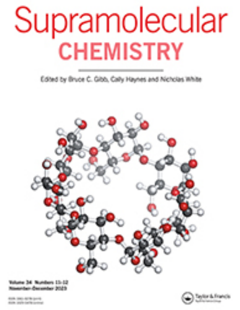

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# Is the spontaneity of chemical reactions related to time travel?

Pedro Metola[a], Sean T. Roberts[b] and Eric V. Anslyn[b]

[a]Freshman Research Initiative, The University of Texas at Austin, Austin, TX, USA; [b]Department of Chemistry, The University of Texas at Austin, Austin, TX, USA

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Are you a Star Wars or Star Trek fan? I love both space adventure series, but I am particularly partial to Star Trek. I was 6 years old when the original series premiered (1966), and I first watched it in reruns when I was in junior high. I did so repeatedly for years, including over dinner with my roommate Michael Petty when I was in graduate school at Caltech (1983–1987). Since then, I have watched every Star Trek series (except the animated ones), including the most recent Strange New Worlds, which I believe is the best yet since The Next Generation.

When considering all the Star Trek series, there have been over 50 episodes involving time travel. Two from the original series particularly stand out to me. The first is The City on the Edge of Forever, in which Dr. McCoy injects himself with a dangerous drug on accident, goes a bit crazy, and transports himself to a planet the Enterprise is orbiting. A rescue party including Captain Kirk and Spock beam down to the planet and encounter the Guardian of Forever, which is a sentient time portal. McCoy travels back in time and changes history, and Kirk and Spock follow him to restore the timeline. I will not give away the rest of the episode because I strongly encourage you to watch it. The episode is both romantic and tragic. My second favourite Star Trek episode dealing with time travel is Assignment Earth, in which the Enterprise travels to 1968 Earth for historical research. Kirk and Spock encounter Gary Seven, a being from the future, and his cat Isis, both assigned to this period of Earth's history to prevent WWIII. The plot is fun, complex, and twisted; ultimately it is discovered that the proper timeline has the Enterprise involved in the time travel that occurs in this episode.

Why am I reminiscing about Star Trek episodes? And what does time travel have to do with supramolecular chemistry, or chemistry in general? To make the connections, we must first recognise that chemical reactions are spontaneous, as in unforced or occurring without intervention (we are not discussing reactions that are fuelled, as in an electrochemical transformation that is driven by a current). For example, if we simply allow a solid to sit in the bottom of a flask, with time it may dissolve. Or if we mix reactants, with time a product may form. We do not touch the flask with a magic wand, we do not force the molecules together – in fact, we do nothing more than mix the reagents in a solvent – and *voila*, the change in composition occurs. I am not discussing how fast the reaction occurs (it may occur in a microsecond or over centuries) but only that the change is spontaneous.

To further establish the parallels between time travel and chemistry, allow me to review the 2nd Law of Thermodynamics, which relates to entropy ($S$). Many chemists tend to think of entropy as being synonymous with disorder, but it is better defined as the number of ways ($\Omega$) that the microscopic degrees of freedom in a system can be arranged to create the same macroscopically observable state (Eq. 1):

$$S = k_B \ln \Omega, \tag{1}$$

where $k_B$ is Boltzmann's constant.

Coming back to the Second Law, it states that the total entropy ($S$) of the universe always increases or remains constant and can never decrease. In the context of chemistry, this means that the entropy of our reactions (the system) and their surroundings (the rest of the universe) can either remain constant or increase. The reaction can be a chemical transformation of a product into a reactant, or the supramolecular binding of a guest to a host.

Thus, $\Delta S_{universe}$ is always positive, and this change is irreversible! This irreversibility fundamentally sets the difference between the past and the future, or what is called the "arrow of time". Now we see the connection to time travel. We cannot travel into the past because that would inherently decrease the entropy of the universe and break the 2nd Law of Thermodynamics.

**CONTACT** Eric V. Anslyn anslyn@austin.utexas.edu Department of Chemistry, The University of Texas at Austin, 105 E 24th St, Austin, TX 78712, USA

Let us keep developing this idea further, increasingly making a tie to chemical transformations. One goal of this analysis is to review, but better explain (in our opinion), many of the lessons taught in freshman chemistry and the first semester of physical chemistry that focus on thermodynamics. For that purpose, I am now about to do a bunch of maths to connect time travel into the past to chemical reactivity, so try not to fall asleep.

Entropy is not energy and consequently does not need to be conserved. A mathematical way of stating the Second Law is given here (Eq. 2), separating the entropy of the system and that of its surroundings.

$$\delta S_{sys} + \delta S_{surr} \geq 0 \tag{2}$$

Clausius showed that the integral of all changes in entropy is greater than or equal to the integral of the sum of energy placed into states (see definition of a state given below) that can accept that energy, divided by the temperature of each state. [1] Basically, this means that energy distributes into all possible states and therefore maximises entropy. Thus, an infinitesimally small change ($\delta$) in the entropy of the surroundings ($\delta S_{surr}$) is equal to the infinitesimal heat transferred to the surroundings ($\delta q_{surr}$) divided by the surrounding's temperature (Eq. 3).

$$\delta S_{surr} = \delta q_{surr}/T_{surr} \tag{3}$$

Eq. 3 makes sense when one considers that at higher temperatures the entropy change created from a given transfer of heat is less than at a lower temperature because the disorder is already greater at higher temperature. To understand this, we need a fundamental comprehension of what is temperature and what is a state. Temperature is a measure of the occupancy of states. A state is a chemical or physical configuration with a specific quantum energy level that is, or is not, occupied. As an example, if there are 100 possible states (let us say akin to the stretching vibrational levels of a bond), only one state (the lowest energy) is occupied at zero Kelvin. You may remember this as the zero-point energy for a bond stretch. As you raise the temperature, other states become occupied. At some high temperature, nearly all the states are occupied. It follows then that the change in entropy by adding energy at higher temperature is less because there are fewer empty states to occupy.

Any heat transferred to the surroundings must come from the system (Eq. 4).

$$\delta q_{surr} = -\delta q_{sys} \tag{4}$$

With some simple manipulations of the above equations, we arrive at Eq. 5.

$$\delta S_{sys} - \delta q_{sys}/T_{surr} \geq 0 \tag{5}$$

For a process at constant pressure, the heat transferred to the surroundings is equal to the enthalpy change (Eq. 6).

$$\delta q_{sys} = \delta H_{sys} \tag{6}$$

We combine equations, and with the assumption that this is for an isothermal system where the temperature of the system and surroundings is the same, we drop the subscripts, giving Eq. 7.

$$\delta S - \delta H/T \geq 0 \tag{7}$$

Rearranging and multiplying by $T$, we find Eq. 8 for a spontaneous change.

$$\delta H - T\delta S \leq 0 \tag{8}$$

When considering an integrated total difference per mole, rather than an infinitesimally small change, we arrive at an expression relevant for any spontaneous change (Eq. 9).

$$\Delta H - T\Delta S \leq 0 \tag{9}$$

Alternatively, we can write this in terms of the Gibbs free energy ($G$), which is defined as $G = H - TS$. At constant temperature then, we get Eq. 10, which describes how the Gibbs free energy must change for a process to spontaneously occur.

$$\Delta G \leq 0 \tag{10}$$

We have arrived at the lesson you learned in introductory chemistry: endergonic changes do not occur. But for some of us this lesson was not derived from the 2nd Law of Thermodynamics, and it almost certainly was not tied to the evolution of time in a forward fashion, which cannot be reversed by time travel into the past.

You may be wondering, how can $\Delta S$ for a reaction be negative? To understand this, we must return to what the Second Law of Thermodynamics says, i.e. the total entropy of the universe can never decrease. Our reaction flasks are not isolated from their surroundings. Heat is continually being exchanged with the outside world (Eq. 5), and this compensates for any associated entropy decrease within the flask.

Now, let us analyse $\Delta G$ in greater detail to understand why chemical reactions are spontaneous. Our discussion above shows that whenever a chemist sets up a chemical reaction and a spontaneous process commences, the system (reactant (R) and solvent) is necessarily out of equilibrium and proceeds in accordance with the 2nd Law of Thermodynamics, to increase the entropy of the universe. With time this reactant generates a system additionally consisting of the product (P).

Each compound, R and P, has a chemical potential ($\mu$) defined as the extent to which the Gibbs free energy of the system changes as the activity ($a$) of that species changes. Activity is the effective mole fraction of a solute in a solution, and therefore $\Delta\mu$ can be expressed as $\Delta G/n$ (n = number of moles). Recall, activity is akin to concentration (and below we will make a parallel to pressure). Chemical potential is analogous to potential energy, such as the energy stored in a brick raised off the ground that can be released by dropping the brick. The chemical potential is free energy that can be released by changing the composition of the system.

Remember, all energy is relative. To determine how the energy of a system will change as the chemical potential of R or P changes, chemists define reference chemical potentials ($\mu^o$)for R and P, and correction terms ($RT\ln(a)$) derived from thermodynamics for a change away from the reference involving the species' activity (Eq. 11).

$$\mu_{(R\,or\,P)} = \mu^o{}_{(R\,or\,P)} + RTln(a_{R\,or\,P}) \tag{11}$$

But where did $RT\ln(a)$ come from as a correction term? So many chemists just accept this term and have no idea where it came from. To explain this, we need to take an interlude and discuss the ideal gas law and mixing. So, hold tight while we take a right turn in the discussion.

## Interlude

$RT\ln(a)$ arises from the free energy of mixing. Yes, that is right, mixing! To understand this, we must dig into some fundamental thermodynamics. Once again, do not let your eyes glaze over. This interlude is worth it.

The expression of the Gibbs free energy first given in 1873 [2] defines it as the following (a):

a. $G = U + PV \quad TS$

where $U$ is the system's internal energy (energy associated with all bond energies, vibrations, etc.), $P$ is its pressure, $V$ is its volume, and $G$, $T$, and $S$ represent the usual quantities discussed thus far. If we consider how $G$ changes as we vary temperature, pressure, volume, etc. we have Eq. b.

b. $\delta G = \delta U + \delta(PV) \quad \delta(TS) = \delta U + P\delta V + V\delta P \quad T\delta S \quad S\delta T$

This looks complicated! But if we think about the energy change for a system, we can relate this to the work that it does and the heat that it exchanges with its surroundings (Eq. c) {a future Eric's Corner will discuss what is work, and what is a fuel, and how these terms are being used in supramolecular chemistry, in that discussion we will need many of the conclusions from this Eric's Corner}:

c. $\delta U = \delta w + \delta q$

This turns out to be nothing but the First Law of Thermodynamics, which states that energy must be conserved. To calculate $\delta U$, we can consider a process wherein the system and surroundings are in equilibrium. In this case, the work is related to the change in the volume of the system $\delta w = -P\delta V$ and the heat transferred is given by the Clausius expression $\delta q = T\delta S$. Plugging this in to $\delta G$, we get some terms that fortuitously cancel, and we are left with Eq. d:

d. $\delta G = V\delta P \quad S\delta T$

Now, if the mixing does not change the temperature, $\delta T = 0$ (an isothermal mixing), we get Eq. e.

e. $\delta G/\delta P = V$

Given this, we can make the connection between the pressure of a gas and the mixing of a solute in a solvent. In a thought experiment, we can imagine a gas starting all on the left side of a vessel and then expanding to occupy the entire vessel. Consequently, the pressure of the gas equilibrates across the entire vessel and the change in Gibbs free energy during the equilibration of the gas is the expression just given by Eq. e. Analogously, let us say a solute is added to the top of a solvent. With time it diffuses and mixes into the solvent. It is clear the two concepts are the same. But, with a solution, it is the activity of the solute that is changing during the process, not the pressure, and hence the chemical potential of the system is changing.

Solving Eq. e requires an integration, Eq. f.

f. $\int \delta G = \int V\delta P$

And of course, $V = nRT/P$ (ideal gas law), and so we have Eq. g.

g. $\int \delta G = \int nRT(\delta P/P) = nRT\int(\delta P/P)$

Solving the integration yields Eq. h.

h. $\Delta G = \mathrm{n}RT\ln(P_f/P_i)$, or expressed alternatively, $\Delta G/\mathrm{n} = RT\ln(P_f/P_i)$

Thus, we can express change in Gibbs free energy as a function of the changing pressure across a vessel due to mixing. As discussed above, the change in pressure is akin to changing the activity of a chemical in a solution. With this analogy, and remembering that as alluded to above, $\Delta G/n$ is equal to $\Delta\mu$, we get Eq. i. Thereby, this is the correction factor used in Eq. 11 to calculate how chemical potential for a species changes from a defined reference chemical potential when its activity changes. Is it not wild that the $RT\ln(a)$ factor arises from the free energy of mixing?

i. $RT\ln(P_f/P_i) \approx RT\ln(a_{R\,or\,P}) = \mu_{(R\,or\,P)} \quad \mu^o{}_{(R\,or\,P)}$

We can now return to our original story.

Let us look at how a system's free energy changes during a reaction. To do this, we can define the extent