Process Spontaneity, Entropy and Gibbs Free (Available) Energy

Dr Anand M Shivapuji

Chief Architect- www.thermofluidscitech.com

November 21, 2021

Contents

1 Pre-requisites

Elementary thermodynamics

2 Discussion

Processes can be spontaneous or non spontaneous. Spontaneous processes continue on their own after the initial nudge or push and without any subsequent effort required. Some examples would be cooling of hot water kept in the open, melting of ice exposed to atmospheric temperature higher than the melting point, burning of say wood or paper or gas after the initial ignition, rolling down of a ball down the hill after the push from the top etc. Non spontaneous process will not take place on their own and require continuous external effort. If a cup of water has to be frozen then it has to be placed in the refrigerator which takes in electricity to freeze the water. Similarly, if a cup of water has to be heated then the kettle has to be placed on the burner and if a ball has to be taken uphill then it has to be carried all the way up and just a small initial push will not enable it to climb the top. In summary, spontaneous processes proceed without the requirement of any external efforts while non spontaneous processes require continuous efforts to take them to completion.

Thermodynamics, through the definition of entropy, provides an analytical approach to establish the nature of a process as being spontaneous or non-spontaneous. The second law of thermodynamics states that the any process that results in an increase in the entropy of an **ISOLATED SYSTEM** is spontaneous while a process that results in reduction of entropy of the **ISOLATED SYSTEM** is non spontaneous. It is important to note the applicability of entropy change to an **ISOLATED SYSTEM** in establishing spontaneity of a process. Thus;

$\Delta S_{isolated\ system} > 0$ Process is spontaneous

$\Delta S_{isolated\ system} < 0$ Process is non spontaneous

Practical systems are all basically open and/or closed systems that undergo some thermodynamic process. As such, analysis of the entropy change for such systems will **not** give an indication of the spontaneity of the process. Towards analysing the spontaneity of such practical systems, the scope of investigation is extended from the system to also include the surrounding. Thus, the entropy change of the system and the surrounding together, basically the entropy change of the universe is/can be analysed to establish the spontaneity of the process. Since the universe is an isolated system, a process within the universe that results in entropy increase of the universe is then designated to be spontaneous and vice versa. By definition the

---

entropy change of the universe is the sum of entropy change of the system and the surrounding. Mathematically, the entropy change is presented as in equation 1.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} \tag{1}$$

Considering entropy change of the system and the surrounding through reversible processes, the definition of $\Delta S = \dfrac{Q_{i-f}}{T}$ is invoked to arrive at equation 2 from equation 1.

$$\Delta S_{universe} = \frac{Q_{system}}{T_{system}} + \frac{Q_{surrounding}}{T_{surrounding}} \tag{2}$$

In equation 2, Q_{system} and $Q_{surrounding}$ correspond to the heat transfer associated with the system and the surrounding while T_{system} and $T_{surrounding}$ correspond to the absolute temperature at which the heat transfer takes place for the system and surrounding respectively. In the analysis of system and its surrounding, it is important to note that during any reversible process, the energy transfer across the system boundary results in equi-magnitude changes in the energy levels of the system and surrounding. If energy is added to the system, that energy has to come from the surroundings and as such, energy gain of the system comes at the expense of energy lost by the surrounding. The vice-versa holds true. In reference to equation 2, Q_{system} and $Q_{surrounding}$ can be replaced in terms of Q_{i-f} as;

$$Q_{system} = Q_{i-f} \qquad \text{and} \qquad Q_{surrounding} = -Q_{i-f}$$

Invoking in equation 2, equation 3 is arrived at.

$$\Delta S_{universe} = \left\{ \frac{Q_{i-f}}{T_{system}} \right\} + \left\{ \frac{-Q_{i-f}}{T_{surrounding}} \right\}$$

$$\Delta S_{universe} = \left\{ \frac{Q_{i-f}}{T_{system}} \right\} - \left\{ \frac{Q_{i-f}}{T_{surrounding}} \right\} \tag{3}$$

In equation 3, heat is hypothetically added to the system and lost by the surroundings. If heat is lost by the system and gained by the surroundings, the signs for system and surrounding heat transfer will change.

Exploring a few examples of assessing spontaneity, consider heat of 10 kJ being transferred from the system to the surrounding when the system temperature is at 400 K while the surrounding is at 298 K. By intuition this is a spontaneous process considering that heat is flowing from a high temperature region to low temperature region. Assessing the spontaneity through the universe entropy change of the universe approach,

$$\Delta S_{universe} = \left\{ \frac{-10,000}{400} \right\} + \left\{ \frac{10,000}{298} \right\} = 8.56 J/K$$

Since the entropy change of the universe is positive, which means entropy is generated, the process is spontaneous.

Reversing the scenario, for the same temperature conditions, if heat is transferred from the surrounding to the system then basically heat is being transferred from a low temperature region to a high temperature region and intuitively this is a non spontaneous process and requires external effort. Evaluating the universe entropy change for this process,

$$\Delta S_{universe} = \left\{ \frac{10,000}{400} \right\} + \left\{ \frac{-10,000}{298} \right\} = -8.56 J/K$$

Since the entropy change of the universe is negative, which means entropy is destroyed, the process is non-spontaneous.

Reverting back to the question of assessing the spontaneity of a process executed by a non isolated system using entropy as the yardstick, referring to equation 3, change in entropy of both the system and the surrounding will have to be analysed. A simple mathematical rearrangement of equation 3 can provide a better and simpler expression for the assessment of process spontaneity. In equation 3, reverting the expression of entropy change for the system to be represented as ΔS_{system} the following expression can be arrived at;

$$\Delta S_{universe} = \Delta S_{system} - \frac{Q_{i-f}}{T_{surrounding}}$$

From the first law of thermodynamics, for a constant pressure process (isobaric process) the heat transfer across the system boundary equals the enthalpy change for the process. This is established based on a simple derivation as below;

$$\delta Q = \delta W + dU \; ; \; \delta Q = pdV + dU \; ; \; \delta Q = pdV + d[H - pV] \; ; \; \delta Q = pdV + dH - pdV - V\,dp \; ; \; \delta Q = dH$$

Thus, the entropy change for universe equation takes the form (with $T_{surrounding} = T$);

$$\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H}{T}$$

With additional mathematical rearrangement of multiplying through out by $-T$ and rearranging the terms, equation 4 as presented below is arrived at.

$$-T\Delta S_{universe} = \Delta H - T\Delta S_{system} \tag{4}$$

The left hand side of equation 4 is basically what is famously know as the **Gibbs Free Energy**. It may be noted that the term free can be sometimes confusing and as such a more appropriate term of **Gibbs Available Energy** should be preferably used. Thus, equation 4 can be represented as;

$$\Delta G = -T\Delta S_{universe} = \Delta H - T\Delta S_{system} \tag{5}$$

On the RHS size of equation 5, since the parameter change terms are applicable only to the system, subscripts can be eliminated and the generalized equation can be represented as in equation 6.

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

In regards to equation 6, it is important to note that it is applicable under the constraints of reversible, constant temperature (isothermal) and constant pressure process.

Referring to equation 6, it can be noted that for spontaneous processes, as the Entropy increase, the Gibbs Available Energy decreases (due to the negative sign of $T\Delta S_{universe}$) and vice versa. Thus for;

- Spontaneous process, $\Delta S_{universe}$ increases and ΔG decreases

- Non spontaneous process, $\Delta S_{universe}$ decreases and ΔG increases

- Equilibrium state has $\Delta S_{universe} = 0$ and $\Delta G = 0$