Educación
Química

Comunicación

Revisiting Spontaneity: Addressing Student Misconceptions in Basic Chemistry Courses

Revisitando la Espontaneidad: Abordando las Concepciones Erróneas de los Estudiantes en Cursos Básicos de Química

Julio José Andrade-Gamboa[1] y Edgardo R. Donati[2]

Resumen

Este trabajo analiza concepciones alternativas comunes entre estudiantes de cursos introductorios de química sobre la espontaneidad de los procesos termodinámicos. Sostiene que estos errores derivan menos de la dificultad matemática que de malentendidos sobre las condiciones de aplicación de los criterios termodinámicos. El análisis se centra en el uso incorrecto de la variación de la energía libre de Gibbs (ΔG), en particular cuando se aplica fuera de condiciones de temperatura y presión constantes o a procesos que implican trabajos distintos del trabajo presión–volumen. Mediante ejemplos como las expansiones de gases ideales, se aclara que ΔG funciona tanto como criterio de espontaneidad como medida del trabajo útil máximo en procesos reversibles. Asimismo, se explica que los procesos no espontáneos pueden ocurrir cuando son impulsados por intervenciones externas. Finalmente, se subraya la importancia de las representaciones tridimensionales P–V–T y se enfatiza que la espontaneidad depende de la combinación de contribuciones entálpicas y entrópicas, destacando la necesidad de definiciones rigurosas en termodinámica.

Palabras clave: espontaneidad termodinámica, energía libre de Gibbs, concepciones alternativas en química, enseñanza de la termodinámica, entropía, entalpía.

Abstract

This paper analyzes common misconceptions among introductory chemistry students about the spontaneity of thermodynamic processes. It argues that these errors stem less from mathematical difficulty than from misunderstandings about the conditions under which thermodynamic criteria apply. The discussion focuses on the frequent misuse of Gibbs free energy change (ΔG), particularly when it is applied outside conditions of constant temperature and pressure or to processes involving work other than pressure–volume work. Through examples such as ideal gas expansions, the paper clarifies that ΔG is both a criterion for spontaneity and a measure of maximum useful work in reversible processes. It also explains that non-spontaneous processes can occur when driven by external inputs. Finally, it highlights the value of three-dimensional P–V–T representations and emphasizes that spontaneity depends on both enthalpic and entropic contributions, underscoring the importance of precise definitions in thermodynamics.

Keywords : thermodynamic spontaneity, Gibbs free energy, chemistry misconceptions, thermodynamics education, entropy, enthalpy.

CÓMO CITAR:
Andrade-Gamboa, J J. y Donati, E. R. (2026, enero-marzo). Revisiting Spontaneity: Addressing Student Misconceptions in Basic Chemistry Courses. ***Educación Química, 37***(1). http://dx.doi.org/10.22201/fq.18708404e.2026.1.91582

---

[1] Universidad Nacional del Comahue Argentina.
[2] Universidad Nacional de La Plata Argentina.

Introduction

Learning, encompassing both formal and informal contexts, is fundamentally based on the construction of concepts and descriptions through the integration of elements available within an individual's cognitive framework and externally acquired information. Alternative conceptions (ACs) represent conceptualizations that are either erroneous or, at the very least, divergent from those endorsed by established scientific theories. These conceptions originate from the formation of inaccurate connections between novel concepts and pre-existing cognitive structures, leading to the development of flawed interpretations that often exhibit persistence and impede the assimilation of subsequent knowledge directly or indirectly linked to these initial conceptualizations. In 1997, the Committee on Undergraduate Science Education (CUSE) published a seminal handbook on science instruction, which identified ACs as a primary obstacle to effective science learning. Consequently, the development of educators' awareness regarding the existence, diverse typologies, and underlying causes of ACs can significantly facilitate the positive modification of these conceptions, fostering the acquisition of more rigorous and pedagogically efficacious scientific explanations for natural phenomena. Specifically, students' ACs are nurtured by inaccurate prior knowledge, associative reasoning patterns, the preferential use of intuition as a primary driver of thought processes, incomplete reasoning sequences, the individual's stage of cognitive development, the extent of their existing knowledge base, and vernacular or linguistic challenges arising from the use of terms, metaphors, or analogies that possess everyday significations distinct from their precise scientific meanings. Furthermore, the pedagogical approach and the language employed by instructors constitute a significant source for the generation of numerous ACs, and even, although often met with resistance, instructors' own ACs regarding the subject matter intended for instruction can contribute to this phenomenon.

In the context of chemistry education, didactic research has revealed a substantial prevalence of ACs, investigated their probable genesis, and proposed potential strategies to promote conceptual change towards robust scientific understanding. Thermodynamics stands out as one domain wherein ACs significantly amplify the difficulties associated with comprehension and learning. In particular, fundamental concepts within this topic, such as heat and temperature, exert a strong impact due to their usage and understanding at a colloquial level that markedly differs from their scientific definitions (Granville, 1985; Van Roon, Van Sprang, and Verdonk, 1994; Carson and Watson, 1999; Andrade-Gamboa, Donati, & Mártire, 2001; Brundage, Meltzer, and Singh, 2024a, 2024b; Salame, Fadipe, and Akter, 2025). Furthermore, the majority of its concepts inherently involve a degree of complexity, and it is common for even some textbooks and instructors to describe them in a flawed and inaccurate manner; this not only hinders the modification of ACs but often leads to their amplification and increased complexity and intricacy. Some of these complications are discussed in Donati, Andrade-Gamboa, & Mártire (1995), Vasini & Donati, 2005.

The second law of thermodynamics primarily serves the purpose of interpreting and predicting the spontaneity of processes. This principle stands as one of the most resilient against the advent of new theories and explanations; however, it simultaneously presents significant challenges for complete comprehension due to its integration of a rigorous mathematical foundation with interpretations that are not necessarily intuitive.

In particular, the multiple interpretations surrounding the meaning of entropy (a subject of ongoing debate among specialists; Ben-Naim, 2011; Lambert, 2012) and certain ambiguities regarding its calculation contribute to the generation of numerous ACs concerning the conception of process spontaneity. Precisely due to this inherent complexity, the pedagogical methodologies employed for this topic and the instructors' own ACs frequently serve as sources for the development and/or exacerbation of students' ACs.

In this paper, we will undertake a review of various ACs, which is not intended to be exhaustive (an inherently impossible endeavor) but rather representative of those that our extensive university-level experience has allowed us to identify.

Fundamental formulations of thermodynamics

Thermodynamics is a scientific discipline concerned with the study of material systems in relation to the exchanges and transformations of energy and the physical and chemical processes involved between different states of equilibrium. It is founded upon two fundamental principles that arise from a generalization based on exhaustive observations. Thermodynamics holds relevance across physics, chemistry, biology, geology, and in applications for the design of materials and thermal machines.

The formulations of thermodynamics (which can be found in any standard textbook, such as Barrow, 1978; Metiu, 2006; deVoe, 2020) make use of the following quantities:

- Principal Thermodynamic Functions: Internal energy (U), enthalpy (H), entropy (S), Gibbs free energy (G). The interrelationships between these functions are:

$$H = U + PV \qquad (1)$$

$$G = H - TS \qquad (2)$$

These thermodynamic functions are also termed state functions, as each can be conceived as a difference between the initial (i) and final (f) states between which a transformation occurs. Thus, the variations $\Delta U = U_f - U_i$, $\Delta H = H_f - H_i$, $\Delta S = S_f - S_i$, and $\Delta G = G_f - G_i$ are of significance. As these thermodynamic functions are intrinsic properties of each state, their variations are independent of the path taken to carry out the process.

- **Energy Transfer Processes:** heat (Q) and work (W)
- **State Variables:** temperature (T), pressure (P), volume (V).

The system under thermodynamic study is considered to be immersed in surroundings, and together they constitute the so-called universe (not in a cosmological sense). The system can be, for example, a liquid contained within a glass vessel, and the surroundings a thermostatic bath.

To describe the behavior of a phenomenon, it is useful to conceive different models or types of systems that are idealizations attempting to approximate real behaviors (Figure 1). For this purpose, the permissive or prohibitive nature of the boundary separating the system from the surroundings is considered in relation to the possible exchanges between them (Biel Gayé, 1998). If the boundary allows the exchange of matter, it is termed permeable, and the system is said to be open. Conversely, if the boundary is impermeable, the system is closed. If an impermeable boundary permits the transfer of heat, it is called diathermal; otherwise, it is an adiabatic boundary, and the system is also termed adiabatic. If an impermeable boundary is also adiabatic, it is called an insulating boundary, and the system is classified as isolated.

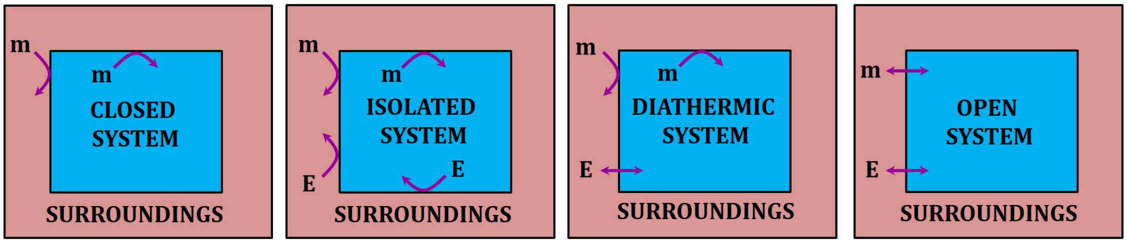

FIGURE 1. Types of systems (E: energy; m: matter).

The first law of thermodynamics is an application of the principle of conservation of energy and, for a differential change, is expressed as:

$$dU = \delta Q + \delta W \qquad (3)$$

where the symbol δ represents an inexact differential (one that depends on the path). For a finite change, the first law is expressed as:

$$\Delta U = Q + W \qquad (4)$$

for which Q is the heat transferred to the system and W is the work done by the system. For the application of this expression, it is necessary to bear in mind the sign convention[1] shown in Figure 2. The surroundings are conceived as a mechanical reservoir (for work exchange) and a thermal reservoir (for heat exchange).

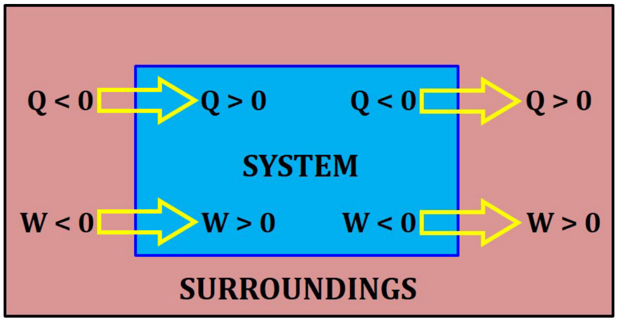

FIGURE 2. Sign convention for heat and work transfers.

In this article, we will consider systems for which, unless otherwise specified, the sole type of work involved is pressure-volume work (i.e. expansion-compression work), and gases or vapors exhibit ideal behavior. For such cases, the differential work is given by $\delta W = -P_{ext}dV$, where P_{ext} is the external pressure exerted on the system. For finite work associated with a volume change from an initial value, V_i, to a final value, V_f, it must be calculated as[2]

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV \qquad (5)$$

The state function that is key in relation to the spontaneity or non-spontaneity of a process is entropy. The differential change in entropy for a system is defined as:

$$dS_{sys} = \frac{\delta Q_{rev}}{T_{sys}} \qquad (6)$$

---

[1] Historically, another sign convention was employed that referenced the system for measuring both Q and W. Expressions 3 and 4 were then written as $dU = \delta Q - \delta W$ and $\Delta U = Q - W$, respectively and $\delta W = P_{ext}dV$.

[2] Under the old sign convention, equation 5 was expressed with a positive sign

where δQ_{rev} is the infinitesimal amount of heat involved when the process between the initial and final states is carried out in a reversible manner. From a theoretical standpoint, a reversible path is one that occurs through an infinite number of infinitesimal steps, each representing a state of thermal, mechanical, and chemical equilibrium. In practical terms, processes tend to approximate reversibility when, at every stage of their progression, the temperature and/or pressure of the surroundings exhibit minimal differences with respect to the pressure and temperature of the system (when they are in mechanical or thermal contact with the surroundings), and no chemical reactions are evolving within the system. When these conditions are not met, processes occur irreversibly.

Any change in the entropy of the system is associated with a change in the entropy of the surroundings (unless the system is isolated). This change is given by:

$$dS_{surr} = \frac{\delta Q_{surr\ (rev)}}{T_{surr}} \qquad (7)$$

where the heat is that received or released by the surroundings and carries the opposite sign to that released or received by the system (notably, from the surroundings' perspective, the type of process undergone by the system—reversible or irreversible—has no bearing, a concept we will explore in detail subsequently). Finite entropy changes are obtained by integrating equations 6 and 7.

The second law of thermodynamics establishes the possibility or impossibility of a process occurring. The former is denoted as spontaneous, and the latter as non-spontaneous. More than one formulation of this principle exists (Barrow, 1978). One such formulation states that in a spontaneous process, the change in entropy of the universe (ΔS_{univ}), which is equal to the sum of the entropy changes of the system (ΔS_{sys}) plus those corresponding to the surroundings (ΔS_{surr}), is greater than zero. Under such conditions, the system evolves until it reaches the state of equilibrium. If a process is reversible, meaning the system is permanently in equilibrium throughout it, the entropy of the universe will not change, such that for that process ΔS_{univ} is 0. In general, it will hold that:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0 \qquad (8)$$

If the system is isolated, and *only in that case*, equation 8 reduces to $\Delta S_{sys} \geq 0$.

The criterion of spontaneity should be interpreted in terms of the possibility of occurrence; however, phenomena evaluated as spontaneous, that is, thermodynamically favorable, might be impeded in their progression due to kinetic barriers.

The variations of the other state functions (ΔH and ΔG) are obtained by integrating the differential expressions of their definitions (equations 1 and 2) for the conditions imposed by the phenomenon under study. The basic formulations derived for specific cases that will be used during the discussion of the different ACs are summarized in Table 1.

TABLE 1. Basic thermodynamic formulas and equations.

CONDITIONS	FORMULAS-EQUATIONS	EQUATION NUMBER
EXPANSION-COMPRESSION WORK W		
General equation	$-\int_{V_i}^{V_f} P_{ext}\, dV$	5
Constant external pressure processes	$-P_{ext}\Delta V$	9
Reversible isothermal expansion-compression processes (ideal gas)	$-nRT \ln\left(\frac{V_i}{V_f}\right) = -nRT \ln\left(\frac{P_f}{P_i}\right)$	10
HEAT Q		
Isobaric heating-cooling processes	$nC_p \Delta T$	11
Isochoric heating-cooling processes	$nC_V \Delta T$	12
Phase change processes (pc) (P, T constants)	ΔH_{pc}	13
INTERNAL ENERGY CHANGE ΔU		
General equation	$Q + W$	4
Isothermal processes (ideal gas)	0 $(Q = -W)$	14
Isochoric processes (expansion-compression work only)	Qv	15
ENTHALPY CHANGE ΔH		
General equation	$\Delta U + \Delta(PV)$	16
Isothermal processes (ideal gas)	0	17
Isobaric processes (expansion-compression work only)	Q_p	18
Chemical processes (chemical reactions) (P, T constants)	$\sum_{n_p} n_p \Delta H_{fn,p} - \sum_{n_r} n_r \Delta H_{fn,r}$	19

ENTROPY CHANGE ΔS		
General equation	$\int \frac{\delta Q_{rev}}{T}$	20
Isothermal processes	$\frac{Q_{rev}}{T}$	21
Isothermal expansion-compression processes (ideal gas)	$nR\ln\left(\frac{V_i}{V_f}\right) = nR\ln\left(\frac{P_f}{P_i}\right)$	22
Isobaric heating-cooling Processes	$nC_p \ln\left(\frac{T_f}{T_i}\right)$	23
Isochoric heating-cooling Processes	$nC_v \ln\left(\frac{T_f}{T_i}\right)$	24
General processes at constant P and T	$\frac{\Delta H}{T}$	25
Phase change processes (pc) (P, T constants)	$\frac{\Delta H_{pc}}{T_{pc}}$	26
Chemical processes (chemical reactions) (P, T constants)	$\sum n_p S_p - \sum n_r S_r$	27
GIBBS FREE ENERGY CHANGE ΔG		
General equation	$\Delta H - \Delta(TS)$	28
Processes with useful work (other than expansion-compression work)	W_{useful}	29
Processes with only expansion-compression and reversible work	$\int_{P_i}^{P_f} VdP - \int_{T_i}^{T_f} SdT$	30
Processes with only expansion-compression work (P, T constants)	$-T\Delta S_{univ} = \Delta H - T\Delta S$	31
Chemical processes (chemical reactions) (P, T constants)	$\sum_{n_p} n_p\, \Delta G_{fn,p} - \sum_{n_r} n_r\, \Delta G_{fn,r}$	32

n: amount of substance in moles; C: molar heat capacity; R: universal gas constant.

Subscripts. P: constant pressure; V: constant volume; fn: formation; p: products; r: reactants; i: initial; f: final; ext: external; rev: reversible; pc: phase changes.

Key misconceptions observed in the application of spontaneity criteria

The following section details some of the alternative conceptions (ACs) that we have frequently identified in the understanding of process spontaneity through thermodynamics. Illustrative calculation examples are also included.

1) Exothermic processes are (always) spontaneous

Among the most commonly observed initial ACs are those that equate a decrease in thermal and/or mechanical energy with the condition for spontaneity. Consequently, even well after the introduction of the second law, students often associate exergonic processes ($\Delta G < 0$) with exothermic processes ($\Delta H < 0$)[3] and tend to judge the spontaneity of a process based on enthalpic changes (see eq. 5 and 6). Numerous reasons account for this AC, ranging from simple terminological confusion to a more profound misunderstanding influenced by teaching methodology. Regarding the latter cause, it is frequent for exothermic processes that are also (or frequently are) spontaneous, such as combustion, to be used as examples of spontaneous processes. Furthermore, and as occurs with other ACs, the confusion between exergonic and exothermic processes might have become established through the discussion of topics preceding the treatment of spontaneity from the perspective of the second law. Thus, it is common for instructors (and textbooks) to discuss examples to demonstrate the direction of processes or even to introduce natural and spontaneous processes where the direction of the process is dictated by a decrease in potential energy without further consideration. Examples of this reasoning include the falling of objects due to gravitational attraction, the attraction of charges due to electrostatic forces, the elastic action of a spring, or even chemical bonding. It is logical that this reasoning fosters a strongly ingrained AC in the student's mind that links the search for a minimum energy state with the natural and spontaneous direction of processes. This AC is also often not easily perceived by instructors (who use these examples only in another context or as mere introductions but do not reflect –perhaps due to a lack of conscious consideration– on their impact on students' conceptions of spontaneity) and, therefore, do not make efforts to modify it subsequently.

To exemplify our argument, we will use the free fall of an object due to gravitational attraction. This process (and the others mentioned above) is indeed spontaneous, and this condition is often justified by indicating that the system tends to reach a minimum potential energy state (inducing the aforementioned AC). However, during free fall, there is no decrease in the system's energy but rather a reconversion of the form of energy it originally possessed. In the simplest case of a fall in a vacuum (thus avoiding the consideration of friction), the system's energy does not change, as the decrease in potential energy is offset by an increase in kinetic energy. This demonstrates that the argument of potential energy decrease is essentially incorrect and a possible source of the AC we are discussing.

We will not elaborate on the thermodynamic explanation of why an object falls; suffice it to say that this process does not violate the second law; rather, as the latter dictates, the entropy of the system (which, in this case, can be considered isolated) increases during the phenomenon. The issue becomes complicated when explaining how this increase

---

[3] It is important to clarify that only when the process does not involve any work other than PV work, does it hold true that at constant pressure a $\Delta H < 0$ corresponds to a release of heat and a $\Delta H > 0$ corresponds to an absorption of heat.

occurs unless the final impact of the object on a surface is incorporated, where energy is transferred from the system to the surface (which incorporates it in more chaotic and entropic forms). In any case, this example, especially without the final impact on a surface, is not the simplest to illustrate the spontaneity of natural processes, much less to use it as an introduction to the reasons that justify it.

Other examples, such as the expansion of a gas into a larger volume or the flow of heat in a rod from a hot end to the rest, seem more appropriate as naturally spontaneous processes (their inverses being clearly non-spontaneous) to then complete the description with the use of the entropy change of the universe or the change in Gibbs free energy (see eq. 5 and 6).

2) An increase in entropy (of the system) guarantees spontaneity

The use of the entropy change of a non-isolated system to define the spontaneity or non-spontaneity of a process is a misconception to which many students often adhere. This AC can originate from multiple reasons: a) the mere simplification of the correct statement of the second law (during a spontaneous process, the entropy of an isolated system or the universe must increase); b) a weak prior discussion or an incorrect understanding of system, surroundings, and universe, and especially of an isolated system; c) the instructor's use of "spontaneous" examples where the system clearly increases entropy, "forgetting" the reference to the universe.

In this case, in addition to the obvious emphasis on the correct use of this statement of the second law, it is important to show with examples that there are spontaneous processes in which the entropy of the system decreases, although with a greater increase in the entropy of the surroundings; a very clear example of this is the existence of life, as Erwin Schrödinger aptly explained (1986). Some examples are more suitable for demonstrating this point even before students learn to quantitatively calculate entropy changes; among these, phase transitions are probably the simplest examples, as the identification of entropy associated with disorder in different states of aggregation is quite intuitive.

The melting process is associated with an increase in the entropy of the system since the liquid state is clearly more disordered than the solid state. To demonstrate this, we will use 1 mole of ice undergoing a phase transition at 0 °C (273 K) and 1 atmosphere ($\Delta H_{melting} = 6028$ J/mol). The process occurs at constant temperature. Thus, if the pressure remains constant, the entropy change will be (equation 25):

$$\Delta S_{syst} = \frac{Q_{rev}}{T_{syst}} = \frac{\Delta H}{T_{syst}} = \frac{6028\ \mathrm{J}}{273\ \mathrm{K}} = 22.08\ \mathrm{J\ K^{-1}}$$

which is positive, confirming the expected increase in entropy.

Can we say that the melting process is spontaneous without any further consideration? Certainly not.

If this system has as its surroundings a freezer in which the temperature is -18 °C (255 K), the entropy change of the surroundings will be given by the same equation (25) we saw for the system, but now applied to the surroundings:

$$\Delta S_{surr} = \frac{Q_{surr}}{T_{surr}}$$

The heat received by the surroundings (Q_{surr}) must be equal to the heat released by the system (Q_{syst}) with the opposite sign; that is, the energy extracted from the system and transferred in the form of heat is absorbed by the surroundings. Therefore:

$$\Delta S_{surr} = \frac{Q_{surr}}{T_{surr}} = \frac{-Q_{sys}}{T_{surr}} = -\frac{\Delta H}{T_{surr}} = -\frac{6028\ J}{255\ K} = -23.64\ J\ K^{-1}$$

In the last calculation, it has been taken into account that the processes undergone by the surroundings (in this case, the heat transfer from the system) are always considered reversible by the definition of surroundings (we will return to this in point 4), and that, for the same reason, it incorporates the heat originating from the system without altering its temperature at all. Finally, for the universe:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 22.1\ J\ K^{-1} - 23.6\ J\ K^{-1} = -1.56\ J\ K^{-1}$$

which indicates that the process is non-spontaneous, as we know (ice will not spontaneously melt inside a freezer that has a temperature much lower than the melting point of water at a pressure close to or equal to 1 atmosphere). Here we have a process in which the entropy change of the system is positive but does not occur spontaneously unless we change the temperature.

Now, if the same mole of ice is taken out of the freezer and placed on a countertop at 20 °C (293 K), the entropy change of the surroundings will be:

Now, obviously, the entropy change of the universe (ΔS_{univ} = 22.08 – 20.57 = 1.51 J/K) will be positive, confirming what we know from everyday experience (ice melts spontaneously at temperatures above 0 °C and a pressure of 1 atmosphere). Figure 3 schematically illustrates the results of the preceding calculations.

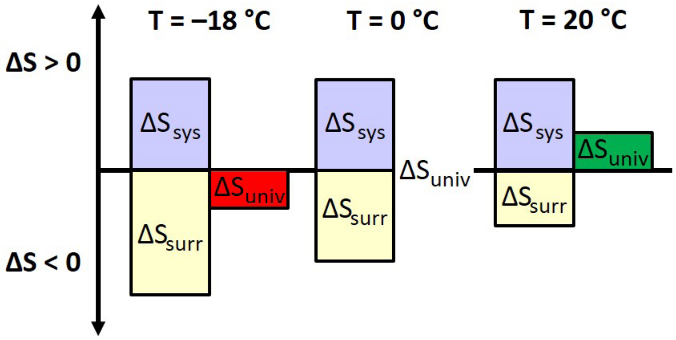

FIGURE 3. Representation of entropic changes for ice melting at different temperatures.

The preceding example demonstrated that processes with an increase in entropy for the system may not be spontaneous under certain conditions. Similarly, processes in which the system decreases its entropy can be spontaneous under specific conditions. A straightforward example is the reverse of the process we just discussed: solidification is a process with a decrease in entropy; in fact, the solidification of 1 mole of water will have an entropy change equal to -22.1 J/K (which is the negative of the entropy of fusion). However, in this case, the entropy change of the surroundings will be exactly the opposite of that found for melting. Obviously, the sum to obtain the entropy change of the universe will be positive, which confirms that the solidification of water at -18 °C is a spontaneous process.

Although phase transitions allow for intuitive conclusions regarding this AC, other processes clearly show that to define the spontaneity of a process, the entropy change of the universe, and not the entropy of the system alone (unless it is isolated), must be analyzed. We can simply consider the heating of a piece of iron – let's say 100 g –, initially at 20 °C (293 K), when it is thrown into a fire with red-orange flames at a temperature of approximately 1000 °C (1273 K), while maintaining constant pressure.

Since the melting point of iron (1538 °C) is higher than this temperature, the only thing that will happen to the metal is that it will heat isobarically and irreversibly from Ti = 293 K to Tf = 1273 K (for iron, C_p = 25.1 J/mol).

The entropy change of our system (the 100 g ≈ 1.79 mol of iron) will be (equation 23):"

$$\Delta S_{sys} = nC_P \ln\left(\frac{T_f}{T_i}\right) = 1.79\ \text{mol} \times 25.1\ \text{J mol}^{-1}\ \text{K}^{-1}\ \times \ln\left(\frac{1273\ \text{K}}{293\ \text{K}}\right) = 66.1\ \text{J K}^{-1}$$

In this case, the entropy of the system increases, but we know that it is necessary to consider the entropy change of the universe. In this scenario, the entropy change of the surroundings, whose temperature remains constant at 1273 K, will be:

$$\Delta S_{surr} = -\frac{Q_{sys}}{T_{surr}} = -\frac{nC_P\,\Delta T}{T_{surr}} = -\frac{1.79\ \text{mol}\ \times 25.1\ \text{j K}^{-1}\text{mol}^{-1} \times 980\ \text{K}}{1273\ \text{K}} = -34.6\ \text{J K}^{-1}$$

where equation 11 has been used to calculate the heat.

The entropy change of the universe, as expected, is positive (ΔS_{univ} = 66.1 J/K – 34.6 J/K = 31.5 J/K), characteristic of a spontaneous process. Nevertheless, and despite the entropy change of the system still being positive, it would have been impossible for the same piece of iron, placed in an environment at 20 °C, to heat up to 1000 °C (or even to 20.1 °C).

Let us finally consider the chemical reaction corresponding to the decomposition of water:

$$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

The enthalpy and entropy change values at 20 °C per mole of water for the system (in this case, the reaction itself) are ΔH = 286 kJ and ΔS = 163 J/K, respectively (calculated from equations 19 and 26 using tabulated data).

These values indicate that it is an endothermic process with a significant increase in entropy, as the products are gases and the reactant is a liquid. Since the process occurs at constant temperature and pressure, the entropy change of the surroundings will be:

$$\Delta S_{surr} = -\frac{\Delta H}{T_{surr}} = -\frac{286000\ \text{J}}{298\ \text{K}} = -960\ \text{J K}^{-1}$$

Then, the entropy change of the universe is:

$$\Delta S_{univ} = 163\ \text{J/K} - 956\ \text{J/K} = -793\ \text{J/K}$$

indicating that this process, despite the system increasing its entropy, is not spontaneous. Obviously, it is the reverse process (the formation of water) that would be spontaneous under these conditions, as the entropy change of the universe would be positive (793 J/K).

3) The calculation of entropy change via the reversible process... only for the reversible pathway

The calculation of entropy change from the reversible heat divided by the absolute temperature (integrated appropriately if the temperature is not constant) generates in students a feeling, even without full conscious awareness, that "cheating" is occurring because the actual process is not taken into account when calculating this change; a variation of this feeling is that the student retains the idea that S cannot be a state function since it is necessary to find a particular path to perform the calculation of its change. Thus, when faced with a transformation carried out between the same states but via different paths, they may calculate the entropy change of the system, sometimes correctly using the corresponding reversible heat, and other times simply using -incorrectly- the heat involved in the specific path. These errors are often linked to ACs about the meaning of "state of the system" and "variables" and "state functions," as well as about "reversible paths" and "system in equilibrium."

In this case, it is essential to discuss these concepts in more detail; in particular, the exceptional nature of an ideal reversible path should be made clear, distinguishing it from all others and explaining that, as it requires the maximum possible heat transfer, it will therefore yield the maximum possible value for the property linked to entropy and disorder. Other, irreversible paths involve a smaller amount of heat than the reversible path, but if the system reaches the same final state, the entropy cannot change because it is a state function representative of that state. In this case, some analogies can work adequately, provided that the potential drawbacks of analogies in teaching scientific concepts are understood, especially those that demand a high degree of abstraction, as is the case with thermodynamic concepts.

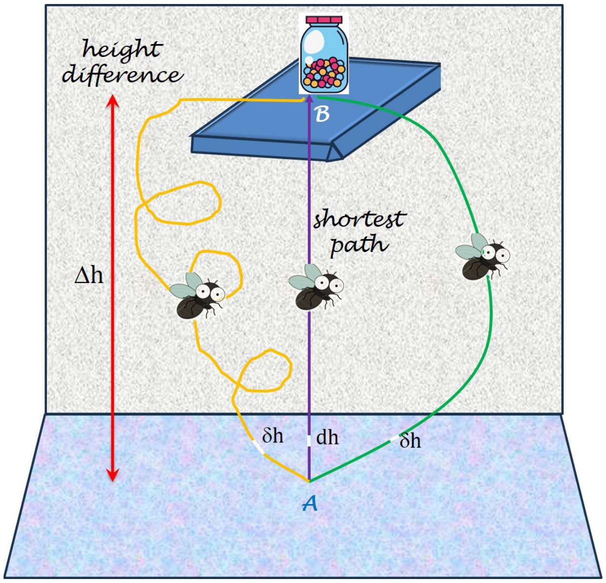

FIGURE 4. The fly's paths from A to B.

Imagine we want to measure the difference in height (Δh) between a fixed point on the floor (point A) and a jar of candies located on a shelf (point B), as shown in Figure 4. To determine this, we have an altimeter (an instrument that measures altitude) calibrated to zero at the fixed point on the floor (point A); to reach point B, a fly with the altimeter attached is used. At the base of the candy jar (point B), there are some drops of honey to motivate the fly to perform the task. Imagine we also attach an odometer (an instrument that measures distance traveled) to the fly. The fly can go from A to B via infinite paths (only three of the possible paths are distinguished in the figure), and for each of them, the odometer will show different values (indicating the different effort the fly must make for each path to reach its goal). In contrast, the altimeter will systematically show the same value (in our analogy, height is a "state function"); furthermore, there is only one path where the measurement with the odometer will coincide with that of the altimeter: this differential path is distinguished from the rest because it is the shortest possible between A and B (at least in a Euclidean space) and is the straight line connecting these points. In the figure, infinitesimal path elements are depicted as white segments along each path. For the shortest path, these infinitesimal elements directly correspond to the infinitesimal changes in height. Consequently, for this specific path, the infinite summation (the integral) of these infinitesimals yields the net change in height between A and B

$$\Delta h = \sum dh$$

In contrast, along the other paths, the infinitesimal displacements constitute inexact differentials of height (δh), and their infinite sum will not correspond to Δh

$$\Delta h \neq \sum \delta h$$

This way, we aim to show that the sum of inexact differentials doesn't yield the change in a state function (like height). Similarly, entropy is an intrinsic property of the system's state, and to measure its changes, the path that is perfectly distinguishable from all others (the reversible path) is selected.

4) The entropy change of the surroundings is not calculated in the same way as for the system and/or is not a state function like that of the system

Even students who have mastered the calculation of the entropy change of the system encounter difficulties when they need to calculate it for the surroundings. Primarily, they fail to understand why in this case "it is not the reversible heat" that is used for the calculation, but rather the actual heat exchanged by the surroundings during the process. They also find it difficult to accept that different paths between two states (of the system) correspond to different entropy changes (of the surroundings), suggesting that the entropy of the surroundings "is not a state function." In these cases, undoubtedly, the alternative conception lies in the concept of "surroundings," which is usually described very superficially and insufficiently for students new to the topic. It must be emphasized that the surroundings, from a thermodynamic perspective, are sufficiently large that their state variables are not affected by the processes undergone by the system, and therefore, the history of the system does not transcend the boundaries of the "universe." This allows all changes undergone by the system, both reversible and irreversible, to result in essentially reversible changes for the surroundings because their state variables are not modified beyond an infinitesimal amount. On the other hand, the erroneous idea that the entropy of the surroundings is not a state function (since each path entails a different change in its entropy) stems from an insufficient discussion about what actually occurs in the surroundings when the system moves between the same initial and final states but along different trajectories. Thus, it could be shown that for the system to move between the same states but via different paths, the intervention of the surroundings must necessarily be different, either supplying or absorbing more or less heat and/or receiving or performing more or less work.

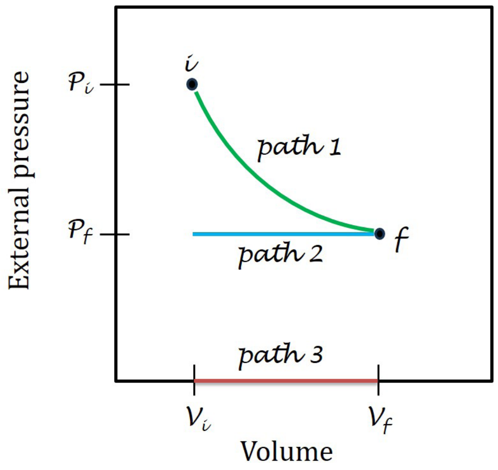

FIGURE 5. Different processes for an ideal gas

As an example, let's consider the isothermal expansion of n moles of an ideal gas between the initial (i) and final (f) states carried out through different paths, as shown in Figure 5 with different colors. Path 1 (in green) corresponds to the process carried out reversibly with the gas in permanent equilibrium. Path 2 (in light blue) indicates the process carried out against a constant external pressure equal to the final pressure. Finally, path 3 (in orange) is the expansion into a vacuum until the final volume is reached, at which point an external pressure equal to the final pressure is re-established. For all three paths, the variations of the state functions are the same. Regardless of their differences, all three paths are isothermal and involve an ideal gas. The internal energy of an ideal gas can be assumed to be solely translational kinetic energy (in monatomic molecules) or with vibrational and rotational contributions to both kinetic and potential energy (in the case of polyatomic molecules); in any case, these energies depend only on temperature. Therefore, in isothermal processes, the internal energy does not change ($\Delta U = 0$), and as indicated in equation 15, the heat is equal to the negative of the work:

$$Q = -W$$

The general expression for expansion work is (equation 5):

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV$$

In path 1, the reversible path, the external pressure can be replaced by the pressure of the gas (since at every point along the path, the external pressure is at most an infinitesimal amount less than the gas pressure), which, in turn, can be replaced by its equivalent from the ideal gas law:

$$W_{rev} = -\int_{V_i}^{V_f} \frac{nRT}{V}\, dV$$

Because the number of moles and the temperature are constant, the work results in (equation 10):

$$W_{rev} = -\, nRT \ln(V_f/V_i)$$

from which

$$Q_{syst} = -\, W = nRT \ln(V_f/V_i)$$

This heat (positive) is transferred from the surroundings to the system, so the heat for the surroundings will be:

$$Q_{surr} = -\, nRT \ln(V_f/V_i)$$

Because the process is isothermal, the entropy change of both the system and the surroundings can be calculated by dividing the corresponding heat by the temperature, thus:

$$\Delta S_{sys} = nR \ln(V_f/V_i)$$
$$\Delta S_{surr} = -\, nR \ln(V_f/V_i)$$

It can be observed that the sum of the entropy changes of the system and the surroundings (that is, the entropy change of the universe) will be zero, consistent with what is expected for a reversible process according to the second law.

In the cases of paths 2 and 3, the entropy change of the system must be exactly the same as that calculated for path 1, since entropy is a state function. However, the entropy change of the surroundings cannot have the same magnitude and opposite sign as that of the system because the process is spontaneous, and the entropy change of the universe must be greater than zero. This does not mean that the entropy of the surroundings is not a state function. For the system to end up in the same final state, the surroundings contribute differently than they did in the case of path 1.

In path 2, although for this path it is also true that Q = –W, the values are different from those of path 1. Since the external pressure remains constant and equal to the final pressure, P_f, the gas does work against this pressure, and the calculation reduces to equation 10:

$$W = -\, P_{ext}\Delta V = -\, P_f\Delta V$$

therefore

$$Q_{sys} = P_f\Delta V$$

While the heat delivered by the surroundings (reversibly, even though the system received it irreversibly) will be:

$$Q_{surr} = -\, P_f\Delta V$$

Thus, the entropy change for the surroundings:

$$\Delta S_{surr} = -P_f\Delta V/T$$

It can be verified using values that this variation of the surroundings is, in absolute value, smaller than the entropy change of the system, so the entropy change of the universe is greater than zero.

Finally, in path 3, the isothermal expansion into a vacuum, Q = –W still holds. However, since it is an ideal gas, the work done against a vacuum is zero, and consequently, the heat is also zero. Therefore, the surroundings do not transfer any heat for the system to reach the final point through this path. In this case, the entropy change of the surroundings is 0.

In summary, in all three paths, the entropy change of the system is the same (because the system undergoes the process between the same states), but the entropy changes of the surroundings are not the same because their contribution is different in each case to allow the system to move between the same states. Clearly, the entropy of the surroundings is also a state function, and that is why in path 3, where its contribution is zero, the entropy does not change and remains the same as at the beginning. In other words, the entropy change of the surroundings is not a function of the state of the system but of the surroundings themselves, and the states of the latter are not shown in the figure. The states of the surroundings depend only on the exchange of heat and/or work with the system, regardless of how these processes occur in the system.

5) A negative change in Gibbs free energy indicates the spontaneity of a process

It is common for students to use the Gibbs free energy change (ΔG) as a criterion for spontaneity without remembering the implicit conditions for its use: constant pressure and temperature, and processes where only pressure-volume work is involved. Again, the use of inadequate examples or the lack of proper discussion can reinforce this AC, which consists of "forgetting the fine print." It is very frequent in basic courses to analyze isothermal or isobaric expansion processes of ideal gases, and in these cases, precisely, the Gibbs free energy change criterion is not applicable, although the entropy change of the universe criterion, which has no restrictions, can be applied.

Closely related to this AC is the erroneous idea that the Gibbs free energy change cannot be calculated in cases where it cannot be used as a criterion for spontaneity. Obviously, it is possible to calculate it, although the result cannot be used to infer the spontaneity of the process.

To illustrate this point, we will first recall how the spontaneity criterion using the Gibbs free energy change is derived.

The second law states that the entropy of the universe (or that of an isolated system) must increase in a spontaneous process; that is, ΔS_{univ} must be greater than zero. If we restrict the analysis to isothermal processes (of major interest to chemists), the entropy change of the surroundings will depend on the actual amount of energy transferred as heat. Then, remembering that for the surroundings, every process will be reversible since their conditions will not change appreciably, i.e., $Q_{surr} = -Q_{sys}$, we can write:

$$\Delta S_{surr} = \frac{Q_{surr}}{T} = -\frac{Q_{sys}}{T}$$

If we impose the additional condition of constant pressure, also frequent in chemical processes, then the actual amount of energy transferred as heat will coincide (as long as the work is only pressure-volume work!) with the enthalpy change ($Q_{sys} = \Delta H$):

$$\Delta S_{surr} = \frac{\Delta H}{T}$$

With this last expression, we can write for $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0$:

$$\Delta S_{univ} = \Delta S_{sys} + \frac{\Delta H}{T} \geq 0$$

and multiplying both sides by –T, we arrive at equation 31:

$$-T\Delta S_{univ} = -T\Delta S + \Delta H = \Delta H - T\Delta S \qquad (31)$$

Because we have multiplied by a negative quantity, the terms of the previous inequality must be ≤ 0. In the equation, the subscript "sys" has been omitted, but it should be emphasized that all variations are of system properties. The second term of the equation corresponds to the finite change in the Gibbs free energy function (equation 31), ΔG, at constant T and P, and when only pressure-volume work is involved. Therefore, we arrive at:

$$\Delta G = -T\Delta S_{univ} \qquad (33)$$

Since the entropy change of the universe will be zero in a reversible process, positive in a spontaneous process, and negative in a non-spontaneous one, it is concluded that for a process at constant pressure and temperature and if there is no work other than pressure-volume work:

$\Delta G = 0$ (reversible process)

$\Delta G < 0$ (spontaneous process)

$\Delta G > 0$ (non-spontaneous process)

One way to remember the "fine print" is to rewrite this by placing that information in the form of subscripts:

$\Delta G_{P,T,We\text{-}c} = 0$ (reversible process)

$\Delta G_{P,T,We\text{-}c} < 0$ (spontaneous process)

$\Delta G_{P,T,We\text{-}c} > 0$ (non-spontaneous process)

where P, T, and We-c, indicate constant P and T, and only expansion-compression work, respectively.

Next, we will see some typical examples where the Gibbs free energy is incorrectly used as a criterion for spontaneity.

In the previous section (item 4), the case of the reversible isothermal expansion of an ideal gas (path 1) was examined. There, we verified that the entropy changes of the system and the surroundings are equal but opposite in sign, causing the entropy change of the universe to be zero, as expected for a reversible process.

To calculate the Gibbs free energy change, we must use equation 31; for this, we must calculate the enthalpy change ΔH using equation 16:

$$\Delta H = \Delta U + \Delta(PV)$$

As we have already seen, in an isothermal expansion process for an ideal gas, ΔU is 0; furthermore, in an isotherm, an ideal gas obeys Boyle's law (PV = constant), so $\Delta(PV)$ is 0, and consequently, ΔH is also 0. Therefore:

$$\Delta G = -T\Delta S$$

which, using equation 22, is solved as:

$$\Delta G = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

and will take a negative value, thus suggesting that the process is spontaneous when in reality it is a reversible process. This apparent contradiction is not such; the Gibbs free energy criterion cannot be applied in this case because, although the process is at constant temperature, the pressure of the gas varied gradually from its initial value P_i to its final value P_f. In conclusion, the calculation gives the change in Gibbs free energy for the isothermal expansion of an ideal gas can be performed without problems, but it cannot be used as a criterion for spontaneity.

The reversible isobaric expansion of an ideal gas (item 4, path 2) is the other common case of an inappropriate use of Gibbs free energy as a criterion for spontaneity. Initially, let's clarify that for the change to be reversible, the variable being modified (the temperature) should do so infinitesimally; to achieve this, the system should be in a thermostat whose temperature is slowly and gradually increased between the initial (T_i) and final (T_f) temperatures. Since the process is not isothermal, equation 31 cannot be used. The appropriate calculation expression is obtained from equation 29, integrating under the conditions of constant pressure, reversible process, and only pressure-volume work. This implies solving the integral:

$$\Delta G = -\int_{T_i}^{T_f} S\,dT$$

Calculating the change in Gibbs free energy using this last expression is somewhat complicated since it requires a function that gives the dependence of absolute entropy on temperature (which is one of the results of the third law of thermodynamics). Such an analysis is beyond the scope of this article, and it will suffice to remember that absolute entropy is a positive quantity for all temperatures (Barrow, 1978); because of this, the integral indicated above will be positive, but the negative sign affecting it will lead to a negative value of ΔG, suggesting a spontaneous process. Again, we find an apparent contradiction since the process is actually reversible; in reality, this criterion is again being applied under conditions for which it is not valid (the temperature must be constant).

Finally, we will see the inconsistency that arises when ΔG is applied as a criterion of spontaneity when P and T are constant, but there is work other than pressure-volume work. When there is work W' other than pressure-volume work (for example, electrical work, surface work, etc.), it is necessary to consider it in the thermodynamic expressions. Thus, this work should be contained in the corresponding term of equation 3. If we separate the work into two terms, one corresponding to pressure-volume work and another that includes any other form of work, equation 3 will be:

$$dU = \delta Q + \delta W + \delta W'$$

Then, using the previous equation in the differential expression of equation 2, and under the sole condition that the process occurs reversibly, we arrive at:

$$dG = VdP - SdT + \delta W'_{rev} \qquad (34)$$

from which it is concluded that for a reversible change to be reflected in the spontaneity criterion based on Gibbs free energy ($dG = 0$), not only must T and P be constant, but also dW'_{rev} must be zero.

The typical example of the intervention of work other than compression-expansion work is that of a battery or galvanic cell. In this type of device, electrical work is performed given by (Lladó & Jubert, 2011):

$$W_{elec} = -\, nFE$$

where n is the number of electrons that circulate, F is the charge (in coulombs, C) of one mole of electrons (Faraday constant; 96485 C/mol), and E (> 0) is the electromotive force (EMF), which is an electrical potential expressed in V (volts) delivered by the device. If, at constant pressure and temperature, an opposing external electrical potential is applied that differs infinitesimally from the value of E, the electrochemical process will develop reversibly. In such a case, expression 34 reduces to:

$$dG = \delta W_{elec,rev}$$

so that for a finite reversible process:

$$\Delta G = W_{elec,rev} = -nFE \qquad (35)$$

which is negative. Therefore, when there is work other than pressure-volume work, even at constant pressure and temperature, the change in Gibbs free energy is not a criterion for spontaneity. For example, for the reaction:

$$Zn(s) + Cu^{2+}(ac,\ 1M) \rightarrow Zn^{2+}(ac,\ 1M) + Cu(s)$$

the thermochemical values at 25 °C (298 K) are (Llado & Jubert, 2011), $\Delta H = -219$ kJ; $\Delta S = -21$ J/K, from which one can calculate (equation 30):

$$\Delta G = \Delta H - T\Delta S = -219000\ J - 298\ K\ (-21\ J/K) = -212742\ J$$

Therefore, in a reaction vessel, it should proceed spontaneously at 25 °C, as is observed experimentally. If two electrodes are available to form a battery (called a Daniell cell):

$$Zn(s)|Zn^{2+}(1\ M)\ ||\ Cu^{2+}(1\ M)\ |Cu$$

And the measured EMF is E = 1.102 V. Therefore, the reversible electrical work when the process is carried out by opposing an electrical potential that differs by no more than an infinitesimal amount from E will be:

$$W_{elec,rev} = -nFE = -2\ mol \times 96485\ C/mol \times 0.00102\ kV = -212.7\ kJ$$

which coincides with the value of ΔG in accordance with equation 35.

The reaction that occurs spontaneously in a reaction vessel ($\Delta G < 0$) does so reversibly (at equilibrium) in the Daniell cell if an external potential (opposing the cell's operation) infinitesimally smaller is applied. If the applied external electrical potential is less than the EMF, the reaction in the cell proceeds spontaneously, while if the applied external electrical potential is greater, the reaction will proceed spontaneously in the reverse direction. There is an evident link between the operation of electrochemical cells against an applied external potential and the expansion-compression of an ideal gas, which constitutes an excellent analogy Vasini & Donati, 2001. Then, for this case, the spontaneity criterion can be reformulated, at constant pressure and temperature, as (Gislason & Craig, 2013):

$\Delta G - W_{elec} = 0$; proceso en la pila reversible ($W_{elec} = W_{elec,rev}$)

$\Delta G - W_{elec} < 0$; proceso en la pila espontáneo

$\Delta G - W_{elec} < 0$; proceso en la pila no espontáneo

This result can be generalized, at constant P and T, by replacing the electrical work with work of any other type different from pressure-volume work in the previous conditions.

6) ΔG as a criterion for spontaneity is only useful for chemical reactions

It is extremely important to emphasize that the criterion based on the entropy change of the universe and the one that uses the Gibbs free energy change of the system are equivalent. Each offers advantages and disadvantages. The increase in the entropy of the universe is a universal criterion of spontaneity without any restriction, but it requires knowing the entropy change not only of the system but also of the surroundings. On the other hand, the Gibbs free energy change has the advantage of being calculated only for the system, but it is restricted to three conditions that were explicitly indicated in the previous section.

An additional advantage of using Gibbs free energy in predicting the spontaneity of processes is its ability to handle temperature changes. As we have already mentioned in previous sections, processes that occur at constant pressure and temperature and with only pressure-volume work must have an associated negative Gibbs free energy change to be spontaneous, while if it is positive, they do not occur on their own. In general, there is a weak dependence of enthalpy and entropy changes on temperature for many processes that meet the conditions for applying this spontaneity criterion given by equation 31. If we accept the "constancy" of ΔH and ΔS with respect to temperature, then the expression of ΔG as a function of T has a graphical representation that is a straight line: the y-intercept will always be ΔH, and the slope will be given by –ΔS. As shown in Figure 6, there will be two quadrants, an upper one ($\Delta G > 0$) corresponding to non-spontaneous processes, and a lower one ($\Delta G < 0$) corresponding to spontaneous processes. The horizontal line at $\Delta G = 0$ is the space corresponding to reversible processes (at equilibrium). ΔG will be equal to ΔH at 0 K, and therefore, endothermic processes will initially be located in the upper quadrant and exothermic processes in the lower quadrant, as represented by the red and green points, respectively, in Figure 6. Then, there will be four lines, each corresponding to different combinations of signs for ΔH and ΔS. In the case of an endothermic process with negative ΔS, the line will remain in the upper quadrant, indicating that the process will not be spontaneous under any temperature conditions (case 1). If, on the other hand, the endothermic reaction has positive ΔS, the slope is negative, and for some temperature, the line will cross into the lower quadrant (case 2). These are processes that, although not spontaneous at low temperatures, become spontaneous at high temperatures. Similarly, for exothermic processes, there will be two possibilities: if ΔS is negative, the line represents spontaneous processes at low temperatures but becomes non-spontaneous at high temperatures (case 3). Finally, for exothermic processes with positive ΔS, the line will remain within the lower quadrant, and this will indicate that the process is spontaneous for all temperatures (case 4).

This analysis clearly shows that, at constant pressure and temperature, and provided that the only type of work is pressure-volume work, spontaneity depends on two aspects that are the two terms ΔH and TΔS, which we could indicate as the energetic and entropic contributions, respectively. It is the combination of both that defines the nature of the process under analysis. This is the appropriate conceptual tool to combat the frequent AC of students who consider that exothermic processes are always spontaneous and endothermic ones never are.

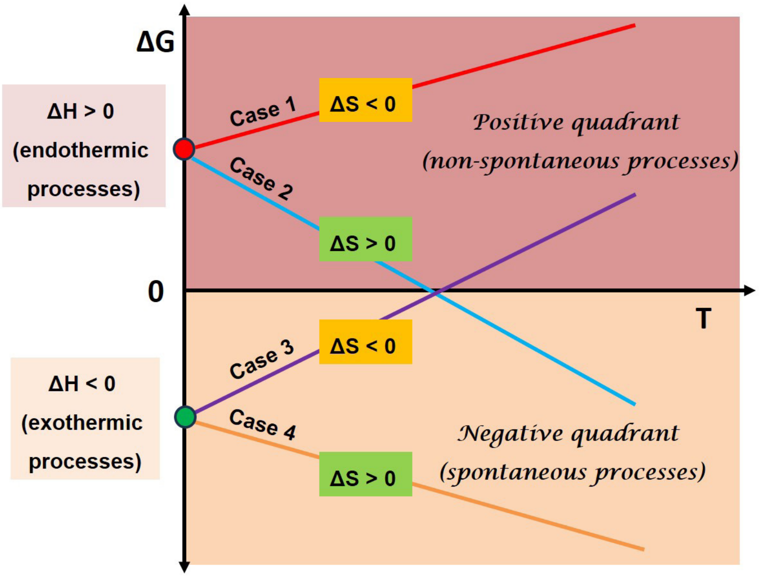

FIGURE 6. Conditions for spontaneity or non-spontaneity.

Next, examples of chemical reactions for each of the four cases will be presented.

- Case 1

Among the many reactions that fit this case, we can highlight photosynthesis (glucose synthesis), which is a crucial process for life on our planet:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(ac) + 6O_2(g)$$

This is an endothermic reaction ($\Delta H > 0$) with an increase in order ($\Delta S < 0$). Therefore, it is a reaction that does not occur spontaneously under any temperature conditions. However, and fortunately, it occurs "naturally." We will discuss this in a later section.

- Case 2

As an example, the decomposition of calcium carbonate can be given by:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

This reaction is endothermic and has a clear increase in entropy (a gas is formed from a solid). Therefore, this reaction is spontaneous at high temperatures where the entropic contribution dominates.

- Case 3

A reaction that corresponds to this case is the formation of NH_3, which we represent below:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

This exothermic reaction has a clear decrease in entropy (halving the number of gaseous moles), so it occurs spontaneously only at low temperatures.

- Case 4

The reactions between alkali metals and water are included in this case. The following equation shows this process for sodium:

$$2Na(s) + 2H_2O(l) \rightarrow H_2(g) + 2NaOH(ac)$$

since it is a case of an exothermic reaction with an increase in entropy, it will be spontaneous at all temperature conditions.

As anticipated, it is necessary to emphasize that the spontaneity criterion based on the Gibbs free energy change can be applied to any process (chemical or physical) that occurs at constant pressure and temperature, and for which any work involved is only pressure-volume work.

If we apply the spontaneity criterion given by ΔG (at constant P and T and only pressure-volume work) to the case of ice melting at 1 atm, which was treated as an example in item 2, the following will be verified:

Around 0 °C (273 K): $\Delta G = 6028\ \text{J} - 273\ \text{K} \times 22.08\ \text{J/K} = 0$ (reversible; equilibrium)

Around –18 °C (255 K): $\Delta G = 6028\ \text{J} - 255\ \text{K} \times 22.08\ \text{J/K} = 397.6\ \text{J} > 0$ (non-spontaneous)
Around 20 °C (293 K): $\Delta G = 6028\ \text{J} - 293\ \text{K} \times 22.08\ \text{J/K} = -441.4\ \text{J} < 0$ (spontaneous)

The change from one modality to another occurs precisely at the melting temperature (0 °C), for which the process is in equilibrium.

The equivalence between the two spontaneity criteria can be demonstrated by dividing these values of ΔG by the temperature of the experiment (eq. 33) to verify that they coincide with the values calculated in item 2 for ΔS_{univ}.

Another illustrative example is the transition of tin between the gray and white allotropes:

$$Sn(white) \rightarrow Sn(gray)$$

The represented process is exothermic and exhibits a decrease in entropy since gray tin has a less compact and ordered structure than white tin. Due to this, it falls within case 3, being spontaneous only at low temperatures. This process had an impact on several historical events (Andrade-Gamboa, 2023).

Cases type 1 and type 4 are the only ones for which, knowing only the signs of ΔH and ΔS (+/– and –/+, respectively), it can be affirmed that, regardless of the temperature, the process will be non-spontaneous (case 1) or spontaneous (case 4). Figure 6 clearly shows that the incorrect consideration of ΔS_{syst} as a criterion for spontaneity will yield the correct result only in a strictly accidental manner for cases 1 and 4.

7) The change in Gibbs free energy only serves as a criterion for spontaneity

The use of the Gibbs free energy change as a criterion for spontaneity is undoubtedly its most relevant application. However, its very name suggests another very important application: the change in G is “free” energy to be used. Equation 29, which has been derived for a reversible process at constant T and P, is of general validity for all types of work other than pressure-volume work. This work can be used as an energy source, and hence it is called useful work. Therefore:

$$\Delta G = W_{useful,rev}$$

If the process is irreversible, the expression that links ΔG with the useful work is:

$$\Delta G = Q_{irrev} - Q_{rev} + W_{useful,irrev}$$

which allows us to conclude that for an irreversible process with $\Delta G < 0$, it is not possible to have all the free energy available as useful work, and part of it will be lost as heat. Consequently, the closer the irreversible process is to a reversible one, the greater the proportion of free energy that can be used in useful work. Therefore, reversible useful work is the maximum possible. A battery provides us with an electrical potential generated by a spontaneous chemical reaction that can be used to light an electric bulb, charge a mobile phone, etc. In the case of rechargeable batteries, once they are depleted (the electrochemical reaction is at equilibrium shifted towards products), they are recharged by reversing the chemical reaction towards the reactants through the application of an external electrical potential.

8) Non-spontaneous processes cannot occur under any circumstances

The exemplification of non-spontaneous processes based on certain natural processes can lead students to solidify the AC that reverse processes are unnatural and consequently impossible. In reality, it is possible to carry out a process that is non-spontaneous on its own through external intervention, and, on the other hand, nature employs this type of action to “naturally” produce phenomena that would not occur without such intervention. Although the Clausius statement, which is one of the formulations of the second law of thermodynamics, tells us that it is not possible to build a device that operates in a cycle and whose only effect is to transfer heat from a colder body to a hotter body, this does not prevent the existence of refrigerators that obtain the necessary work from their electrical connection to force a process that would not occur spontaneously. Precisely, this shows that it is necessary to carefully discuss the meaning of the phrase “non-spontaneous” to avoid producing the AC indicated in the title. Even when this aspect is clarified, another derived AC (closely linked to the first case we discussed) should be avoided, which is maintaining an energetic view devoid of the entropic contribution. Thus, many students who intimately associate exothermic and exergonic processes assume that endothermic processes will not be spontaneous and that, to produce them, an amount of heat equivalent to the enthalpy change must be supplied. As we have discussed, this extrapolation is incorrect, and everyday life constantly shows us this; for example, if a car brakes abruptly, the tires will heat up due to friction with the asphalt; however, it has never been seen that heating the tires causes the car to start moving.

In reality, to produce a non-spontaneous process, it is necessary to invest work from outside the system equivalent to the positive Gibbs free energy change, as exemplified by the process of recharging a battery. Similarly, the non-spontaneous process of photosynthesis, presented in item 6, is produced in green plants (and some algae) thanks to chlorophyll molecules that act as photoelectric cells, transforming sunlight into an electron current that does the electrical work to produce glucose. This cellular mechanism is common to all biological processes. The electron transport chains that all living organisms possess consist of a series of coupled redox pairs of decreasing potentials that generate a cascade of electrons from the highest to the lowest redox potential. In this way, the free energy available in the original redox process is better utilized. This was the inspiration for the quote by biochemist Albert Szent-Györgyi (1893–1986), Nobel Prize in Physiology or Medicine (1937): “What drives life is a little electric current, maintained by the sunshine!” (de Rosnay, 1993).

9) Isothermal expansion processes against a constant external pressure are the same as isobaric processes

It is common and appropriate to use P vs. V graphs (like Figure 5) to represent the processes that an ideal gas undergoes, including cases where thermodynamic concepts such as heat, work, and changes in internal energy, enthalpy, or entropy are intended to be shown. These processes include isothermal processes (which actually occur in a slice at constant T of the P-V-T surface) but also those in which the temperature changes (in which what is represented is the projection of the three-dimensional change onto the P-V plane). These include reversible processes, but also irreversible ones where the gas, obviously, is not in equilibrium except before and after the process. For most teachers, the differentiation may be obvious, and the graphical use can be carried out mechanically during teaching without the pertinent clarifications that allow students to take the corresponding precautions. This can lead to different alternative conceptions in the average student.

As an example, imagine 1 mol of ideal gas that is initially at 400 °C and 2 atm (represented by point Ia in the graph of Figure 7a) in a container with a movable lid. If the pressure is suddenly decreased to 1 atm, the gas will expand spontaneously until it doubles its volume (point IIIa). The graph represents the process by a horizontal line (in red) that shows the increase in the volume of the gas doing work against a constant external pressure of 1 atm.

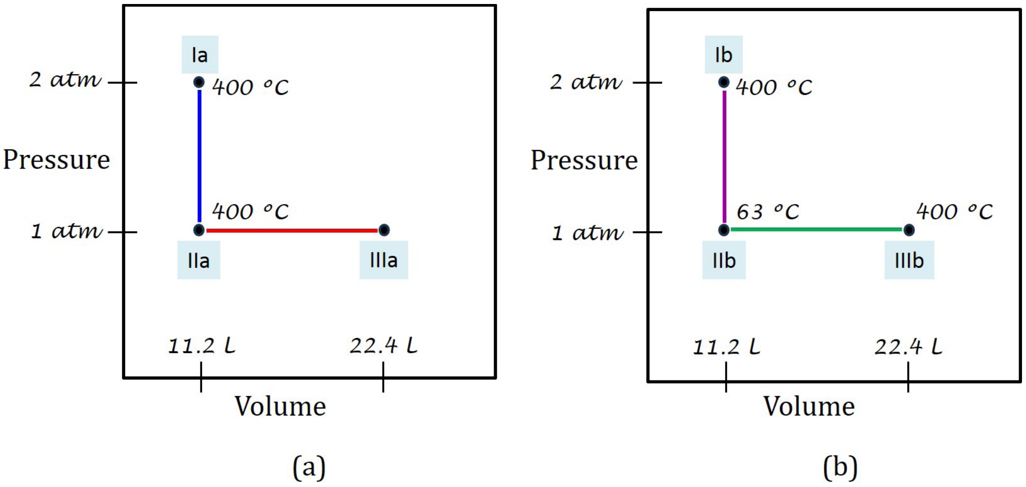

FIGURE 7. Are these the same trajectories in a as in b?

On the other hand, the graph in Figure 7b shows 1 mol of ideal gas at 400 °C and 2 atm (initially point Ib) whose pressure decreases reversibly to 1 atm and 63 °C (point IIb). Then it expands by isobaric heating until it reaches a final temperature of 400 °C (green line). The two paths correspond to the same initial and final state (Ia ≡ Ib and IIIa ≡ IIIb), but the state represented by point IIa is different from the state given by point IIb, so the vertical trajectories (blue and violet lines), between each other, and the horizontal trajectories (red and green lines), between each other, are different. In each case, the apparent equivalence is only in the fact that the P-V projections of these lines are coincident. Usually, this type of graph accompanies a narrative without explicitly stating the temperatures at each state, so the distinction of the nature of the trajectories based on the graphical representation leads to a frequently observed AC whereby students understand the process represented in the graph of Figure 7a as the combination of two "reversible" processes, one isochoric (represented by the blue line) and one isobaric (represented by the red line). However, this is incorrect. The blue line, in reality, doesn't represent a process undergone by the system; instead, it solely depicts the change in external pressure (not the gas pressure). Therefore, it's more appropriate to omit its representation to prevent this error (as done in Figure 5). On the other hand, the red line does represent the system's volume increase and consequently indicates the system's evolution, so it should be included. Nevertheless, even this line doesn't describe the pressure of the gas, as it varies from an initial 2 atm to a final 1 atm in a way that we cannot precisely represent because the gas is NOT in equilibrium until the process concludes at the right end of the red line (point IIIa). Therefore, the complete path Ia-IIa-IIIa is irreversible. Thus, the P-V projections do not allow us to graphically differentiate between reversible and irreversible paths in this type of process.

Although, for this type of representation, the isotherm (hyperbola) at T = 400 °C connecting points Ia and IIIb could be added to graph 7a, and in graph 7b, in addition, the isotherm at T = 63 °C (which would pass through point IIb); it may still not be sufficiently clear to discern for students. In these cases, it is extremely useful, and therefore our proposal, to use three-dimensional graphs that clearly show the behavior of an ideal gas, in this case, adding the T coordinate.

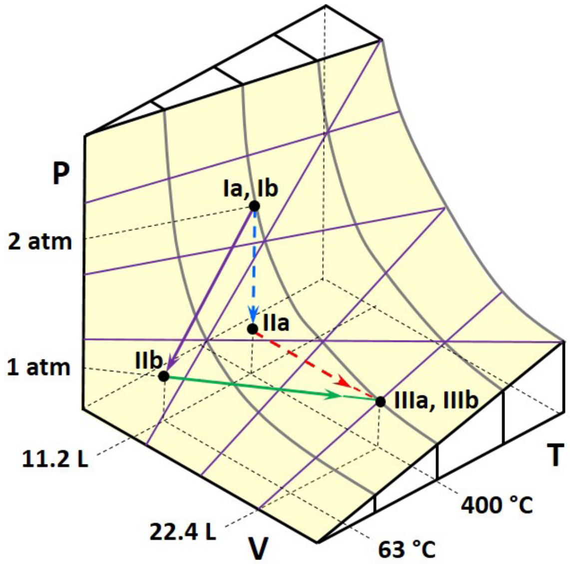

Figure 8. P-V-T surface for one mole of ideal gas.

Figure 8 shows a graph of the surface represented by all the P-V-T points that correspond to equilibrium situations for 1 mol of ideal gas and the trajectories of Figure 7 using the same colors. Any process that moves on that surface will be a reversible process, as occurs for the paths Ia/Ib–IIb (violet line) and IIb–IIIa/IIIb (green line). The first is an isochoric cooling (V = 11.2 L) from 400 °C to 63 °C (with the consequent decrease in gas pressure from 2 atm to 1 atm), and the second consists of an isobaric heating (P = 1 atm) from 63 °C to 400 °C. The path Ia/Ib–IIIb (which has not been represented in Figure 7 and is analogous to path 1 of Figure 5) corresponds to a reversible isothermal expansion (T = 400 °C) from an initial volume of 11.2 L to a final volume of 22.4 L. It must be insisted that to achieve these changes reversibly, the gas should undergo infinitesimally small changes in pressure, volume, and/or temperature. If it is an isothermal expansion, the external pressure should be decreased infinitesimally, while if it is an isobaric expansion or an isochoric compression, the surroundings should infinitesimally modify their temperature, allowing infinitesimal changes in volume or pressure, respectively.

Perhaps the most relevant utility of the P-V-T graph is in the description of the paths in Figure 7a. Point IIa is below the equilibrium surface. It could represent a metastable state of the gas that then evolves to reach the equilibrium state IIIa on the P-V-T surface, but the corresponding trajectory (below that surface), and which would be a description of the variation of the gas pressure in different non-equilibrium states, is indeterminate. In a real process, perhaps the gas will not even reach state IIa.

Conclusions

The alternative conceptions associated with the concept of spontaneity of processes discussed in this work demonstrate their detrimental effects on thermodynamic calculations, leading to contradictions even in cases where everyday experience provides the correct answer. However, this circumstance can serve as a valuable starting point for teaching key thermodynamic aspects. The difficulty in employing thermodynamic formulations at a basic level lies not in the mathematical aspects but in the precise understanding of the restrictions governing their application. Both in textbooks and in teaching practice, omissions can inadvertently contribute to these misconceptions.

To effectively address and prevent these alternative conceptions, a strong emphasis must be placed on fundamental definitions and concepts. This includes a rigorous treatment of the system and surroundings, the various types of thermodynamic processes (isothermal, isobaric, isochoric, adiabatic), the crucial concept of equilibrium (thermal, mechanical, chemical), and the distinction between reversible and irreversible processes.

Furthermore, meticulous attention must be paid to the 'fine print' that indicates the specific conditions under which a given equation or criterion is applicable. For instance, the Gibbs free energy change (ΔG) as a criterion for spontaneity is only valid under conditions of constant pressure and temperature and in the absence of non-expansion work. Failure to emphasize these limitations leads directly to the alternative conceptions explored in this paper.

Therefore, pedagogical strategies should consistently reinforce these foundational principles and explicitly highlight the conditions of applicability for each thermodynamic tool and concept. Utilizing illustrative examples, including those where intuition might initially lead to incorrect conclusions, followed by a detailed analysis based on the correct application of thermodynamic principles, can be particularly effective. The discrepancies arising from the misapplication of these principles should be used as learning opportunities to deepen understanding and promote more robust conceptual frameworks in students.

References

Andrade-Gamboa, J. (2023). ¿Qué peste la del estaño? Tres desastrosos momentos en la historia. *Los Andes*. https://www.losandes.com.ar/sociedad/que-peste-la-del-estano-tres-desastrosos-momentos-en-la-historia

Andrade Gamboa, J., Donati, E. R., & Mártire, D. O. (2001). An analogy for teaching the difference between heat and temperature. *Chem 13 News*, (297), 8–11.

Barrow, G. M. (1978). *Química física* (Tomo I). Reverté.

Ben-Naim, A. (2011). Entropy: Order or information. *Journal of Chemical Education*, 88(5), 594–596. https://doi.org/10.1021/ed100922x

Biel Gayé, J. (1998). *Curso sobre el formalismo y los métodos de la termodinámica* (Vol. 1). Reverté.

Brundage, M. J., Meltzer, D. E., & Singh, C. (2024a). Investigating introductory and advanced students' difficulties with change in internal energy, work, and heat transfer using a validated instrument. *Physical Review Physics Education Research*, 20, 010115. https://doi.org/10.1103/PhysRevPhysEducRes.20.010115

Brundage, M. J., Meltzer, D. E., & Singh, C. (2024b). Investigating introductory and advanced students' difficulties with entropy and the second law of thermodynamics using a validated instrument. *Physical Review Physics Education Research*, 20, 020110. https://doi.org/10.1103/PhysRevPhysEducRes.20.020110

Carson, E. M., & Watson, J. R. (1999). Undergraduate students' understanding of enthalpy change. *University Chemistry Education*, 3(2), 46–51. https://edu.rsc.org/download?ac=517085

Committee on Undergraduate Science Education, & National Research Council. (1997). *Science teaching reconsidered: A handbook*. National Academy Press.

de Rosnay, J. (1993). *Qué es la vida*. Biblioteca Científica Salvat.

DeVoe, H. (2020). *Thermodynamics and chemistry*. https://www2.chem.umd.edu/thermobook/

Donati, E. R., Andrade Gamboa, J., & Mártire, D. O. (1995). Misconceptions induced by chemistry teachers. *Chem 13 News*, (241), 20–21.

Gislason, E. A., & Craig, N. C. (2013). Criteria for spontaneous processes derived from the global point of view. *Journal of Chemical Education*, 90(5), 584–590. https://doi.org/10.1021/ed300570u

Granville, M. F. (1985). Student misconceptions in thermodynamics. *Journal of Chemical Education*, 62(10), 847–848. https://doi.org/10.1021/ed062p847

Lambert, F. L. (2012). The misinterpretation of entropy as "disorder". *Journal of Chemical Education*, 89(3), 310. https://doi.org/10.1021/ed2002708

Lladó, M. L., & Jubert, A. H. (2011). Trabajo útil y su relación con la variación de energía de Gibbs. *Educación Química*, 22(3), 271–276. https://doi.org/10.1016/S0187-893X(18)30144-7

Metiu, H. (2006). *Physical chemistry: Thermodynamics*. Taylor & Francis.

Salame, I. I., Fadipe, O., & Akter, S. (2025). Examining difficulties, challenges, and alternative conceptions students exhibit while learning about heat and temperature concepts. *Interdisciplinary Journal of Environmental and Science Education*, 21(2), e2510. https://doi.org/10.29333/ijese/15997

Schrödinger, E. (1986). *¿Qué es la vida? El aspecto físico de la célula viva*. Ediciones Orbis.

Van Roon, P. H., Van Sprang, H. F., & Verdonk, A. H. (1994). "Work" and "heat": On a road towards thermodynamics. *International Journal of Science Education*, 16(2), 131–144. https://doi.org/10.1080/0950069940160203

Vasini, E., & Donati, E. R. (2005). Thermodynamics concepts: Some considerations on the use in introductory courses of chemistry. *Journal of the Argentine Chemical Society*, 93(1–3), 177–184.

Vasini, E. J., & Donati, E. R. (2001). Uso de analogías adecuadas como recurso didáctico para la comprensión de los fenómenos electroquímicos en el nivel universitario inicial. *Enseñanza de las Ciencias*, 19(3), 471–477. https://doi.org/10.5565/rev/ensciencias.3995

Recepción: 2025-05-22. ▪ Aceptación: 2025-08-31.