Work Degrading and the Reversible to Irreversible Transition in Chemical Reactions

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Abstract

A thermodynamic analysis performed on a simple ideal-gas chemical reaction with the help of the van't Hoff Equilibrium Box, among other thermodynamic notions, produces results concurrent with those of a previously published study in that infinite-time irreversible paths composed of a sequence of equilibrium states are possible. The purely thermodynamic methodology emerging from these studies allows the thermodynamic characterization and further graphical representation of irreversible processes and is simpler than that embodied by the Postulate of Local Equilibrium in that no recourse is made in it of kinetic considerations.

Keywords: thermodynamics, entropy, reversible and irreversible chemical reactions, postulate of local equilibrium, work-degrading path

1. Introduction

"... The real power of classical thermodynamics ..." says Miller, "... stems from the fact that only a small number of state variables are required to determine the properties of a uniform equilibrium system ..." (Miller, 1995). The restriction to systems in equilibrium being a reflection of the fact that "... strictly speaking, thermodynamic variables such as entropy ... are not well defined except at thermodynamic equilibrium, and their precise meaning becomes less clear the further the system deviates from this state ..." (Parlin et al., 1955). A similar consideration can be made for the temperature variable "... the temperature of a system is a concept which can be unambiguously applied only to systems in states of thermal equilibrium ..." (Tolman & Fine, 1948). These limitations find a good exemplification in the process known as a 'free expansion', this is, the expansion of a gas against a vacuum. Here, "... while the gas is streaming out into the vacuum, turbulent phenomena appear which not only weaken the homogeneity and our ability to describe the state of the gas by two variables but also cast doubt on the concept of the thermodynamic 'state'" (Haase, 1990). The combination of the previous considerations with the fact that irreversible processes are commonly conceived as a succession of non-equilibrium states bound by the initial and final equilibrium conditions of the process, could lead us to the erroneous conclusion that irreversible processes are beyond thermodynamic description. The reality of things is that an almost complete knowledge of the thermodynamics of irreversible processes can be provided by classical thermodynamics (*CT*) by focusing its attention on the equilibrium states constituting the initial and final conditions of these processes. By doing this *CT* can determine the changes in the relevant state functions associated to the irreversible transit. If needed, an alternate path constituted by a succession of equilibrium states -the so called reversible path-connecting the said initial and final states can be devised and the entropy evaluated by the proper integration along it of $\delta q / T$. All this knowledge apart, one limitation still stands: *CT* lack of capability for making statements as to the *step-by-step* changes sustained by the thermodynamic variables along the actual succession of non-equilibrium states. This is what Tolman and Fine are referring to when stating "... thermodynamics is adequate for the exact treatment of irreversible entropy production on passage from an initial to a final state of equilibrium, without reference to the violence of the intervening irreversible behavior, and this is often all that is needed ..." (Tolman & Fine, 1948). The impossibility of integration of $\delta q / T$ and the consequential impediment for its graphical representation alongside an irreversible path are vivid examples of the incompleteness of the picture provided by *CT* of irreversible processes.

Thermodynamicists have, however, found a roundabout way to this obstacle. By bringing into the conceptual edifice of *CT* what is known as *The Postulate of Local Equilibrium* (*PLE*), the noted limitation appears to be overcome. In the case of closed systems-the systems of interest in chemical thermodynamics-this postulate

assumes that an irreversible process can be thought as constituted by a succession of cells "…of short duration, with each occupying the whole system…" (Garfinkle, 2002); and that each of these cells, in the words of Moore, can, at a time t, be "… isolated from its surroundings and allowed to come to equilibrium, so that at $t + \delta t$, the P and T of the cell can be specified. The Postulate of Local Equilibrium is that we can take the P and T at any point in the original non-equilibrium system at time t to be equal to the P and T in the corresponding cell when equilibrium is reached at $t + \delta t$" (Moore, 1972); Here δt represents what is called the time of relaxation. Invocation of this postulate permits ascribing to every non-equilibrium state appearing in the irreversible path the properties of its reversible 'image'. This procedure allows then the use of the concepts and techniques of classical thermodynamics for the analysis of the irreversible path. The adoption by *CT* of *PLE* comes, however, at the price of including in its catalog of variables the "time of relaxation", *strictu sensu* a kinetic, and as such an extra classical-thermodynamic concept.

The overcoming of the noted thermodynamic limitation brought about by *PLE* can be seen in the chemical literature in the forms of graphs depicting the *step by step* evolution of *S* (the total entropy), or/and *G* (the Gibbs energy), or/and *A* (the Helmholtz energy) along the succession of non-equilibrium states defining the path of irreversible chemical reactions (Castellan, 1974; Davies, 1972; Hill, 1966; McEachern, 1979; Kauzmann, 1967; Pimentel & Spratley, 1970). In most of these graphs the thermodynamic variable ξ, known as the *extent of reaction or degree of advancement*, is used to follow the evolution of the reaction (Moore, 1972).

It has been recently shown, however, that *PLE* is not the only way to proceed towards the thermodynamic determination of the irreversible path. This new approach, originally exemplified via the comparison of the reversible and irreversible versions of an ideal gas isothermal expansion, claims to be purely thermodynamic on reason of not including the 'time of relaxation' in its discourse (Íñiguez, 2013). To understand the reasoning behind this alternative approach; to apply it to the occurrence of chemical reactions, as well as to obtain from it counterexamples to some accepted notions about irreversible processes is what the discussion that follows will attempt to achieve.

2. Antecedents

In what follows a thermodynamic analysis for the *reversible* occurrence of the following isothermal, ideal-gas isomerization reaction will be presented

$$1A(1bar,T) \rightarrow 1B(1bar,T) \tag{1}$$

The occurrence of the reversible reaction will be analyzed in two steps. Along the four processes constituting Step I, we will carry on the standard reaction until that point in which n moles out of the original 1 mole of *A* are isomerized into $nB(1bar,T)$. The $(1-n)$ moles of *A* remaining and the n moles of *B* produced are found at the end of Step I separate of one another, and each of them at $1bar$ and temperature T, i.e.

$$1A(1bar,T) \rightarrow (1-n)\,A(1bar,T) + nB(1bar,T) \tag{2}$$
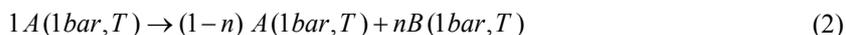
Step II take these gases at these conditions and mix them in a reversible fashion in order to produce, with the help of an inhibitor or negative catalyst, a non-reacting mixture of temperature *T* in which their respective partial pressures are P_A and P_B, with $P_A + P_B = 1$ *bar*, i.e.

$$(1-n)\,A(1bar,T) + n\,B(1bar,T) \rightarrow [(1-n)A(P_A,T),\,n\,B(P_B,T)] \tag{3}$$
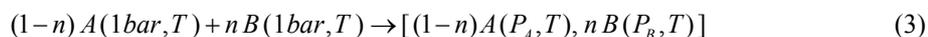
The fact that in reaction (1) as well as in its re-expression given in (2) the ideal gases appear in their standard states -pure gases at 1 *bar* of pressure- is what imparts the "standard" qualifier to this reaction (Denbigh, 1968). Finally, in Step III the transit of the reaction from reversible to irreversible will be produced via the degradation into heat of the reversible work by it produced.

Let us now center our attention in the situation depicted in Figure 1. In it C_A and C_B are cylinders fitted with frictionless pistons. Their connection to the constant volume reaction box C_R includes, respectively, valves V_A and V_B -initially closed-as well as semi-permeable membranes M_A, and M_B. The former being permeable only to ideal gas *A* and the latter to ideal gas *B*. The reaction box contains a large amount of a mixture of gases *A* and *B* at their respective equilibrium pressures P_{Aeq}, $P_{B,eq}$, at temperature T, i.e. $A(P_{Aeq},T) = B(P_{Beq},T)$. The pressure inside the box is constant and equal to $P_{C_R} = P_{A,eq} + P_{B,eq}$. The pistons have been properly coupled to a reversible mechanical reservoir (*MR*)-not shown-whose function is to safe keep or provide the work either produced or demanded by the operation (Callen, 2007). Initially, while cylinder *A* contains 1 mole of *A* at 1 *bar* and temperature *T*, cylinder *B* is empty, with its piston in its extreme leftmost position. Initially, the pressures keeping these pistons in place are 1 *bar*, and $P_{B,eq}$, respectively. The reaction box and the cylinders are in thermal contact with a reversible heat reservoir (*HR*)-not shown-of temperature *T* (Callen, 2007). The reversible qualifier attached to the heat and mechanical reservoirs stems from the fact that all processes taking place within

them are reversible (Callen, 2007). Gases *A*, *B*, as well as their equilibrium mixture in the reaction box constitute the thermodynamic system (*sys*); with the heat and mechanical reservoirs constituting the surroundings. Combined, system and surroundings constitute the universe of the process. The mechanical device constituted by reaction box, cylinders, pistons, valves, and semi-permeable membranes is called *the van't Hoff Equilibrium Box (VHEB)*. Alternative descriptions of this device can be found in the chemical literature (Fermi, 1956; Kauzmann, 1967; Smith & Van Ness, 1965).
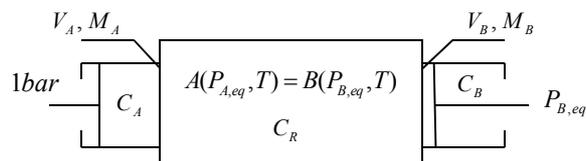
Figure 1. The van't Hoff Equilibrium Box is here depicted at the beginning of Step I. Here valves V_A and V_B are closed; cylinder C_A contains 1 mole of *A* at 1 *bar* and temperature *T*; cylinder C_B is empty, and the reaction box (C_R) contains a large amount of the equilibrium mixture of *A* and *B*, $A(P_{Aeq},T) = B(P_{Beq},T)$

3. A Brief Review of the Thermodynamics of Ideal Gases

It will serve us well to briefly review here those concepts of the thermodynamics of ideal gases which will be extensively used in the analysis to be presented below.

Let us recall that the internal energy (*U*) of ideal gases –such as the systems to be dealt with below- is a sole function of the temperature (Maron & Prutton, 1965). For isothermal changes of condition such as ideal-gas expansions or compressions the first law expression ($\Delta U_{sys} = Q_{sys} - W_{sys}$) reduces to $Q_{sys} = W_{sys}$. The fact that the sign convention for this form of the first law makes positive quantities out of heat absorbed and work produced, and negative quantities out of their respective opposites, allows us to understand that $Q_{sys} = W_{sys}$ means that the performance of any amount of work by our system has to be accompanied by a concomitant absorption on its part of an equivalent amount of heat from the heat reservoir (Q_{HR}), or vice versa, i.e.

$$Q_{sys} = -Q_{HR} \tag{4}$$

The fact that any work done by the system is work done on the mechanical reservoir, and vice versa, allows us to write

$$W_{sys} = -W_{MR} \tag{5}$$

For the heat reservoir, whose only function is heat exchange, the first law expression reduces to $\Delta U_{HR} = Q_{HR}$. For the mechanical reservoir, whose sole function is the exchange of energy as work, it takes the following form $\Delta U_{MR} = -W_{MR}$.

Under reversible conditions the work done by/on *n* moles of the system in an isothermal (*T*) expansion/compression from an initial pressure P_i to a final pressure P_f is given by

$$W_{sys} = n R T \ln(P_i / P_f) \tag{6}$$

The fact that in these processes any heat exchanged is reversible heat allows us to re-express Equation (4) in terms of the individual as well as combined entropy changes of these bodies

$$\Delta S_{sys} = Q_{sys} / T, \quad \Delta S_{HR} = Q_{HR} / T \tag{7}$$

$$\Delta S_{sys} + \Delta S_{HR} = 0 \tag{8}$$

4. Step One: A Standard and Reversible Chemical Reaction

Process 1. The mole of gas *A* in cylinder C_A is expanded isothermally (*T*) and reversibly from *1 bar* to P_{Aeq}. At the end of this process the pressure keeping this piston in place is P_{Aeq}. In accordance with the discussion presented in Section 3, the different changes associated to this process are the following

$$\Delta U_{sys,1} = 0 \tag{9}$$

$$W_{sys,1} = Q_{sys,1} = -Q_{HR,1} = -W_{MR,1} = -RT \ln P_{A,eq} \tag{10}$$

$$\Delta S_1 = \Delta S_{sys,1} + \Delta S_{HR,1} = -R \ln P_{A,eq} + R \ln P_{A,eq} = 0 \tag{11}$$

At the conclusion of this process both valves are opened for Processes 2 and 3 to take place.

Process 2. Under infinitesimal pressure gradients n moles of gas $A(P_{A,eq}, T)$ are introduced, $0 \langle n \leq 1$, and n moles of gas $B(P_{B,eq}, T)$ simultaneously removed from the reaction box. The constant temperature and constant pressure work done on gas A in pushing it into the reaction box can be evaluated by noticing that under these conditions any volume change can be traced to a change in the number of moles of the gas, i.e. $P_{A,eq} dV_A = RT dn_A$. This fact allows us to write the integrated expression for the work involved in terms of the change in the number of moles as: $W_{A,2} = RT \, \Delta n_A = RT(n_{f,A} - n_{i,A})$. The sub-indexes here used make reference to the changes experienced by gases A or B in process 2. In the previous expression $n_{i,A}$ and $n_{f,A}$ stand for the initial and final number of moles of A in the process being considered, i.e. $n_{i,A} = 1$ and $n_{f,A} = (1-n)$. The proper substitution of these values in the previous work expression leads to

$$W_{A,2} = -nRT \tag{12}$$

The work associated to the removal step can be similarly evaluated. Here $W_{B,2} = RT(n_{f,B} - n_{i,B})$ with $n_{i,B} = 0$, and $n_{f,B} = n$. Therefore

$$W_{B,2} = nRT \tag{13}$$

The calculation of W via the equivalent expression $W = P\Delta V$ can be seen in Kauzmann (1967).

The combination of the work associated to these two processes determines the work of the system for Process 2, i.e.

$$W_{sys,2} = W_{A,2} + W_{B,2} = 0 \tag{14}$$

This result allows writing the following equations

$$W_{MR,2} = 0 \tag{15}$$

$$Q_{sys,2} = W_{sys,2} = 0 \tag{16}$$

$$\Delta U_{sys,2} = 0 \tag{17}$$

$$Q_{HR,2} = -Q_{sys,2} = 0 \tag{18}$$

$$\Delta S_2 = \Delta S_{sys,2} + \Delta S_{HR,2} = 0 \tag{19}$$

Process 3. Upon disturbance of the equilibrium composition in the box as a consequence of the introduction/removal operations of Process 2, the reaction mixture proceeds to restore it via the conversion of A into B, i.e.

$$nA(P_{A,eq}, T) \rightarrow nB(P_{B,eq}, T) \tag{20}$$

This reaction, it should be understood, is concomitant, i.e. simultaneous to the introduction/removal process before described. The fact that reaction (20) takes place *at equilibrium*, corresponds with

$$W_{A \rightarrow B,3} = 0 \tag{21}$$

This notion-equivalent to that which can be written in terms of the Gibbs free energy: $\Delta G_{A \rightarrow B,3} = 0$ (Maron & Prutton, 1965)-can be properly rationalized considering that if a reversible chemical reaction produces work in its way to equilibrium and consumes work in getting away from it, then no production nor consumption of work can be associated to a reaction taking place at equilibrium. The sub index just introduced refers to the conversion of A into B taking place in process 3. Insertion of Equation (21) in the expression for the first law applied to reaction (20) produces $\Delta U_{A \rightarrow B,3} = Q_{A \rightarrow B,3}$. Now, the enthalpy and internal energy changes for this reaction are related by the following expression: $\Delta H_{A \rightarrow B,3} - \Delta U_{A \rightarrow B,3} = (\Delta PV)_{A \rightarrow B,3}$. For this isothermal and constant total mole number reaction we also have that $(\Delta PV)_{A \rightarrow B,3} = RT(\Delta n)_{A \rightarrow B,3} = 0$. If so, $\Delta H_{A \rightarrow B,3} = \Delta U_{A \rightarrow B,3}$. This result permits rewriting $\Delta U_{A \rightarrow B,3} = Q_{A \rightarrow B,3}$ as follows

$$\Delta H_{A \rightarrow B,3} = Q_{A \rightarrow B,3} \tag{22}$$

Now, the pressure independence of the enthalpy function of ideal gases (Denbigh, 1968) allows us to establish the following identity

$$\Delta H_{A \rightarrow B,3} = \Delta H[nA(P_{A,eq}, T) \rightarrow nB(P_{B,eq}, T)] = n\,\Delta H[A(1bar, T) \rightarrow B(1bar, T)] = n\Delta H^o \tag{23}$$

In the previous equation $\Delta H[A(1bar, T) \rightarrow B(1bar, T)]$ represents the enthalpy change for reaction (1), in other words, for the transformation of 1 mole of A into 1 mole of B under standard conditions i.e. ΔH^o. The fact that in Equation (20), the embodiment of Process 3, it is not 1 but n the moles of A being transformed into B is what explains the product: $n\,\Delta H^o$. These considerations allow writing equation (22) as follows:

$$n\,\Delta H^o = Q_{A \rightarrow B,3} \tag{24}$$

The fact that in Process 3 the system is represented by the reaction mixture undergoing the transformation represented by reaction (20) allows us to write, with base in Equation (21), the following equations for the work exchanged in this step between system and mechanical reservoir

$$W_{sys,3} = W_{A \rightarrow B,3} = 0 \tag{25}$$

$$W_{MR,3} = 0 \tag{26}$$

The previously quantified heat exchanges, and the entropy changes to they associated will be now written as follows

$$Q_{sys,3} = Q_{A \rightarrow B,3} = n \Delta H^o \tag{27}$$

$$Q_{HR,3} = -n \Delta H^o \tag{28}$$

$$\Delta S_{sys,3} = n \Delta H^o / T, \quad \Delta S_{HR,3} = -n \Delta H^o / T, \quad \Delta S_3 = \Delta S_{sys,3} + \Delta S_{HR,3} = 0 \tag{29}$$

The adequate combination of Equations (25) and (27) produce, in agreement with the preceding discussion, the following energy change for Process 3

$$\Delta U_{sys,3} = n \Delta H^o \tag{30}$$

At the conclusion of this process–simultaneous to the conclusion of Process 2, both valves are closed.

Process 4. Here, the amounts of A and B in C_A and C_B at the end of Processes 2 and 3, namely $(1-n) A(P_{A,eq}, T)$ and $nB(P_{B,eq}, T)$, will be now compressed isothermally (T) and reversibly to a final pressure of 1 bar. The energy/entropy changes associated to these operations are given below. The sub-indexes used make reference to the changes experienced by A or B in Process 4.

$$W_{A,4} = Q_{A,4} = -Q_{HR,A,4} = -W_{MR,A,4} = (1-n) RT \ln P_{A,eq} \tag{31}$$

$$W_{B,4} = Q_{B,4} = -Q_{HR,B,4} = -W_{MR,B,4} = nRT \ln P_{B,eq} \tag{32}$$

$$\Delta S_{A,4} + \Delta S_{HR,A,4} = 0 \tag{33}$$

$$\Delta S_{B,4} + \Delta S_{HR,B,4} = 0 \tag{34}$$

The total changes for system and reservoirs in Process 4 are given below

$$W_{sys,4} = W_{A,4} + W_{B,4} = Q_{sys,4} = -Q_{HR,4} = -W_{MR,4} = (1-n) RT \ln P_{A,eq} + nRT \ln P_{B,eq} \tag{35}$$

$$\Delta S_4 = \Delta S_{A,4} + \Delta S_{HR,A,4} + \Delta S_{B,4} + \Delta S_{HR,B,4} = 0 \tag{36}$$

The total changes for Step I.

The reaction Box.

No change remains in the reaction box as a consequence of the previous processes. The n moles of gas B removed from it were replenished by reaction $nA(P_{A,eq}, T) \rightarrow nB(P_{B,eq}, T)$, with the constancy of its temperature assured by the action of the heat reservoir.

The Cylinders

Cylinders A and B experience changes in their respective conditions as a consequence of the processes described. Thus, while the former originally contained 1 mole of $A(1bar, T)$; at the end it contains only $(1-n)$ moles of this gas at these same conditions. The latter, originally empty, is found at the end containing n moles of $B(1bar, T)$. Note then that the four processes constituting Step I have managed to transform the original $1 A(1bar, T)$ into pure A and B in the amounts and conditions given by: $(1-n) A(1bar, T)$ and $n B(1bar, T)$. In other words these four processes combined to bring forward the standard reaction given by Equation (2).

The System

The work performed by the system in Step I, quantified in Equations (10), (14), (25), and (35), amounts to

$$W_{sys,I} = -RT \ln P_{A,eq} + 0 + 0 + (1-n)RT \ln P_{A,eq} + nRT \ln P_{B,eq} \tag{37}$$

Upon simplification, Equation (37) reduces to

$$W_{sys,I} = nRT \ln (P_{B,eq} / P_{A,eq}) \tag{38}$$

Recognition of the fact that the pressure quotient in the previous equation is the equilibrium constant K for reaction (1) at temperature T, combined with the fact that (Maron & Prutton, 1965)

$$\Delta G^o = -RT \ln K \tag{39}$$

Allows writing Equation (38) as follows

$$W_{sys,I} = -n\,\Delta G^o \tag{40}$$

The heat exchanged by the system in each of the processes constituting Step I has been evaluated in Equations (10), (16), (27), and (35). It amounts to

$$Q_{sys,I} = -RT\ln P_{A,eq} + 0 + n\Delta H^o + (1-n)RT\ln P_{A,eq} + nRT\ln P_{B,eq} \tag{41}$$

Simplification of this equation, followed by its combination with Equation (39) produces

$$Q_{sys,I} = n\left(\Delta H^o - \Delta G^o\right) \tag{42}$$

The defining equation of the Gibbs energy ($G = H - TS$) allows writing the previous expression as

$$Q_{sys,I} = nT\,\Delta S^o \tag{43}$$

According to the first law, the total energy change experienced by the reaction system in Process I, is given by the combination of Equations (43) and (40), i.e.

$$\Delta U_{sys,I} = n\,T\,\Delta S^o - (-n\,\Delta G^o) \tag{44}$$

The same comments made in reference to $n\,\Delta H^o$ in Equation (23) apply to $n\,\Delta G^o$ and $nT\,\Delta S^o$ terms in Equations (40) and (43).

A simple algebraic argument using the defining equation for the Gibbs energy allows rewriting the previous expression as

$$\Delta U_{sys,I} = n\Delta H^o = Q_{sys,I} - W_{sys,I} \tag{45}$$

This last expression sheds light on the fact that the ultimate energy source fueling the production of work as well as the heat exchanged with the heat bath by the standard reaction is the heat released by it in its unfolding, as measured by the standard enthalpy change, properly ponderated by the number of moles n actually isomerized.
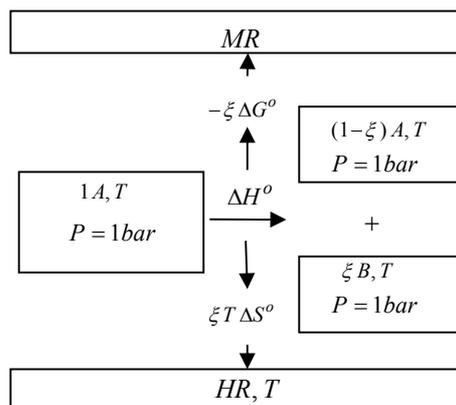
Figure 2. The standard reaction produced in the van't Hoff Equilibrium Box through the four processes of Step I

The Mechanical Reservoir

The changes experienced by the mechanical reservoir are those given in Equations (10) (15), (26), and (35). Substitution of the values given by these equations, followed by adequate simplification leads to

$$W_{MR,I} = n\Delta G^o \tag{46}$$

The Heat Reservoir

The changes associated to the heat reservoir are, in turn, given by Equations (10), (18), (28), and (35). Their combination and further simplification produce

$$Q_{HR,I} = -nT\Delta S^o \tag{47}$$

The total entropy change for Step I, evaluated via the combination of Equations (11), (19), (29), and (36), in accordance with the demand imposed by the second law to reversible processes, is identical with zero

$$\Delta S_I = 0 \tag{48}$$

A summary of the changes produced by Step I have been represented in Figure 2.

The Degree of Advancement

The thermodynamic variable ξ with units of *mole*, known as the *extent of reaction* or *degree of advancement*, is defined for a chemical reaction as $\xi = \Delta n_i / \nu_i$, with ν_i representing the stoichiometric coefficient-a positive number for products and negative for reactants- and Δn_i the change in number of moles of species *i* at the point where ξ is being evaluated (Moore, 1972). In reference to reaction (1) ξ becomes

$$\xi = [\Delta n_A / (-1)] = [(n_{A,f} - n_{A,i}) / (-1) = [(1-n) - 1] / (-1) = n \, mol \tag{49}$$

Or as

$$\xi = \Delta n_B / 1 = (n_{B,f} - n_{B,i}) / 1 = n - 0 = n \, mol \tag{50}$$

The substitution of *n* by ξ allowed by the previous result, already present in Figure 2, will also be used in the following discussions.

5. Step II: Reversible Mixing of the Products of the Standard Reaction

Let us now take each of these gases in the condition they have at the end of Step I and deposit them, without change, in the indicated cylinders of the apparatus shown in the left hand side of Figure 3. This device-whose walls appropriately support the required amount of a negative catalyst or inhibitor for reaction (1)-has been appropriately coupled to a mechanical reservoir as well as a to heat bath of temperature *T*. The left hand side piston incorporates a membrane permeable only to gas *A*, and the right one a membrane permeable only to gas *B*. Being this so, the gases mix upon reaching the space between the pistons. Even if these gases exert no force on their respective pistons, they exert their respective pressures on the opposite ones. The achievement of a reversible mixing under these conditions calls for the application to the left hand piston of an external pressure opposite and infinitesimally smaller than that exerted on it by *B*, as well as of the similar application in the right piston of a pressure equally smaller than that exerted on it by *A* (Klotz & Rosenberg, 1986).
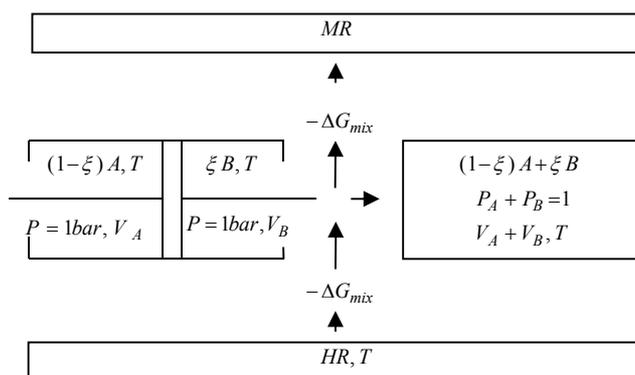
Figure 3. The reversible mixing of the indicated amounts of *A* and *B* manages to transform an amount of heat $-\Delta G_{mix}$ absorbed from the heat reservoir into an equivalent amount of work deposited in the mechanical reservoir

The continued diffusion of the gases through these membranes marks the transit of gases A and B from their respective smaller initial volumes V_A and V_B to the larger and common volume $V_A + V_B$. Thus perceived the mixing process turns out to be nothing more than two simultaneous expansions, two isothermal and reversible expansions if note is taken of the constraints upon which they proceed. Via the opposed and outward motion of the pistons, these expansions manage to transform into work an equivalent amount of heat absorbed from the heat reservoir. Further characterization of the mixing process demands specification of its initial and final conditions. The former, represented by the unmixed gases, is given by $(1-\xi) A (1 \, bar, T, V_A)$ and $\xi B (1 \, bar, T, V_B)$. The latter-represented by the gases coexisting at the same temperature *T* in a common volume $V_A + V_B$, exerting there partial pressure P_A and P_B -can be properly specified considering that

$$P_A = (1-\xi) RT / (V_A + V_B) \; and \; P_B = \xi \, RT / (V_A + V_B) \tag{51}$$

and also that

$$P V_A = (1-\xi) RT, \quad P V_B = \xi \, RT \tag{52}$$

Here P has been introduced to designate the (1 bar) pressure of each of these gases before the mixing takes place. The appropriate one to one combination of equations (51) with (52) leads to $P_A = PV_A/(V_A + V_B)$ and $P_B = PV_B/(V_A + V_B)$. Their addition leads, finally, to $P_A + P_B = P = 1\,bar$. This last result, in combination with the division of any of the expressions given in (51) by the other leads to

$$P_A = 1 - \xi \ \ and \ \ P_B = \xi \tag{53}$$

As noted above, in each of the two isothermal and reversible expansions subsumed by the mixing process we find gases A and B producing work out of heat absorbed from the heat reservoir. For the initial and final conditions previously specified the total amount of work produced by the system in this Step II amounts to

$$W_{sys,II} = -W_{MR,II} = W_A + W_B = (1 - \xi)RT\ln(1/P_A) + \xi RT\ln(1/P_B) \tag{54}$$

The Gibbs energy changes sustained by these gases along their mixing path will now be written. For each of them we can write $dG = VdP - SdT$ (Bevan Ott & Boerio-Goates, 2000). For constant temperature changes this equation reduces to $(\partial G/\partial P)_T = V$, and for ideal gases to $(\partial G/\partial P)_T = nRT/P$. The evaluation of the Gibbs energy changes calls for the proper integration of this equation. To do this we have to recognize that for A, $n = 1 - \xi$, and the limits of integration go from $P = 1$, to $P = P_A$; For B, on the other hand, $n = \xi$, and the integral goes from $P = 1$ to $P = P_B$. The addition of the results produced by these integrals leads to the Gibbs energy change of the mixing process

$$-\Delta G_{mix} = (1 - \xi)RT\ln(1/P_A) + \xi RT\ln(1/P_B) \tag{55}$$

A simple inspection of Equations (54) and (55) makes evident that

$$W_{sys,II} = -\Delta G_{mix} \tag{56}$$

Let us now introduce here the fact that the isothermal mixing of ideal gases takes place without change of internal energy (Denbigh, 1968), i.e.,

$$\Delta U_{sys,II} = 0 \tag{57}$$

From this result and our discussion in Section 3, we can also write

$$Q_{sys,II} = -Q_{HR,II} = -W_{MR,II} = -\Delta G_{mix} \tag{58}$$

$$\Delta S_{II} = (Q_{sys,II}/T) + (Q_{HR,II}/T) = 0 \tag{59}$$

Additional discussions on the reversible mixing of ideal gases can be found in the chemical literature (Planck, 1990; Fast, 1970; Waser, 1966)

6. The Total Changes for the Reversible Reaction

The isomerization reaction in its reversible transit from $1\,mole\,A(1\,bar, T)$ to the ξ-mixture $[(1 - \xi)A(P_A, T), \xi B(P_B, T)]$, has left the following total changes

From Equations (57) and (45); (40) and (56); (43) and (58); (46) and (58); (47) and (58); and (48) and (59), we can respectively, write

$$\Delta U_{sys,total}(\xi) = \xi \Delta H^o \tag{60}$$

$$W_{sys,total}(\xi) = -\xi \Delta G^o - \Delta G_{mix} \tag{61}$$

$$Q_{sys,total}(\xi) = \xi T\Delta S^o - \Delta G_{mix} \tag{62}$$

$$W_{MR,total}(\xi) = \xi \Delta G^o + \Delta G_{mix} \tag{63}$$

$$Q_{HR,total}(\xi) = -\xi T\Delta S^o + \Delta G_{mix} \tag{64}$$

$$\Delta S_{u,rev}(\xi) = 0, \quad \forall \xi \tag{65}$$

The sub-indexes used in Equation (65) emphasize the fact that this entropy change is that of the reversible universe and as such it comes from the combined entropy changes of all the bodies involved in the reversible transit of the isomerization reaction from $\xi = 0$ to the ξ-mixture being considered. The fact that with independence of the number of moles of A inserted in the reaction box, this is, with independence of the value ξ might adopt in a particular analysis, in the reversible transit all the heat exchanges take place, as shown by Equation (4), between system and heat reservoir, combined with the fact that each of these exchanges leads, as shown by Equation (8), to a zero entropy change, serve to explain the zero entropy change for the reversible universe as well as its independence from ξ. The reversible condition of this universe, it should be clear, stems from the fact that the amount of work outputted along its course is precisely that required to make the reaction retrace its steps, and in doing so, return with it the heat and mechanical reservoirs-the universe of the process-to their precise original condition, without changes remaining elsewhere. Had any work been lost along its course

the recuperation of the initial condition wouldn't be possible without a change being left in that foreign body called to supply the missing work. In the words of Planck "... The significance of the second law of thermodynamics depends on the fact that it supplies a necessary and far-reaching criterion as to whether a definite process which occurs in nature is reversible or irreversible ... A process which can in no way be completely reversed is termed *irreversible*, all other processes *reversible*. That a process may be irreversible, it is not sufficient that it cannot be directly reversed...The full requirement is, that it be impossible, even with the assistance of all agents in nature, to restore everywhere the exact initial state when the process has once taken place ..." (Planck, 1990).

It needs to be mentioned here that it is the number of moles *n* of *A* introduced into the reaction box in Process 2 what fixes the degree of advancement ξ corresponding to the mixture produced at the end of the reversible mixing step shown in Figure 3. Let us also recognize that the combination of Steps I and II manage to produce the transit from $1 mole\, A\,(1bar, T)$ to the corresponding ξ-mixture in a direct fashion, without ever passing through any intermediate state or degree of advancement i.e. starting with the state of equilibrium represented by *A* at its initial conditions, it ends up at the equilibrium mixture corresponding to the given ξ. Changing the properties of the mixture produced at the end of Step II, say changing the number of moles of *A* and *B* present in it is equivalent to producing a different mixture, and the only way we can do this with the *modus operandi* of the *VHEB* is to go back to it, restore the initial condition represented by $1\, A\,(1bar, T)$, and start the whole process again by inserting a different number of moles of *A*. That any of the mixtures produced this way is an equilibrium mixture stems from the fact that on reason of the negative catalyst, the ξ of any of these mixtures remains constant, unchanging; and any system with unchanging properties is indeed a system in equilibrium (Reiss, 1996). The particular mixture with $\xi = \xi_{eq}$ will be a mixture in equilibrium in the sense explained, and also in equilibrium in regards to chemical reaction. We can take this process to the extreme and produce an infinite number of mixtures by inserting increasing amounts of *A* differing only infinitesimally from the previous one. The ξ-ordering of these mixtures alongside their associated heat and mechanical reservoirs embody in the most detailed way possible the reversible course of the reaction's universe as each of these states will be characterized by a set of equations similar to that composed by Equations (60) to (65) characterizing the condition of the reaction's universe at ξ. This ξ-ordering can find graphical representation via the continuous locus produced, say, by the increase of the partial pressure of product *B* as the reaction proceeds, $P_B(\xi)\, vs.\, \xi$, or by following the evolution of the total entropy change along its course, in terms of $\Delta S_{u,rev}(\xi)\, vs.\, \xi$. This last graph, it shouldn't be difficult to realize, corresponds to the horizontal line $\Delta S_{u,rev} = 0$.

7. Step III: The Reversible to Irreversible Transit

Let us focus our attention on the initial infinitesimal advancement step in which the insertion of dn moles of A into the reaction box causes the reaction to reversibly transit from its initial condition $1\, mole\, A\,(1bar, T)$ characterized by $\xi = 0$, to a degree of advancement $d\xi$. At the conclusion of the reversible mixing step that follows the action of the *VHEB*, we find that the reaction system has transferred to the mechanical reservoir an amount of work dW_{sys}, as well as transferred to the heat reservoir an amount of heat dQ_{sys}. Let us further assume that the appropriate mechanism is available-v.g. the 'paddle-wheel in water' device used by Joule in his measurement of the mechanical equivalent of heat (Schmidt, 1966) to irreversibly transform dW_{sys}, now being released by the mechanical reservoir, into an equivalent amount of heat to be absorbed by the heat reservoir. At the end of this process we find the mechanical reservoir recuperating its initial no-work containing condition; The heat reservoir receiving, in addition to dQ_{sys}, an amount of heat of magnitude dW_{sys}; And the original reversible universe becoming irreversible. The explanation for this last effect is simple. At the end of this work-degrading process the restoration of the original condition of the universe could only be produced at the expense of a permanent change being left on that body called to supply the work we no longer have. This reversible to irreversible transition stands to attention on reason of the fact that it takes place without affecting the equilibrium conditions of the bodies involved. The explanation for this follows: The fact that this work-losing step takes place with the exclusive involvement of the heat and mechanical reservoirs allows us to realize that the reaction mixture is unaffected by it. Along the course of this irreversible process the reaction mixture is simply a spectator, and on reason of this it is found at the end of this work-degrading step in the same equilibrium condition it was at the beginning of it, i.e. at the same composition, temperature, volume and total and partial pressures. As to the reversible heat and mechanical reservoirs it needs to be remembered that these bodies can always be find in states of equilibrium. They transit from initial to final equilibrium conditions via paths constituted by a sequence of equilibrium steps. At the end of the work degrading process we are then left with an irreversible universe constituted by three bodies in equilibrium. If the procedure just described is repeated with each and every one of the infinite number of reversible reaction steps generated in the previous

section, we will end up with an ξ-ordering of equilibrium yet irreversible universes in each of which the condition of the mixture is indistinguishable from that it had in its equilibrium and reversible antecedent, and if so the ordered pairs (P_B, ξ) corresponding to the latter will be carried on, without change, to the former. This way the continuous graph P_B vs. ξ referred to in the previous section marking the evolutionary path of the reversible reaction will find itself doubling as the descriptor of the irreversible reaction course. This result contradicts the common belief that irreversible processes cannot find representation via continuous graphs (Schmidt, 1966).

The fact that the mixture produced in the reversible universe at ξ transfers to the mechanical reservoir the amount of work given by Equation (61), means that it is the degradation into heat of this amount of work what produces the reversible to irreversible transit of the reaction's universe at ξ. The entropy change sustained by the heat reservoir on reason of this irreversible step, quantified by $\Delta S_{W_{lost}}(\xi) = [W_{lost}(\xi)]/T$ (Smith & Van Ness, 1965; Íñiguez, 2013) defines, in combination with the total entropy change of its reversible antecedent, the total or final entropy change $\Delta S_{u,irr}(\xi)$ for the irreversible universe at ξ, i.e.

$$\Delta S_{u,irr}(\xi) = \Delta S_{u,rev}(\xi) + [W_{lost}(\xi)]/T \qquad (66)$$

The previous equation, on reason of $\Delta S_{u,rev}(\xi) = 0$, becomes $\Delta S_{u,irr}(\xi) = [W_{lost}(\xi)]/T$. The fact that $W_{lost}(\xi)$ is given by $-(\xi \Delta G^o + \Delta G_{mix})$ allows us to quantify the entropy change associated to the irreversible universe at ξ as follows:

$$\Delta S_{u,irr}(\xi) = [-(\xi \Delta G^o + \Delta G_{mix})]/T \qquad (67)$$

At this stage, while the mechanical reservoir finds itself devoid of any work, as it originally was, the final condition of the heat reservoir will be given by the combination of Equation (64) with the properly modified form of Equation (67), as follows

$$Q_{HR,final}(\xi) = -\xi T \Delta S^o + \Delta G_{mix} + T \Delta S_{u,irr}(\xi) = -\xi \Delta H^o \qquad (68)$$

In the irreversible universe the whole of the reaction's enthalpy change finds its way to the heat reservoir. The total entropy conditions of the universe before and after the work-degrading step can be specified, for any given ξ as $(\Delta S_{u,rev} = 0, \xi)$, and $(\Delta S_{u,irr}, \xi)$. Graphically this means that at any ξ the point corresponding to the graph $\Delta S_{u,irr}$ vs. ξ will be upwardly displaced in the amount $\Delta S_{W_{lost}}(\xi)$ from that appearing in $\Delta S_{u,rev}$ vs. ξ. Further knowledge about the graph $\Delta S_{u,irr}$ vs. ξ can be obtained via the techniques supplied by the calculus for this purpose. By doing this it is possible to prove (Anton, 1999) that this graph is continuous on $0 \leq \xi \leq 1$, with $\Delta S_{u,irr}(0) = 0$, and $\Delta S_{u,irr}(1) = -\Delta G^o/T$; that it is concave down in $0 \langle \xi \langle 1$; that on $0 \langle \xi \langle 1$ it shows a critical point/relative maximum at $(\xi_{eq}, \Delta S_{u,irr}(\xi_{eq}))$, where $\xi_{eq} = (1 + \exp(\Delta G^o/RT))^{-1}$; that the relative maximum is also an absolute maximum on reason of $\Delta S_{u,irr}(\xi_{eq}) \rangle \Delta S_{u,irr}(0)$ and $\Delta S_{u,irr}(\xi_{eq}) \rangle \Delta S_{u,irr}(1)$. The reaction's universe entropy maximum corresponds, as should be obvious, to the equilibrium state. That is what the sub-index 'eq' indicates on ξ_{eq}: the equilibrium conversion. All these features can be seen in the graph developed for the isomerization of n-butane into iso-butane at 1 *bar* and 298.15 *K* shown in Figure 4.

Another important characteristic of this graph is that it is indistinguishable from that obtained under the aegis of *PLE*. The reason being that the work lost is, at every step, the same in both of these approaches, and if so, each and every point on the irreversible path produced by the former will be identical to that produced by the latter, as both will be equally displaced from their reversible 'image'. If this weren't so, heat could be converted totally into work through the expedient of using the higher work production path for the forward reaction, and the lesser work consuming path for the inverse reaction. At the end of this cycle the *only* changes left will be the disappearance of a certain amount of heat, and the appearance of an equivalent amount of work, in contradiction with the Kelvin-Planck statement of the second law (Klotz & Rosenberg, 1986). It is necessary to point out here that two of the essential ideas behind the Postulate of local Equilibrium are the possibility of isolating the system at any given degree of advancement of the process; and the system reaching its equilibrium condition once a certain period of time, the time of relaxation, has gone by. Now, even if not explicitly recognized by *PLE*, the use of a negative catalyst is indispensable in its *modus operandi* when the system being considered is a chemical reaction. In its absence a reaction system will simply continue to evolve and if so, taking into account that the system has been isolated, alongside changes in composition we will find changes in temperature and pressure. In this situation the condition of the system at $t + \delta t$ referred to by Moore in Section I, will have no relation with that of the system at t for the simple reason that the system at one time and another are different systems, each one corresponding to a different value of ξ; with the ξ at $t + \delta t$ most likely being the one corresponding to the chemical equilibrium condition, ξ_{eq}, as it is only here that for such a system the thermodynamic variables will stop changing. Even if both, PLE and the approach here introduced might achieve the goal of thermodynamically characterizing the irreversible path of chemical reactions, one difference remains, the latter

does without recourse of extra-thermodynamic arguments.

The fact that each of the (P_B, ξ) states constituting the irreversible path of the chemical reaction can only come out-work degrading step mediating-after its reversible antecedent has taken place, means that just like the latter, the former will also demand an infinite amount of time for its completion. If this applies to each of these (P_B, ξ) states, it also applies to their concatenation, i.e. to the irreversible path. The fact that within the accepted formalism of classical thermodynamics it is possible to have irreversible processes evolving either trough non-equilibrium paths at finite times, as well as through equilibrium paths in infinite time, proves that neither time nor the nature of the path are neither sufficient nor necessary conditions for the assessment of irreversibility. Actually, the whole of the argument matter of this paper happens to be subsumed by Equation (66) which can be read as follows: *An irreversible universe is equal to its reversible counterpart plus an entropy change*. It is precisely this equation the one calling attention to the only necessary and sufficient criterion for irreversibility: entropy production. If we agree that it is entropy growth what gives direction to irreversible processes then we will have to recognize the similarities between our reading of Equation (66) and the following proposition made by Kestin in 1984 "...that the distinction between reversible and irreversible processes should be dispensed with entirely: the former being a special case of the latter, only lacking direction..." (Garfinkle, 2000). Classical thermodynamics has proved to be, in reference to the problem above addressed, capable of overcoming its supposed limitations without recourse to extra-thermodynamic notions. This realization brings to mind the following statement voiced by a noted thermodynamicist and material scientist "...thermodynamics is very much alive and growing." (Brostow, 1972).

8. A Numerical Example

The values quoted below for the standard heat of reaction and standard entropy change at 298.15 K for the isomerization reaction of *n*-butane ($n - C_4H_{10}$) into *iso*-butane ($iso - C_4H_{10}$)

$$n - C_4H_{10} \ (1\,bar, 298.15K) = iso - C_4H_{10} \ (1\,bar, 298.15\,K) \tag{69}$$
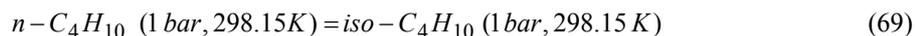
Were calculated from data available in the literature (Stull et al., 1969): $\Delta H^o = -8368\,J\,mol^{-1}$, $\Delta S^o = -15.5\,J\,K^{-1}\,mol^{-1}$. Their combination according to the defining equation of the Gibbs energy produces, in turn, $\Delta G^o = -3752\,J\,mol^{-1}$. When the proper combination of Equations (53) and (55) is substituted in Equation (67) we get the following ξ-explicit expression for $\Delta S_{u,irr}$

$$\Delta S_{u,irr} = -\frac{\xi\,\Delta G^o}{T} - R[(1-\xi)\ln(1-\xi) + \xi\ln\xi] \tag{70}$$

Substitution in the previous equation of the indicated values for ΔG^o, T, alongside $R = 8.3\,J\,K^{-1}\,mol^{-1}$ leads to the following expression

$$\Delta S_{u,irr} = 12.6\,\xi - 8.3[(1-\xi)\ln(1-\xi) + \xi\ln\xi] \ J\,K^{-1} \tag{71}$$

from which the following table was constructed.

Table 1. A number of ordered pairs ($\xi\,mol, \Delta S_{u,irr}\,J\,K^{-1}$) obtained from equation (71) are here shown. The maximum value for $\Delta S_{u,irr}$ is located at an equilibrium conversion of $\xi_{eq} = 0.82$

ξ	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.82	0.9	1.0
$\Delta S_{u,irr}$	0	4.0	6.7	8.8	10.6	12.0	13.1	13.9	14.23	14.24	14.03	12.6

The irreversible path defined by the previous ordered pairs is shown in Figure 4. As previously discussed, an alternative avenue available to gain access to any of the states constituting the said irreversible path is that represented by the concatenation of the reversible path with a work degrading step, as exemplified in Figure 4 for that particular irreversible state characterized by $\xi = 0.6$. As should be clear by now, the difference between this two-step avenue and the one embodied by the actual irreversible path of the reaction boils down to the fact that in the former all the relevant thermodynamic information about the condition of the irreversible universe-the reaction mixture as well as that of its associated reservoirs-at any given ξ is available; a situation not necessarily present along the irreversible path.
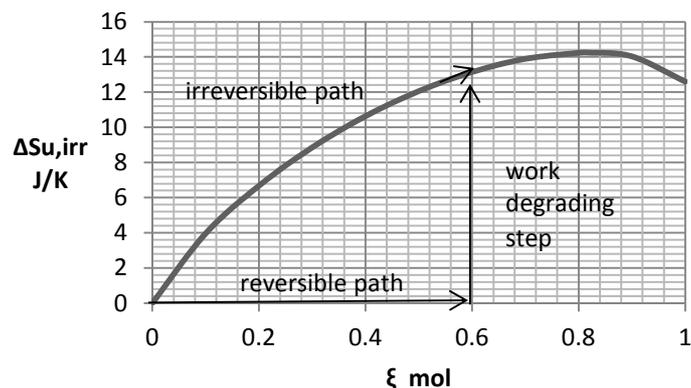
Figure 4. Graphical representation of the numerical data contained in Table 1 for the ideal-gas isomerization of *n*-butane into *iso*-butane

9. Final Comment

The emergence of an infinite-time irreversible path composed by a succession of equilibrium states brings forward a number of conclusions.

1) There is no need to resort to *PLE* in order to apply the analytical tools of classical thermodynamics to the irreversible path.

2) No longer can we depend on the nature of the succession of states, or on time, to assess the irreversibility of a given process.

3) Irreversible processes can be represented as continuous graphs in thermodynamic state space.

4) The only thermodynamic criterion on which irreversibility depends is entropy production.

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