The reversibility is a result of conservative forces controlling the storage and release of energy.

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