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Research Article

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Interrelationship of differential changes of thermodynamic potentials in a system in which a reaction takes place intending to obtain useful work in isentropic conditions–lectures adapted to sensing learners

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Abstract: The educational content of physical chemistry can be a burden for students who are classified as sensing learners (SL). Therefore, for SL, the lecturer must adapt the educational material reflected in standardizing certain procedures (for example, performing and proving similar expressions–differential changes of thermodynamic potentials) and visualization of abstract concepts and expressions. Here is presented the connection of differential changes of thermodynamic potentials in isentropic conditions with useful work (in the system, there is one exothermic reaction in the quasi-static regime) and with the differential change of internal energy in an adiabatic and isochoric composite system (reactive system + corresponding reservoir) as well as with the differential change of internal energy in the isochoric composite system. When defining an isentropic process (or system), the change in entropy that is a consequence of heat exchange and the change in entropy that is a consequence of a chemical reaction is considered. Differential changes in thermodynamic potentials are also shown schematically, facilitating SL's mastery of the material.

Keywords: curriculum; higher education; reaction entropy; de Donder's affinity; learning styles; thermodynamic potential

1 Introduction

There are several divisions in terms of learning style; one division is sensing learners (SL) and intuitive learnings (IL).[1,2] It is believed that SL students prefer observation, collection of data, like to learn facts, and participate in experiments. SL students prefer standard and well-established methods in solving problems. During their studies, IL students apply indirect perception, prefer principles, innovation, new theories, and dislike similar and repetitive tasks. IL students accept symbols more easily than SL students.[1] Lectures on physical chemistry and thermodynamics are full of symbols (mathematical equations) which favors IL students. However, psychological and statistical analyses show that most chemical engineering students belong to the SL group.[3,4] Therefore, it is desirable to adapt lectures to SL students. Although the material is full of mathematical formulas, proving (i.e., deriving) equations can be simplified by standardizing mathematical derivation (suitable for SL). Research in the psychology of learning

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Correction note: Correction added after online publication on March 24, 2025: In the PDF version, the display of equation (33) has been modified to match its presentation on the website.

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indicates that using visual aids, such as pictures, is effective in helping students understand abstract concepts.[5] Consequently, during lectures in physical chemistry, we focus on illustrating the processes represented by specific equations. The standard approach to learning involves visualizing the processes described by these equations.

The goal is to relate the differential changes in thermodynamic potentials (internal energy, enthalpy, Helmholtz free energy, and Gibbs compact energy) related to a system where one reaction occurs (reactive system), considering different conditions in the reactive system. The desire is for students to have a visual representation of differential changes in thermodynamic potentials and to show that if the goal is to obtain useful work (isentropic conditions) – the portion of a chemical reaction's energy changes that can be converted into work usable for practical purposes, such as electrical work or other forms of energy transfer–then differential changes in thermodynamic potentials are reduced to differential changes in the internal energy of a composite system (a system in which the reaction takes place + the corresponding reservoir) that is adiabatic and isochoric or to a composite system that is only isochoric. An identical approach is used for each thermodynamic potential, standardizing the proof, which is convenient for SL students. The material presented in the discussion is suitable for students who have previously completed the definitions of thermodynamic potentials and partial molar quantities.

2 Discussion

2.1 Differential change in internal energy

Consider a closed reactive system in which only one reaction takes place to obtain useful work (analogously, the supply of energy to perform some reaction can be observed).

In general, the differential change in the internal energy of a closed system (**sy**) – which only exchanges energy with the environment (Figure 1) – can be the result of an infinitesimal change in entropy ($\mathrm{d}S_{\mathrm{sy}}$), which is related to the quasi-static transfer of heat between **sy** and the environment ($\delta q_{\mathrm{sy}} = T\mathrm{d}S_{\mathrm{sy}}$); an infinitesimal change in the volume of the system ($\mathrm{d}V_{\mathrm{sy}}$) – i.e., the quasi-static differential pressure-volume work exchanged between **sy** and the environment ($\delta W_V = -p\mathrm{d}V_{\mathrm{sy}}$); and the infinitesimal change in the amount of the i-th reactive component ($\mathrm{d}n^{\mathrm{i}}_{\mathrm{sy}}$) due to the quasi-static reaction[6] – $\mathrm{d}W_{\mathrm{nonV}} = \sum \mu_{\mathrm{i}} \mathrm{d}n^{\mathrm{i}}_{\mathrm{sy}}$ where W_{nonV} denotes the change in internal energy in **sy** due to of a quasi-static chemical reaction, i.e., it represents useful non-pressure-volume work obtained from the system.[7,8]

$$\mathrm{d}U_{\mathrm{sy}} = T\mathrm{d}S_{\mathrm{sy}} - p\mathrm{d}V_{\mathrm{sy}} + \sum \mu_{\mathrm{i}} \mathrm{d}n^{\mathrm{i}}_{\mathrm{sy}} = T\mathrm{d}S_{\mathrm{sy}} - p\mathrm{d}V_{\mathrm{sy}} - A\mathrm{d}\xi_{\mathrm{sy}} = \delta q_{\mathrm{sy}} + \underbrace{\delta W_{\mathrm{V}} + \mathrm{d}W_{\mathrm{nonV}}}_{\delta W}. \tag{1}$$

In equation (1), T, p, and μ are intensive quantities from the system **sy** and are, respectively, temperature, pressure, and chemical potential–which is defined for each component from the system. In **sy**, the change in the amount (mol) of reactive components that belong to the same reaction can be expressed in one extensive quantity (ξ_{sy}) – the degree of progress of the chemical reaction–extent of the chemical reaction.[9,10] The extensive quantity ξ_{sy} as an intensive quantity corresponds to De Donder's affinity of a chemical reaction (Appendix A).[11,12]

$$A = \sum\nolimits_{\mathrm{reactants}} \nu_{\mathrm{i}} \mu_{\mathrm{i}} - \sum\nolimits_{\mathrm{products}} \nu_{\mathrm{j}} \mu_{\mathrm{i}} \tag{2}$$

ν_{i} denotes the stoichiometric coefficients of the reactive components in the observed reaction ($\sum_{\mathrm{reaction}} \nu_{\mathrm{i}}\mathrm{i} = 0$) from **sy**. Equation (1) is the total differential of internal energy in the system **sy**; therefore, it can be expressed with partial differentials of internal energy:

$$\mathrm{d}U_{\mathrm{sy}} = (\partial U/\partial S)_{V_{\mathrm{sy}}, \xi_{\mathrm{sy}}} \mathrm{d}S_{\mathrm{sy}} + (\partial U/\partial V)_{S_{\mathrm{sy}}, \xi_{\mathrm{sy}}} \mathrm{d}V_{\mathrm{sy}} + (\partial U/\partial \xi)_{S_{\mathrm{sy}}, V_{\mathrm{sy}}} \mathrm{d}\xi_{\mathrm{sy}}. \tag{3}$$

Equations (1) and (3) obtain the definitions of intensive quantities using partial derivatives of internal energy: $(\partial U/\partial S)_{V_{\mathrm{sy}}, \xi_{\mathrm{sy}}} = T$, $(\partial U/\partial V)_{S_{\mathrm{sy}}, \xi_{\mathrm{sy}}} = -p$ and $(\partial U/\partial \xi)_{S_{\mathrm{sy}}, V_{\mathrm{sy}}} = -A$. Using the subscript **sy** for the differential changes of extensive quantities and the partial differentials–especially at the beginning–makes it easier for

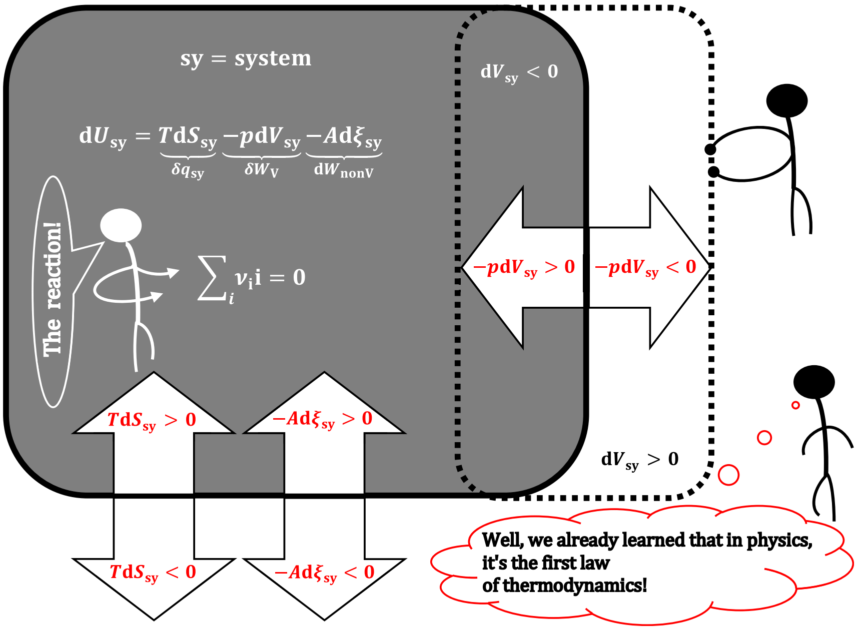

Figure 1: A closed system sy in which a chemical reaction takes place: the differential change in the internal energy of the system.

students to relate the differential changes to physical space (the system where the changes take place) instead of equations (1) and (3) being differential changes of an abstract meaning (Figure 1). Callen[7] to equations (1) and (3) as the fundamental thermodynamic equation in differential form and energy representation. As Kandepudi and Prigogine[11] noted, this equation originally came from Gibbs. Equation (1) illustrates the first law of thermodynamics, which students typically recognize through its definition of the products of intensive quantities and the differential changes of corresponding extensive quantities as infinitesimal heat and work.

According to equation (1), the quasi-static exchange of infinitesimal heat between system **sy** and the environment (δq_{sy}) results in a differential entropy change in **sy** (dS_{sy}):

$$dU^{sy}_{\xi_{sy}V_{sy}} = \delta q_{sy} = TdS_{sy} \rightarrow dS_{sy} = dU^{sy}_{\xi_{sy}V_{sy}}\Big/T. \tag{4}$$

However, there is also a differential change in entropy that is not covered by equations (1) and (3), which is a differential change in entropy due to the infinitesimal progression of the chemical reaction from the system (dS_ξ). So, the total differential change of entropy in **sy** is (Figure 2):

$$dS_T = dS_{sy} + dS_\xi. \tag{5}$$

Suppose in **sy**, i.e., in equations (1) and (3), entropy S_{sy} (entropy related to heat exchange) and volume V_{sy} are constant ($S_{sy}, V_{sy} = const.$). In that case, i.e., the system is rigid (isochoric) and adiabatic (the system does not exchange heat with the environment: $dS_{sy} = 0 \rightarrow TdS_{sy} = \delta q_{sy} = 0$), the differential change of internal energy in system **sy** is:

$$dU^{sy}_{S_{sy}V_{sy}} = -Ad\xi_{sy}. \tag{6}$$

Let reaction $\sum_i \nu_i i = 0$ from **sy** occur quasi-statically and isentropically (approximations for a reversible thermodynamic process),[7,8,13,14] which implies that the differential change of the total entropy in the system is zero ($dS_T = 0$). However, as the reaction proceeds in an adiabatic system ($dS_{sy} = 0$), it follows that under isentropic conditions–according to equation (5) – the equality $dS_\xi = 0$ must also apply (Figure 2). In other words, if equality[5] holds, in **sy** without heat exchange with the environment under the isentropic conditions, the reaction $\sum_i \nu_i i = 0$ does not change the system's entropy. Under isentropic conditions in the case of $dU^{sy}_{S_{sy}V_{sy}} < 0$, the change in $dU^{sy}_{S_{sy}V_{sy}}$ corresponds to the differential (useful) non pressure-volume work (dW_{nonV}) – differential work of a reversible process (δW_{rev}), i.e., the maximum differential work that approaches the value of the differential work of a quasi-static process -

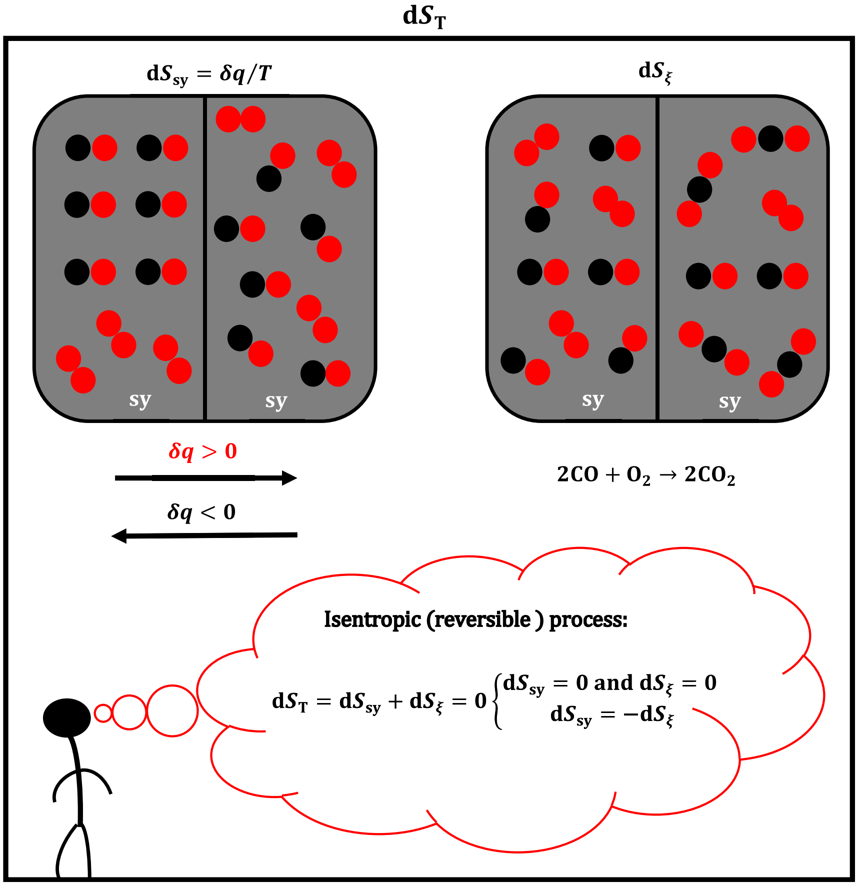

Figure 2: The change in entropy of a system of constant volume is a consequence of the heat exchange between the system (sy) and the environment or the occurrence of a chemical reaction in the system or both processes simultaneously.

$$\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}} = -A\mathrm{d}\xi_{\mathrm{sy}} = \mathrm{d}W_{\mathrm{nonV}} = \delta W_{\mathrm{rev}} \tag{7}$$

that can be obtained from system sy (Figure 3).

During the lecture, usually, a student, after the introduction of equations (6) and (7), asks the following question: what if there is a change in entropy ($\mathrm{d}S_\xi \neq 0$) during the quasi-static reaction $\sum_i \nu_i \mathrm{i} = 0$ in a rigid adiabatic ($\mathrm{d}S_{\mathrm{sy}} = 0$) system? Answer follows from equation (5):

$$0 \neq \mathrm{d}S_{\mathrm{T}} = \mathrm{d}S_{\xi}. \tag{8}$$

Suppose equation (6) is valid, and there is a chemical reaction–a thermodynamic process–in a system with $\mathrm{d}S_\xi \neq 0$. In that case, the thermodynamic process in system **sy** cannot be isentropic or reversible (in a reversible process, the total entropy does not change). Namely, there is no possibility for $\mathrm{d}S_\xi$ compensation due to heat transfer between the system and the environment. However, it should be emphasized to the students that even under conditions $\mathrm{d}S_\xi \neq 0$, if the observed reaction from **sy** is in the quasi-static regime, then equation (6) is still valid, and the same amount of work is obtained as when $\mathrm{d}S_\xi = 0$, i.e., in the quasi-static regime, energy dissipation into heat is negligible. However, due to equality,[8] the reaction generally belongs to an irreversible thermodynamic process in the quasi-static regime. Students from earlier lectures know that if a thermodynamic process is non-isentropic (irreversible), then a smaller amount of useful work is obtained than when the same process is isentropic (reversible), for example, during isothermal irreversible expansion of a system, the environment receives a smaller amount of work in absolute value than during reversible isothermal expansion. This means that if system **sy** in which the reaction $\sum_i \nu_i \mathrm{i} = 0\big| : \mathrm{d}S_\xi \neq 0$ takes place would be isentropic ($\mathrm{d}S_{\mathrm{T}} = 0$), then by absolute value, a higher value of useful work should be obtained than $\left|\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}}\right| = \left|-A\mathrm{d}\xi_{\mathrm{sy}}\right|$. Which is when the isochoric **sy** can quasi-statically exchange heat with the environment. Under these conditions, according to equations (1) and (3), the total differential of internal energy for system **sy** is:

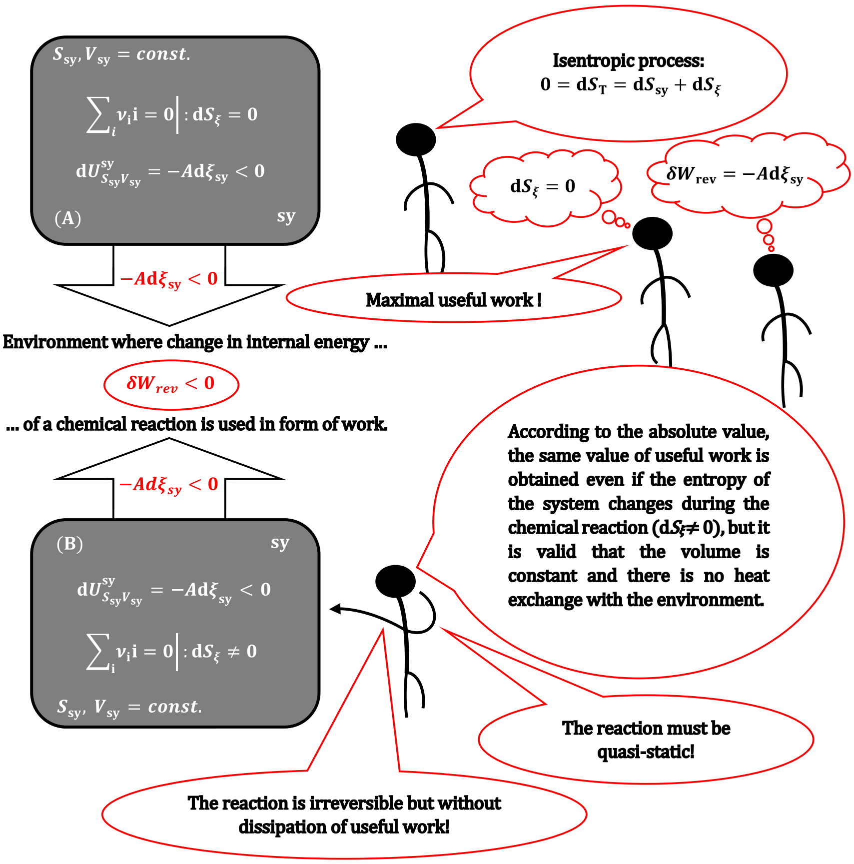

Figure 3: A closed rigid and adiabatic system sy in which a chemical reaction takes place under isentropic conditions (A) and under non-isentropic conditions (B).

$$\mathrm{d}U^{sy}_{V_{sy}} = (\partial U/\partial S)_{S_{sy},\xi_{sy}}\mathrm{d}S_{sy} + (\partial U/\partial \xi)_{S_{sy},V_{sy}}\mathrm{d}\xi_{sy} = T\mathrm{d}S_{sy} - A\mathrm{d}\xi_{sy}. \tag{9}$$

Of course, under isentropic conditions in **sy**, $\mathrm{d}S_{sy} = -\mathrm{d}S_\xi$ applies, so the total differential[9] is:

$$\mathrm{d}U^{sy}_{V_{sy}} = -T\mathrm{d}S_\xi - A\mathrm{d}\xi_{sy}. \tag{10}$$

It follows from equation (10) that if it is $\mathrm{d}S_\xi > 0$, then under isentropic conditions, the inequality holds:

$$\left|\mathrm{d}U^{sy}_{V_{sy}}\right|_{S_T} > \left|\mathrm{d}U^{sy}_{S_{sy}V_{sy}}\right|_{S_T} = \left|\mathrm{d}U^{sy}_{S_{sy}V_{sy}}\right|_{S_{T \neq const.}:\mathrm{quasi-static}} \tag{11}$$

According to the inequality[11] in the case of an isentropic thermodynamic process (chemical reaction) from **sy**, under the conditions $V_{sy} = const.$, a greater amount of useful work is obtained by the absolute value for the quantity $|-T\mathrm{d}S_\xi|$, i.e., for the amount of quasi-static heat required for $\mathrm{d}S_\xi > 0$ compensation, than under adiabatic-isochoric ($S_{sy}, V_{sy} = const.$) conditions (Figure 4).

If the thermodynamic process at $V_{sy} = const.$ conditions in **sy** is not isentropic and quasi-static (reversible), then $T\mathrm{d}S_{sy}$ formally represents the thermal energy supplied to **sy** and represents the energy loss of the useful work $-A\mathrm{d}\xi_{sy}$ (for example, if the useful work from the chemical reaction is used to drive the piston and if friction occurs when the piston moves, then part of $|-A\mathrm{d}\xi_{sy}|$ is lost as frictional thermal energy $|T\mathrm{d}S_{sy}|$, i.e., $-A\mathrm{d}\xi_{sy} < 0$ and $T\mathrm{d}S_{sy} > 0$ are valid, Figure 4).

2.2 Differential change of enthalpy

In general, from the function of internal energy ($U = f(S,V,\xi) \equiv U(S,V,\xi)$), enthalpy ($H$) is defined by a partial Legendre transformation[7,14–16] – in the state function U, the independent variable (extensive quantity) V is replaced by the intensive quantity pressure p (whose values are easily monitored by manometer):

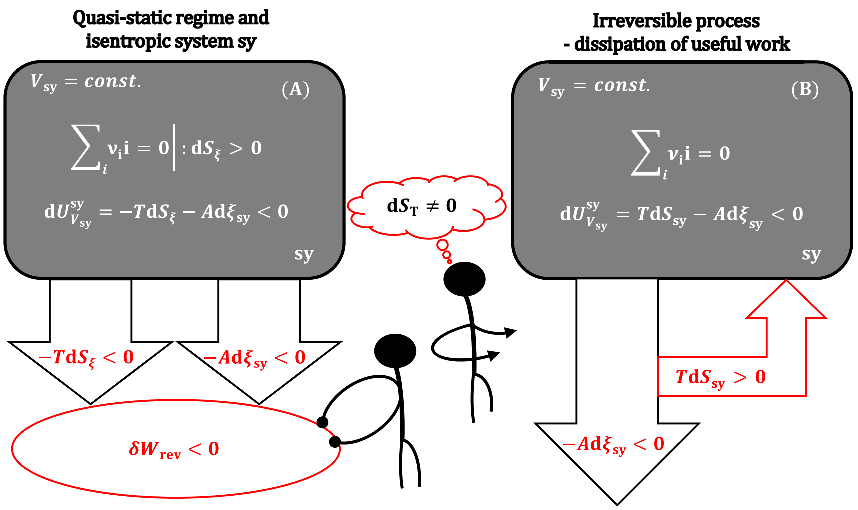

Figure 4: An isochoric system that is isentropic (A) or not isentropic (B).

$$H \equiv U[p] = U(S,V,\xi) + pV \rightarrow H = f(S,p,\xi) \equiv H(S,p,\xi). \tag{12}$$

Differentiation of equation (12) leads to the following expression:

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p. \tag{13}$$

If equation (13) refers to the system **sy** from Figure 1 ($\mathrm{d}H = \mathrm{d}U_{\mathrm{sy}} + p\mathrm{d}V_{\mathrm{sy}} + V\mathrm{d}p_{\mathrm{sy}}$), then by introducing the total differential of internal energy[1] we get:

$$\mathrm{d}H = T\mathrm{d}S_{\mathrm{sy}} - p\mathrm{d}V_{\mathrm{sy}} - A\mathrm{d}\xi_{\mathrm{sy}} + p\mathrm{d}V_{\mathrm{sy}} + V\mathrm{d}p_{\mathrm{sy}}, \tag{13a}$$

$$\mathrm{d}H = T\mathrm{d}S_{\mathrm{sy}} + V\mathrm{d}p_{\mathrm{sy}} - A\mathrm{d}\xi_{\mathrm{sy}}. \tag{14}$$

However, with equation (14), usually a student guesses: professor, you left out the subscript “sy” for the symbol H. Then the professor says: let us wait a while longer; let the subscript be a mystery:

$$\mathrm{d}H_? = T\mathrm{d}S_{\mathrm{sy}} + V\mathrm{d}p_{\mathrm{sy}} - A\mathrm{d}\xi_{\mathrm{sy}}. \tag{14a}$$

In equation (14), the term $T\mathrm{d}S_{\mathrm{sy}}$ comes from equation (1) and, therefore, represents the exchanged heat between isochoric **sy** and the environment: $\delta q^{\mathrm{sy}}_{V_{\mathrm{sy}}} = (\partial U/\partial S)_{V_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}}$. However, since equation (14) is the total differential of enthalpy, the following expression applies to $T\mathrm{d}S_{\mathrm{sy}}$: $\delta q^{\mathrm{sy+surrounding\ with\ }p=const.}_{p_{\mathrm{sy}}} = (\partial H/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}}$. Therefore, the term $T\mathrm{d}S_{\mathrm{sy}}$ simultaneously corresponds to the exchanged heat between **sy** and the heat source both at a constant volume of **sy** (V_{sy}) and at a constant pressure in **sy** (p_{sy}):

$$T\mathrm{d}S_{\mathrm{sy}} = \delta q^{\mathrm{sy}}_{V_{\mathrm{sy}}} = \delta q^{\mathrm{sy+surrounding\ \ with\ \ }p=const.}_{p_{\mathrm{sy}}} = (\partial U/\partial S)_{V_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}} = (\partial H/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}}, \tag{15}$$

$$T\mathrm{d}S_{\mathrm{sy}} = \Big(\partial(U + pV/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}} = (\partial U/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}} + p(\partial V/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}}. \tag{16}$$

Based on equation (15), it can be noted that during the heating of isochoric **sy**, the total supplied thermal energy is spent on increasing the internal energy of the system, while when heating isobaric **sy**, a part of the heat is spent on pressure-volume work ($p(\partial V/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}}$) and the remaining part of the heat increases the internal energy of the system ($(\partial U/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}}$). By introducing the total differential of the internal energy function $U(T,V)$: $\mathrm{d}U_{\mathrm{sy}} = C^{\mathrm{sy}}_V\mathrm{d}T + \pi^{\mathrm{sy}}_T\mathrm{d}V$ (C^{sy}_V = heat capacity of the system at constant volume and π^{sy}_T = internal pressure in the system) into the partial derivative $(\partial U/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}$, equation (16) changes to the form (Appendix B):

$$T\mathrm{d}S_{\mathrm{sy}} = \underbrace{C^{\mathrm{sy}}_V\mathrm{d}T + \pi^{\mathrm{sy}}_T V\alpha^{\mathrm{sy}}_T\mathrm{d}T}_{\text{part of heat which stay in sy}} + \overbrace{p(\partial V/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}}}^{\text{part of the heat }(\text{as }pV\text{ work})\text{ that escapes to the surroundings}} \tag{16a}$$

From the above equation ($\alpha_T^{\mathrm{sy}} = (1/V)(\partial V/\partial T)_p$ is isobaric expansivity), it can be seen that part of the heat at the constant pressure system (**sy**), which is not spent on pressure-volume work, remains in the system in the form of the kinetic energy of particles ($C_V^{\mathrm{sy}}\mathrm{d}T$) and the form of the potential energy of intermolecular interactions ($\pi_T^{\mathrm{sy}} V \alpha_T^{\mathrm{sy}} \mathrm{d}T = \pi_T^{\mathrm{sy}} \mathrm{d}V$). If the same amount of heat is supplied at the constant volume system, then the total amount of heat is spent on the kinetic energy of the particles. At the same time, the potential energy of intermolecular interactions does not change since the system's volume does not change ($\pi_T^{\mathrm{sy}} V \alpha_T^{\mathrm{sy}} \mathrm{d}T = \pi_T^{\mathrm{sy}} \mathrm{d}V = 0$). Considering equation (16) $\delta q_{p_{\mathrm{sy}}}^{\mathrm{sy+surrounding\,with}\,p=const.} \equiv \delta q_{p_{\mathrm{sy}}}^{\mathrm{sy}}$, expression[14] for the isobaric condition is often written in the form $\mathrm{d}H_{p_{\mathrm{sy}}} = \delta q_{p_{\mathrm{sy}}}^{\mathrm{sy}} + \delta W_{p_{\mathrm{sy}}}^{\mathrm{sy}}$, where $\delta W_{p_{\mathrm{sy}}}^{\mathrm{sy}}$ represents the useful work (non-expansion work) obtained from the reaction (i.e., the maximum work under isobaric and reversible conditions), or the minimum work required for some non-spontaneous reaction to take place–for example, the electrolysis of water.[17–19] Of course, under isentropic conditions in the quasi-static regime of the thermodynamic process, i.e., in the case of an infinitely slow reaction, the equalities apply: $\delta q_{p_{\mathrm{sy}}}^{\mathrm{sy}} = T\mathrm{d}S_{\mathrm{sy}}$ and $\delta W_{p_{\mathrm{sy}}}^{\mathrm{sy}} = -A\mathrm{d}\xi_{\mathrm{sy}}$.

If the pressure in **sy** is constant and if **sy** does not exchange heat with the environment (**sy** is adiabatic), then equation (14) is:

$$\mathrm{d}H_{S_{\mathrm{sy}}p_{\mathrm{sy}}}^{?} = -A\mathrm{d}\xi_{\mathrm{sy}}. \tag{17}$$

However, as -$A\mathrm{d}\xi_{\mathrm{sy}}$ derives from the expression for the total differential of internal energy [1], then the following applies:

$$\mathrm{d}H_{S_{\mathrm{sy}}p_{\mathrm{sy}}}^{?} = -A\mathrm{d}\xi_{\mathrm{sy}} = (\partial H/\partial\xi)_{S_{\mathrm{sy}},p_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = (\partial U/\partial\xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = \mathrm{d}U_{S_{\mathrm{sy}}V_{\mathrm{sy}}}^{\mathrm{sy}} \tag{18}$$

In order to understand equation (18) in more detail, it is necessary to return to the differential change in enthalpy from equation (13a) under adiabatic conditions and constant pressure of the system:

$$\mathrm{d}H_{S_{\mathrm{sy}}p_{\mathrm{sy}}}^{?} = -p\mathrm{d}V_{\mathrm{sy}} - A\mathrm{d}\xi_{\mathrm{sy}} + p\mathrm{d}V_{\mathrm{sy}} \tag{19}$$

If in expression,[19] the two terms for pressure-volume work are not shortened, then it can be seen that the first and second terms (-$p\mathrm{d}V_{\mathrm{sy}}$-$A\mathrm{d}\xi_{\mathrm{sy}}$) refer to the differential change of internal energy in **sy**, while the last term–as in absolute value is equal to the first term, but has the opposite sign–it represents pressure-volume work in the environment (i.e., the first term represents the work of the system on the environment, while the last term in equation (19) is the work of the environment on the system). Furthermore, the environment can only change volume at the expense of the system volume $\mathrm{d}V_{\mathrm{sy}} = -\mathrm{d}V_{\mathrm{surrounding}}$; the environment and system **sy** have a constant total volume ($V_{\mathrm{sy}}+V_{\mathrm{surrounding}} = const.$). In a quasi-static change of the state of the system, in order for the system and the environment to be in mechanical equilibrium in each infinitesimal step (volume change), the pressures in **sy** and the environment must be equal, which is possible if the volume of the environment is multiple (infinitely) more significant than the volume of **sy** ($V_{\mathrm{surrounding}} \gg V_{\mathrm{sy}}$). In this way, the change in volume in the environment does not affect the pressure of the environment; therefore, the environment behaves as a reservoir of constant pressure. The **R** symbol will be used as a subscript for physical quantities related to the reservoir ($\mathrm{d}V_{\mathrm{sy}} = -\mathrm{d}V_{\mathrm{R}}$). The last term in equation (19), according to the total differential of internal energy,[1] represents the differential change in the internal energy of the reservoir when its composition does not change (there is no exchange of particles with **sy** and with the environment of the total system (i.e., composite system: **sy** + **R** ≡ **Csy**); also **R** is not a reactive system, i.e., no chemical reaction takes place in **R**). According to equation (19), **R** does not exchange heat with the system or with the environment of **Csy**, which means that **R** is an adiabatic system. Therefore, equation (19) is:

$$\mathrm{d}H_{S_{\mathrm{sy}}p_{\mathrm{sy}}}^{?} = \underbrace{-p\mathrm{d}V_{\mathrm{sy}} - A\mathrm{d}\xi_{\mathrm{sy}}}_{\text{system}} \overbrace{-p\mathrm{d}V_{\mathrm{R}}}^{\text{reservoir}} = \underbrace{-p\mathrm{d}V_{\mathrm{sy}} + \mathrm{d}U_{S_{\mathrm{sy}}V_{\mathrm{sy}}}^{\mathrm{sy}}}_{\text{system}} \overbrace{-p\mathrm{d}V_{\mathrm{R}}}^{\text{reservoir}} = \mathrm{d}U_{S_{\mathrm{sy}}}^{\mathrm{sy}} + \mathrm{d}U_{S_{\mathrm{R}}\xi_{\mathrm{R}}}^{\mathrm{R}} = \mathrm{d}U_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}}^{\mathrm{Csy}}. \tag{20}$$

Therefore, $\mathrm{d}H_{S_{\mathrm{sy}}p_{\mathrm{sy}}}^{?}$ represents the differential change in internal energy in both **sy** and **R**, i.e., it defines the differential change of internal energy in the entire composite system (**sy** + **R** ≡ **Csy**), which is adiabatic (isentropic)

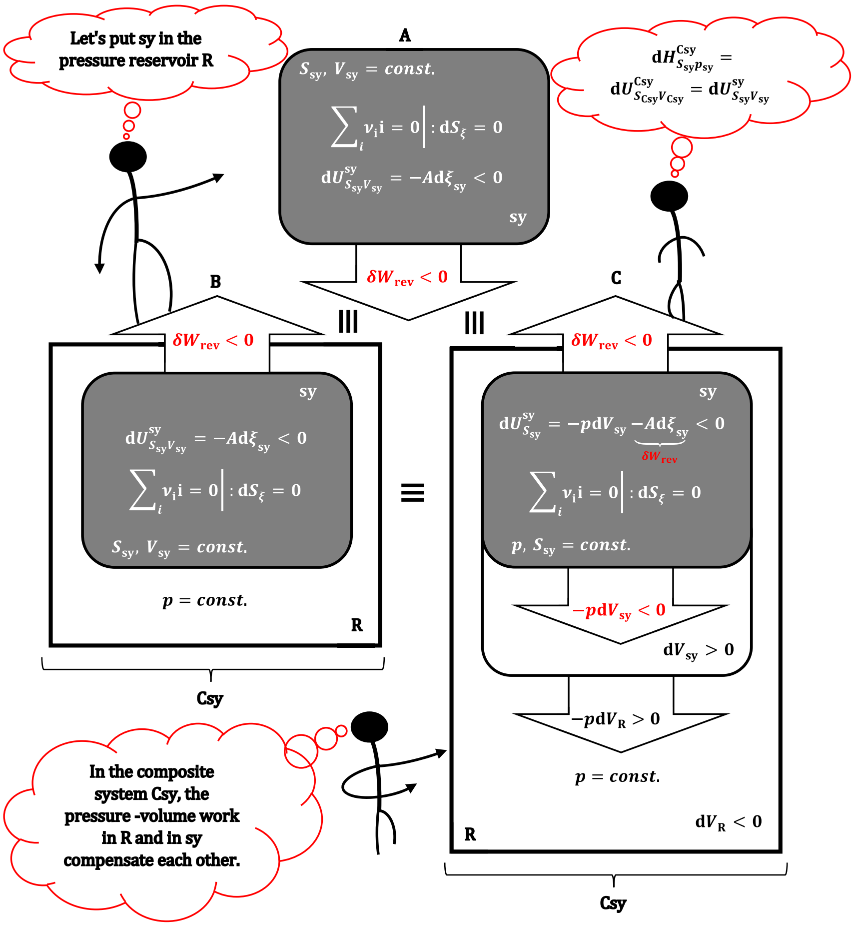

Figure 5: An isochoric adiabatic system (A) is placed in reservoir **R** that provides a constant pressure in sy; formally, first the chemical reaction takes place in the adiabatic and isochoric sy (B) and only then the adiabatic volume changes in sy (system expansion, C) and **R** (reservoir compression, C).

and isochoric (Figure 5). Therefore, instead of the question mark symbol in $\mathrm{d}H^{?}_{S_{sy}p_{sy}}$, the composite system symbol follows:

$$\mathrm{d}H^{Csy}_{S_{sy}p_{sy}} = \mathrm{d}U^{Csy}_{S_{Csy}V_{Csy}}. \tag{21}$$

It is important to emphasize that enthalpy as a function $H(S_{sy}, p_{sy}, \xi_{sy})$ depends exclusively on the parameters of system **sy**. In contrast, the differential enthalpy change (and the finite change) refers to the sum of the system and the pressure reservoir, i.e., to the composite system. Of course, when students learn the properties of enthalpy, in the course of further lectures, superscripts and subscripts for the symbol H are omitted (this also applies to other thermodynamic potentials). Considering, equation (18) the above equality is:

$$\mathrm{d}H^{Csy}_{S_{sy}p_{sy}} = \mathrm{d}U^{Csy}_{S_{Csy}V_{Csy}} = \mathrm{d}U^{sy}_{S_{sy}V_{sy}}; \tag{22}$$

moreover, it has the following equality: $(\partial H/\partial \xi)_{S_{sy},p_{sy}} = (\partial U/\partial \xi)_{S_{sy},V_{sy}}$. Equations (17)–(22) refer to the adiabatic system ($\mathrm{d}S_{sy} = 0$); therefore, for the chemical reaction in system **sy** to be an isentropic thermodynamic process ($\mathrm{d}S_T = 0$), the system's entropy must not change during the progress of the reaction ($\mathrm{d}S_\xi = 0$). It follows that the observed reaction from the system is reversible (i.e., an infinitely slow quasi-static process), which means that in the case of an exothermic reaction ($\mathrm{d}U^{sy}_{S_{sy}V_{sy}} < 0$), the differential change in internal energy of **sy** is equal to the useful work ($\mathrm{d}U^{sy}_{S_{sy}V_{sy}} = \delta W_{rev}$) obtained from **sy** (from the chemical reaction). Let the same reaction from the adiabatic isochoric system **sy** (Figure 5A) take place in the adiabatic isobaric system **sy** (which is in contact with the pressure reservoir **R**). If, formally, in the adiabatic isobaric **sy**, the differential advancement of the chemical reaction occurs first ($\mathrm{d}\xi_{sy}>0$) with a constant volume (Figure 5B) – which is allowed by the property of the total differential,[20] then the differential change of internal energy in **sy** is $\mathrm{d}U^{sy}_{S_{sy}V_{sy}}$, and after the $\mathrm{d}\xi_{sy}$ change, the differential change of volume follows (let $\mathrm{d}V_{\mathrm{sy}}>0$, Figure 5C). After these two infinitesimal steps (which actually take place simultaneously), the differential change in internal energy in **sy** is:

$$\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}} = -p\mathrm{d}V_{\mathrm{sy}} + \mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}}. \tag{23}$$

If the differential changes of internal energy and volume are $\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}} < 0$ and $\mathrm{d}V_{\mathrm{sy}}>0$, then $\left|\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}}\right| > \left|\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}}\right|$ is valid according to equation (23). However, although the reduction of the internal energy of the adiabatic isobaric system is more significant compared to the adiabatic isochoric system, the absolute value of the useful work is not greater than that obtained from the adiabatic isochoric system. Namely, the pressure-volume work $-p\mathrm{d}V_{\mathrm{sy}}$ from equation (23) is the differential internal energy that goes from **sy** to **R** (in the case of $\mathrm{d}V_{\mathrm{sy}}>0$). At the same time, $-p\mathrm{d}V_{\mathrm{R}} = p\mathrm{d}V_{\mathrm{sy}}$ is the differential increase in internal energy in **R** so that in the composite system (Figure 4C), the pressure-volume works in **sy** and **R** are mutually compensated,[20] i.e., in the composite system there has been a redistribution of internal energy ($p\mathrm{d}V_{\mathrm{sy}}$) which remains in the composite system. It follows that the differential change of the total internal energy of the composite system **Csy** ($\mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}}$) – which is equal to the differential change of enthalpy in the adiabatic isobaric system ($\mathrm{d}H^{\mathrm{Csy}}_{S_{\mathrm{sy}}p_{\mathrm{sy}}}$) – according to equation (20) is $\mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}} = \mathrm{d}H^{\mathrm{Csy}}_{S_{\mathrm{sy}}p_{\mathrm{sy}}} = \delta W_{\mathrm{rev}} = \mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}}$ and represents the differential useful work obtained from the adiabatic isobaric system (with an isentropic thermodynamic process) which is in the adiabatic **R** of constant pressure and is equal to the change in the internal energy of the reaction from the adiabatic isochoric **sy** (Figure 5).

If the isobaric **sy** is still located in the adiabatic reservoir of constant pressure **R**, but **sy** is no longer adiabatic, then according to equations (14a) and (20) the differential change of enthalpy in **Csy** is:

$$\mathrm{d}H^{\mathrm{Csy}}_{p_{\mathrm{sy}}} = T\mathrm{d}S_{\mathrm{sy}} - A\mathrm{d}\xi_{\mathrm{sy}}, \tag{24}$$

$$\mathrm{d}H^{\mathrm{Csy}}_{p_{\mathrm{sy}}} = \underbrace{T\mathrm{d}S_{\mathrm{sy}} - p\mathrm{d}V_{\mathrm{sy}} - A\mathrm{d}\xi_{\mathrm{sy}}}_{\text{system}} \overbrace{-p\mathrm{d}V_{\mathrm{R}}}^{\text{reservoir}}, \tag{25}$$

of course, as with equation (20), it applies $\mathrm{d}V_{\mathrm{sy}} = -\mathrm{d}V_{\mathrm{R}}$. Let the differential change of entropy be $\mathrm{d}S_{\xi}>0$ during the differential advancement of the reaction from **sy** (during the reaction, **sy** is formally adiabatic and isochoric). If the thermodynamic process from **sy** is isentropic quasi-static ($\mathrm{d}S_{\mathrm{T}} = 0$ – the maximum useful work is obtained), then in each infinitesimal step of the reaction advancement from **sy**, the change in entropy $\mathrm{d}S_{\xi}$ must be compensated with the departure of heat $q = (\partial U/\partial S)_{V_{\mathrm{sy}}\xi_{\mathrm{sy}}} = T\mathrm{d}S_{\mathrm{sy}} < 0$ from **sy** (formally, the reaction takes place first at adiabatic and isochoric conditions in **sy** and then heat exchange follows at isochoric conditions between **sy** and the environment–the environment of the composite system **Csy**, Figure 6). The differential change of internal energy in the system due to these two thermodynamic processes (reaction and heat exchange) is $\mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}} = -T\mathrm{d}S_{\xi} - A\mathrm{d}\xi_{\mathrm{sy}}$, so equation (25) is:

$$\mathrm{d}H^{\mathrm{Csy}}_{p_{\mathrm{sy}}} = \underbrace{\mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}} - p\mathrm{d}V_{\mathrm{sy}}}_{\text{system}} \overbrace{-p\mathrm{d}V_{\mathrm{R}}}^{\text{reservoir}} = \underbrace{\mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}} - p\mathrm{d}V_{\mathrm{sy}}}_{\text{system}} \overbrace{+p\mathrm{d}V_{\mathrm{sy}}}^{\text{reservoir}}. \tag{26}$$

The reaction and heat exchange is followed by a change in the volume of the system and reservoir under formally adiabatic and isobaric conditions. Since the total volume of the composite system (**Csy**) is constant, when the volume of **sy** and **R** changes, the pressure-volume work compensates each other, meaning that equation (26) turns into equality:

$$\mathrm{d}H^{\mathrm{Csy}}_{p_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{T}}V_{\mathrm{Csy}}} = \mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}} = \delta W_{\mathrm{rev}}. \tag{27}$$

As the total entropy change is zero in the isobaric thermodynamic process (27), it follows that the internal energy change of the composite system (enthalpy change at isobaric conditions) is equal to the maximum useful work (δW_{rev}). From equation (27), it can also be concluded that the same amount of work is obtained (at isentropic conditions) when the reaction takes place at isochoric conditions ($\mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}}$) or when the reaction takes place at isobaric conditions ($\mathrm{d}H^{\mathrm{Csy}}_{p_{\mathrm{sy}}}$) (Figure 6).

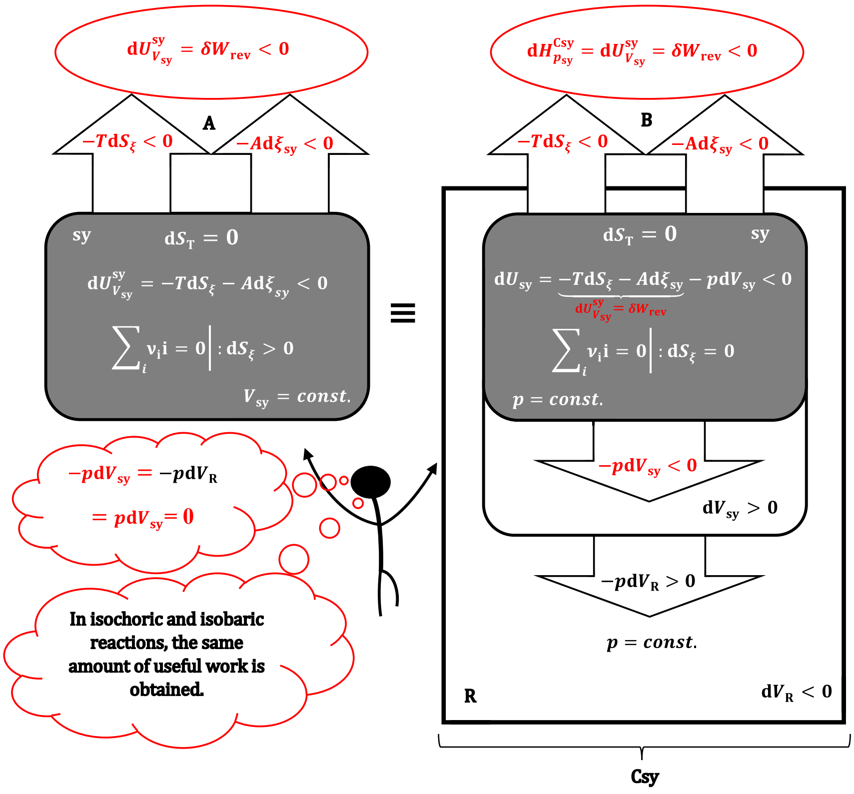

Figure 6: The reaction in the isochoric (A) and isobaric (B) system sy, the isobaric system and the reservoir R form the composite system **Csy**.

2.3 Differential change of helmholtz free energy

Legendre's definition of Helmholtz free energy is[7,14–16]

$$F \equiv U[T] = U(S, V, \xi) - TS \tag{28}$$

Therefore, the Helmholtz free energy is a function $F = f(T,V,\xi) \equiv F(T,V,\xi)$. By differentiating equation (28) and introducing the total differential of internal energy related to system **sy**, the following equation is obtained:

$$dF = TdS_{sy} - pdV_{sy} - Ad\xi_{sy} - TdS_{sy} - SdT_{sy}, \tag{29}$$

and if the volume and temperature in **sy** are constant, i.e., isochoric and isothermal **sy** is observed, then it is:

$$\begin{aligned} dF &= \underbrace{TdS_{sy} - Ad\xi_{sy}}_{\text{system}} - \overbrace{TdS_{sy}}^{\text{reservoir}} = \underbrace{TdS_{sy} + dU^{sy}_{S_{sy}V_{sy}}}_{\text{system}} - \overbrace{TdS_{sy}}^{\text{reservoir}} = -Ad\xi_{sy} = dU^{sy}_{S_{sy}V_{sy}} \\ &= (\partial F/\partial \xi)_{T_{sy},V_{sy}} d\xi_{sy} = (\partial U/\partial \xi)_{S_{sy},V_{sy}} d\xi_{sy}. \end{aligned} \tag{30}$$

Equation (30) corresponds to a chemical reaction during which the entropy of **sy** does not change ($dS_\xi = 0$). Similar to equation (20), in equation (30), the first and second terms refer to the differential change of internal energy in the isochoric system **sy**: $dU^{sy}_{V_{sy}} = TdS_{sy} - Ad\xi_{sy}$. In each infinitesimal step of the quasi-static thermodynamic process (reaction) accompanied by thermal fluctuation, the differential heat (TdS_{sy}) is exchanged with the thermoreservoir (**R**), which is isothermal, isochoric, and non-reactive. If **R** exchanges heat exclusively with **sy**, then heat compensation ($-TdS_{sy} = TdS_R$) occurs in the composite system **(Csy** = **sy** + **R**), and **Csy** remains an isentropic system. Therefore, the last term in equation (30) is the differential change in the internal energy of the thermoreservoir. So, according to equation (30), dF is equal to the differential change of internal energy in the composite system **Csy** under isothermal and isochoric conditions:

$$\mathrm{d}F^{\mathrm{Csy}}_{T_{\mathrm{sy}},V_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}} + \mathrm{d}U^{\mathrm{R}}_{V_{\mathrm{R}}\xi_{\mathrm{R}}} = \mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}}. \tag{31}$$

Considering equations (18) and (30), the equality follows:

$$\delta W_{\mathrm{rev}} = (\partial H/\partial\xi)_{S_{\mathrm{sy}},p_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = (\partial U/\partial\xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = (\partial F/\partial\xi)_{T_{\mathrm{sy}},V_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = \mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}}, \tag{32}$$

or

$$-A = (\partial H/\partial\xi)_{S_{\mathrm{sy}},p_{\mathrm{sy}}} = (\partial U/\partial\xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}} = (\partial F/\partial\xi)_{T_{\mathrm{sy}},V_{\mathrm{sy}}}. \tag{32a}$$

Equation (32) can be interpreted in two ways. Indeed, during the progression of the exothermic reaction (if the goal is to obtain useful work) from **sy**, the entropy of the isochoric and adiabatic system does not change ($\mathrm{d}S_\xi$=0). In each infinitesimal step of the reaction progress, differential useful work is obtained $\delta W_{\mathrm{rev}} = (\partial U/\partial\xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}}$, which is also obtained if **sy** is in contact with the thermoreservoir or reservoir for pressure–the composite system as the entire system (**sy** + **R**) is adiabatic and isochoric. Internal energy equivalent to an infinitesimal amount of heat or infinitesimal pressure-volume work is differently distributed within the composite system. Another interpretation of equality (32) is that during the progress of the reaction, not only does the entropy of **sy** not change, but neither does the volume change nor does it exchange heat with **R**, i.e., **sy** has constant temperature, pressure, and volume.

A reaction whose progress results in a change in the entropy of the system ($\mathrm{d}S_\xi \neq 0$). If, for example, an exothermic reaction occurs in an isothermal and isochoric system, then in some infinitesimal step of the quasi-static reaction progress $-A\mathrm{d}\xi_{\mathrm{sy}} = \mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}} < 0$ is valid, whereby each differential step of the reaction progress can be formally considered to take place in an isochoric and adiabatic system (Figure 7A), the environment of **Csy** (the global environment) from system **sy** receives the differential change in the internal energy of the reaction $\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}}$ (in the case of an isentropic reaction, the equality $\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}} = \delta W_{\mathrm{rev}}$ applies). If during the progress of the reaction

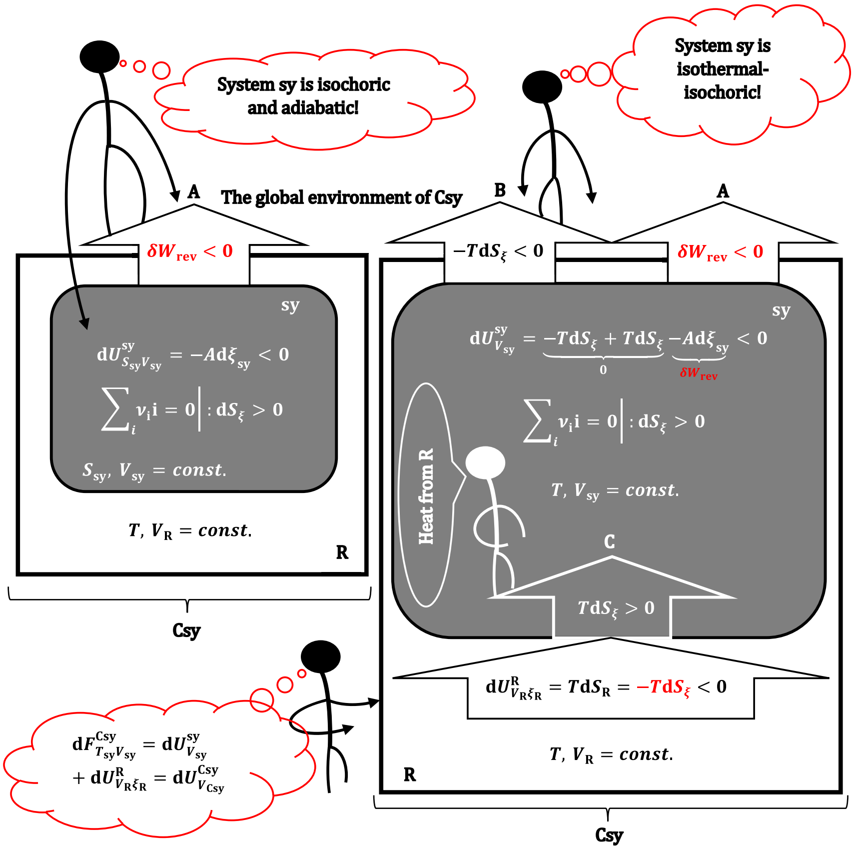

Figure 7: A formal illustration of the differential change in Helmholtz free energy: first, under adiabatic and isochoric conditions, the chemical reaction (A) progresses infinitely, and the entropy of the system increases infinitely, which is then compensated by the departure of differential heat (in the form of useful work) from sy to the global environment at isothermal and isochoric conditions (B), the lost heat from sy is compensated from the thermoreservoir (C).

is $\mathrm{d}S_\xi$>0 and if the quasi-static thermodynamic process in **sy** is isentropic ($\mathrm{d}S_\mathrm{T}$ = 0), then according to equation (5), the equality $\mathrm{d}S_\mathrm{sy}$ = -$\mathrm{d}S_\xi$ is valid, so that equation (30) is:

$$\mathrm{d}F^{\mathrm{Csy}}_{T_\mathrm{sy}V_\mathrm{sy}} = \underbrace{\overbrace{-T\mathrm{d}S_\xi}^{(\text{leav sy to sur. of Csy})} \quad \overbrace{+T\mathrm{d}S_\xi}^{(\text{enter to sy from R})} \quad -A\mathrm{d}\xi_\mathrm{sy}}_{\text{system}} \overbrace{-T\mathrm{d}S_\xi}^{\text{leav R to sy}}. \tag{33}$$

Namely, in equation (30), $T\mathrm{d}S_\mathrm{sy} = \sum \delta q$ can represents the exchanged heat between **sy** and other compartments of the global environment, which means that the first term in equation (33) represents the heat leaving the isochoric and isothermal **sy** (after the infinitesimal progress of the reaction in a formally adiabatic and isochoric system, Figure 7A) to compensate for the infinitesimal increase in entropy ($\mathrm{d}S_\xi$>0) during the progress of the reaction (Figure 7B). However, since **sy** is isothermal, heat $T\mathrm{d}S_\xi$ enters the system from the thermoreservoir (Figure 7C). At the same time, the same amount of heat leaves **R** (-$T\mathrm{d}S_\xi$) so that the heat that compensates for the entropy of the reaction from **sy** comes from the thermoreservoir. It follows that equation (33) is equal to equation (10), i.e., the differential change $\mathrm{d}F^{\mathrm{Csy}}_{T_\mathrm{sy}V_\mathrm{sy}}$ is equal to the differential change in the internal energy of the isochoric system:

$$\mathrm{d}F^{\mathrm{Csy}}_{T_\mathrm{sy}V_\mathrm{sy}} = -T\mathrm{d}S_\xi - A\mathrm{d}\xi_\mathrm{sy} = \mathrm{d}U^{\mathrm{sy}}_{V_\mathrm{sy}} = \delta W_\mathrm{rev} = \mathrm{d}U^{\mathrm{Csy}}_{V_\mathrm{Csy}}\Big| : \mathrm{d}S_\mathrm{T} = 0. \tag{33a}$$

Based on equation (33a), it can be concluded that if $\mathrm{d}S_\xi$ is > 0 in the observed reaction from **sy**, then in each infinitesimal step of the reaction progress, a higher differential useful work is obtained in absolute value than the differential change in internal energy of formally adiabatic and isochoric systems (due to differential progress reactions). On the contrary, if $\mathrm{d}S_\xi$ < 0, the differential useful work is smaller in absolute value than -$A\mathrm{d}\xi_\mathrm{sy}$ since part of -$A\mathrm{d}\xi_\mathrm{sy}$ goes to **R** as heat to compensate for the decrease in reaction entropy in system **sy**.[21] If expressions (10) and (24)–(27) are compared with expression (33a), then the equality follows:

$$\delta W_\mathrm{rev} = \mathrm{d}F^{\mathrm{Csy}}_{T_\mathrm{sy}V_\mathrm{sy}} = \mathrm{d}H^{\mathrm{Csy}}_{p_\mathrm{sy}} = \mathrm{d}U^{\mathrm{sy}}_{V_\mathrm{sy}} = \mathrm{d}U^{\mathrm{Csy}}_{V_\mathrm{Csy}}\Big| : \mathrm{d}S_\mathrm{T} = 0. \tag{34}$$

Namely, if **sy** is in contact with the corresponding reservoir, then the exchanged energy (heat or pressure-volume work) between the system and the reservoir is mutually compensated, i.e., the net effect is to move some of the internal energy from one part of the composite system to another part. In each infinitesimal step of the progress of the reaction, regardless of the presence of **R**, the system **sy** from the composite system behaves as an isochoric system without **R** and with an infinitesimal change in internal energy: $\mathrm{d}U^{\mathrm{sy}}_{V_\mathrm{sy}} = -T\mathrm{d}S_\xi - A\mathrm{d}\xi_\mathrm{sy}$. This change in $\mathrm{d}U^{\mathrm{sy}}_{V_\mathrm{sy}}$ in the global environment **Csy** represents the differential useful work.

2.4 Differential change of gibbs free energy

The definition of the Gibbs free energy from the internal energy $U(S,V,\xi)$ based on the Legendre transformation is[7,14–16]

$$G \equiv U[T,p] = U(S,V,\xi) + pV - TS, \tag{35}$$

which means that G is a function: $G = f(T,p,\xi) \equiv G(T,p,\xi)$. We arrive at the expression (36) by differentiating equation (35) and introducing the total differential of the internal energy related to the system **sy** where one reaction occurs:

$$\mathrm{d}G = T\mathrm{d}S_\mathrm{sy} - p\mathrm{d}V_\mathrm{sy} - A\mathrm{d}\xi_\mathrm{sy} - T\mathrm{d}S_\mathrm{sy} - S\mathrm{d}T_\mathrm{sy} + p\mathrm{d}V_\mathrm{sy} + V\mathrm{d}p_\mathrm{sy}, \tag{36}$$

If **sy** is isotherm and isobar, then the above equation is:

$$\begin{aligned}\mathrm{d}G^{\mathrm{Csy}}_{p_\mathrm{sy}T_\mathrm{sy}} &= \underbrace{T\mathrm{d}S_\mathrm{sy} - p\mathrm{d}V_\mathrm{sy} - A\mathrm{d}\xi_\mathrm{sy}}_{\text{system}} \overbrace{-T\mathrm{d}S_\mathrm{sy} + p\mathrm{d}V_\mathrm{sy}}^{\text{reservoir}} = -A\mathrm{d}\xi_\mathrm{sy} \\ &= (\partial G/\partial \xi)_{T_\mathrm{sy},p_\mathrm{sy}}\mathrm{d}\xi_\mathrm{sy} = \mathrm{d}U^{\mathrm{sy}}_{S_\mathrm{sy}V_\mathrm{sy}} = \mathrm{d}U_\mathrm{sy} + \mathrm{d}U^{\mathrm{R}}_{\xi_\mathrm{R}} = \mathrm{d}U^{\mathrm{Csy}}_{S_\mathrm{Csy}V_\mathrm{Csy}}.\end{aligned} \tag{37}$$

In equation (37), the first three terms represent the differential internal energy change in **sy**. As the H and F functions (thermodynamic potentials) show, appropriate reservoirs of intensive state quantities were required to maintain the system's constant pressure and temperature. Similarly, with the thermodynamic potential G, a p, T-reservoir (**R**) is needed to maintain the constant temperature and pressure in **sy**. The last two terms in equation (37) correspond to the differential internal energy change in **R**. Since the first term ($T\mathrm{d}S_{\mathrm{sy}}$) and the fourth term ($-T\mathrm{d}S_{\mathrm{sy}}$) in equation (37) are equal in absolute value, it means that **R** exchanges heat exclusively with **sy** (analogously, **sy** can exchange heat exclusively with **R**). Similarly, the second term ($-p\mathrm{d}V_{\mathrm{sy}}$) and the last term ($p\mathrm{d}V_{\mathrm{sy}}$) in absolute value are equal to each other and represent the pressure-volume work exchanged between **sy** and **R**. It can be concluded that the differential change of Gibbs free energy (37) under isothermal and isobaric conditions represents a differential change of internal energy in the composite system **Csy** = **sy** + **R** ($\mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}}$). Suppose the composite system **Csy** is adiabatic and isochoric. In that case, it follows that the entropy change of the system (**sy**) during the reaction progress is zero–so that the thermodynamic process as a whole would be isentropic–and the differential change in the internal energy of **Csy**, according to equation (37), is equal to the change in the internal energy of the system (**sy**) itself ($\mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}} = \mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}}$). Energy fluctuations, i.e., thermal and pV fluctuation between **sy** and **R**, compensate for each other (if they exist). Therefore, the differential change $\mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}}$ equals the differential change in internal energy of a formally adiabatic and isochoric system. Suppose a change in the volume of **sy** and thermal fluctuation does not accompany the progress of the reaction from **sy**. In that case, the isobaric-isothermal system is also isochoric-adiabatic (Figure 8). Considering the expression (37) and equality (32), it follows the expansion of equality (32) with the term related to the Gibbs free energy:

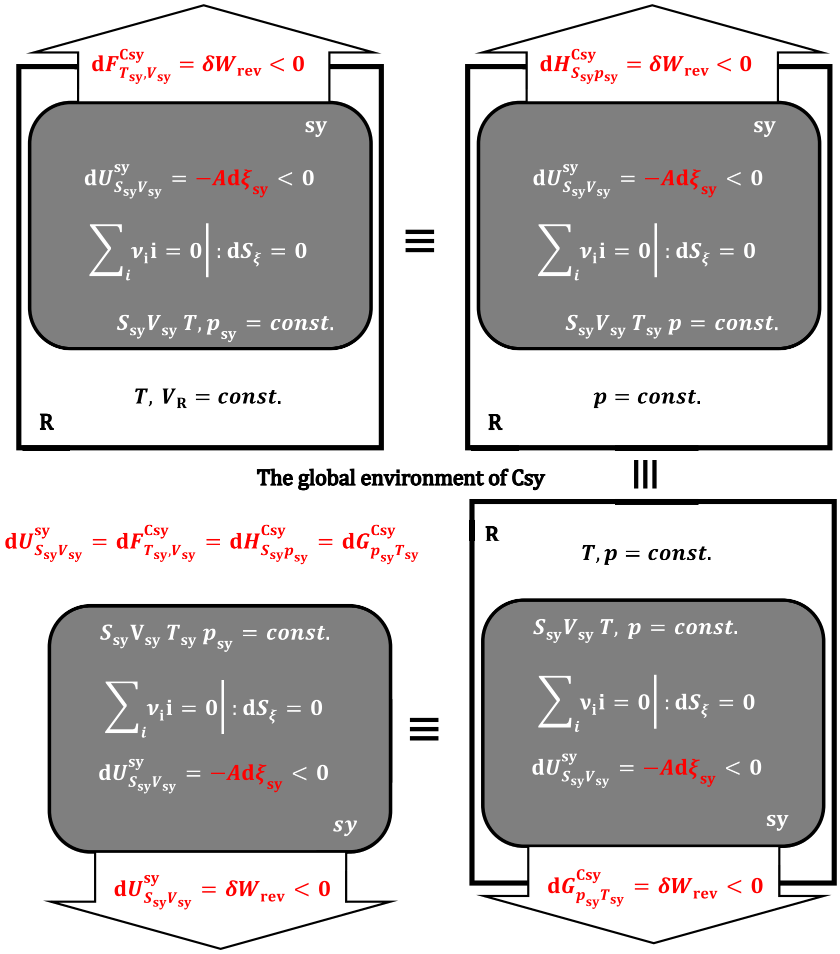

Figure 8: Suppose the reaction progress from sy is not accompanied by a change in the system's volume and a thermal fluctuation with **R**. In that case, every system from the composite system is also an isochoric-adiabatic sy and is equivalent to an isochoric-adiabatic system without **R**.

$$\delta W_{\mathrm{rev}} = (\partial U/\partial\xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = (\partial H/\partial\xi)_{S_{\mathrm{sy}},p_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = (\partial F/\partial\xi)_{T_{\mathrm{sy}},V_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = (\partial G/\partial\xi)_{T_{\mathrm{sy}},p_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = \mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}}, \tag{38}$$

or

$$-A = (\partial U/\partial\xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}} = (\partial H/\partial\xi)_{S_{\mathrm{sy}},p_{\mathrm{sy}}} = (\partial F/\partial\xi)_{T_{\mathrm{sy}},V_{\mathrm{sy}}} = (\partial G/\partial\xi)_{T_{\mathrm{sy}},p_{\mathrm{sy}}}. \tag{38a}$$

Let us now study the system (**sy**) with a *p*,*T*-reservoir when the reaction's progress changes the system's entropy ($\mathrm{d}S_\xi \neq 0$). If, formally, the infinitesimal progression of the exothermic reaction occurs first in a system that is adiabatic and isochoric, then the differential change in internal energy of **sy** is: $\delta W_{\mathrm{rev}} = \mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}} = (\partial U/\partial\xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}}$ (Figure 9A). For example, during the reaction's differential progress, the system's entropy increases infinitesimally ($\mathrm{d}S_\xi > 0$). For the thermodynamic process to be isentropic, differential heat ($-T\mathrm{d}S_\xi$) leaves **sy** to the global environment (in the form of useful work), whereby the reaction entropy in a formally isochoric and isothermal system is compensated (Figure 9B). Since **sy** is an isothermal system, the lost heat is compensated by the input of differential heat from the *p*,*T*-reservoir (Figure 9C). If, during the differential progress of the reaction, the volume of **sy** decreases infinitesimally ($\mathrm{d}V_{\mathrm{sy}} < 0$) under isobaric and isothermal conditions (formally, after the infinitesimal progress of the reaction and the process of infinitesimal heat exchange), then **sy** gains

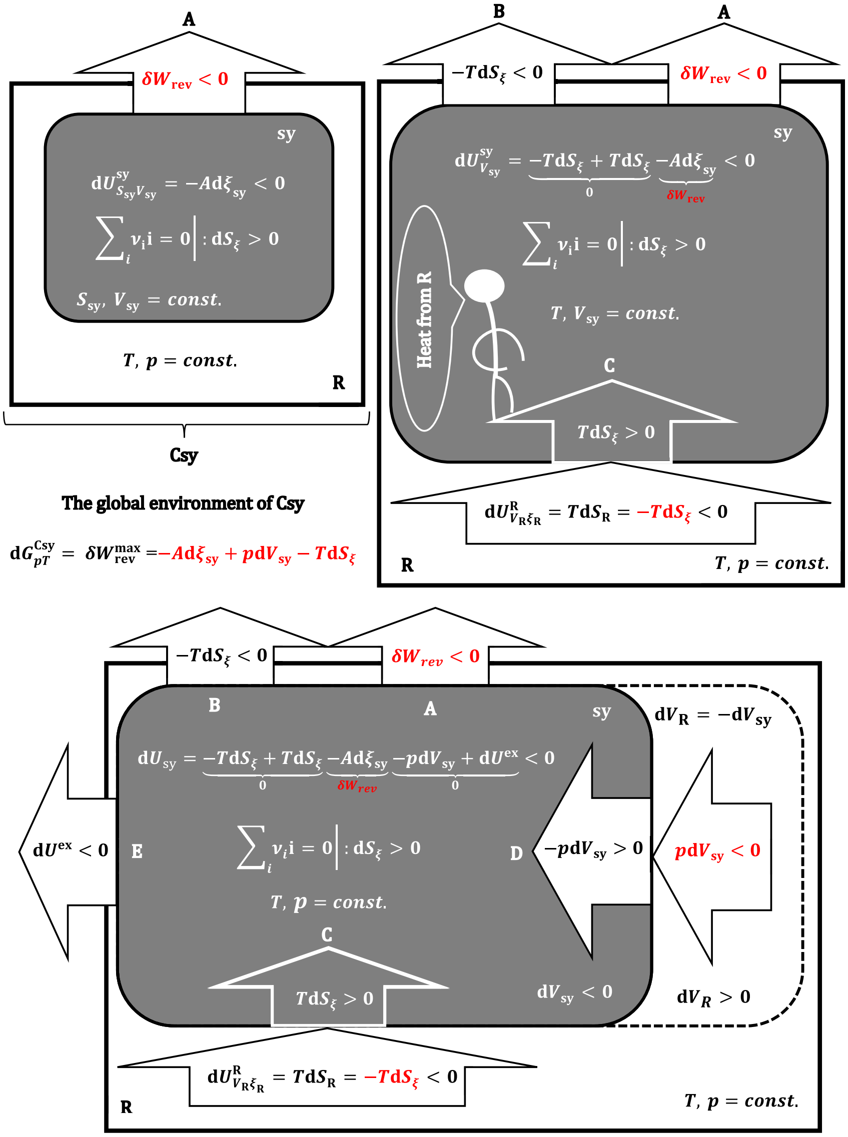

Figure 9: A formal illustration of the differential change in equation (39).

differential energy in the form of pressure-volume work ($-p\mathrm{d}V_{\mathrm{sy}}>0$) from **R** (at the same time, **R** loses differential energy in the form of pressure-volume work ($p\mathrm{d}V_{\mathrm{sy}}<0$); Figure 9D), but as **sy** is isothermal, this differential excess of internal energy ($\mathrm{d}U^{\mathrm{ex}} = p\mathrm{d}V_{\mathrm{sy}}<0$) from **sy** goes to the global environment as useful work (Figure 9E):

$$\mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}} = \underbrace{\underbrace{\overbrace{-T\mathrm{d}S_{\xi}}^{(\text{leav sy to surr. of Csy})}\quad\overbrace{+T\mathrm{d}S_{\xi}}^{(\text{enter to sy from R})}}_{0}\;\underbrace{\overbrace{-p\mathrm{d}V_{\mathrm{sy}}}^{(\text{enter to sy from R})}\;+\;\overbrace{(\mathrm{d}U^{\mathrm{ex}} = p\mathrm{d}V_{\mathrm{sy}})}^{(\text{leav sy to surr. of Csy})}}_{0}\;-A\mathrm{d}\xi_{\mathrm{sy}}}_{\text{system}}$$

$$\overbrace{\underbrace{-T\mathrm{d}S_{\xi}}_{(\text{leav R to sy})}\quad\underbrace{+p\mathrm{d}V_{\mathrm{sy}}}_{(\text{leav R to sy})}}^{\text{reservoir}} = \underbrace{-A\mathrm{d}\xi_{\mathrm{sy}}}_{\text{system}}\overbrace{-T\mathrm{d}S_{\xi}+p\mathrm{d}V_{\mathrm{sy}}}^{\text{reservoir}} = -A\mathrm{d}\xi_{\mathrm{sy}} - T\mathrm{d}S_{\xi} + p\mathrm{d}V_{\mathrm{sy}} = \mathrm{d}U^{\mathrm{Csy}}_{V_{\mathrm{Csy}}} = \delta W^{\max}_{\mathrm{rev}} = \mathrm{d}H^{\mathrm{Csy}}_{pT} - T\mathrm{d}S_{\xi}\Big| : \mathrm{d}S_{\mathrm{T}} = 0. \tag{39}$$

In the above expression, the differential enthalpy change appears, which differs from the differential enthalpy changes introduced by equations (22) and (27) (Figure 10):

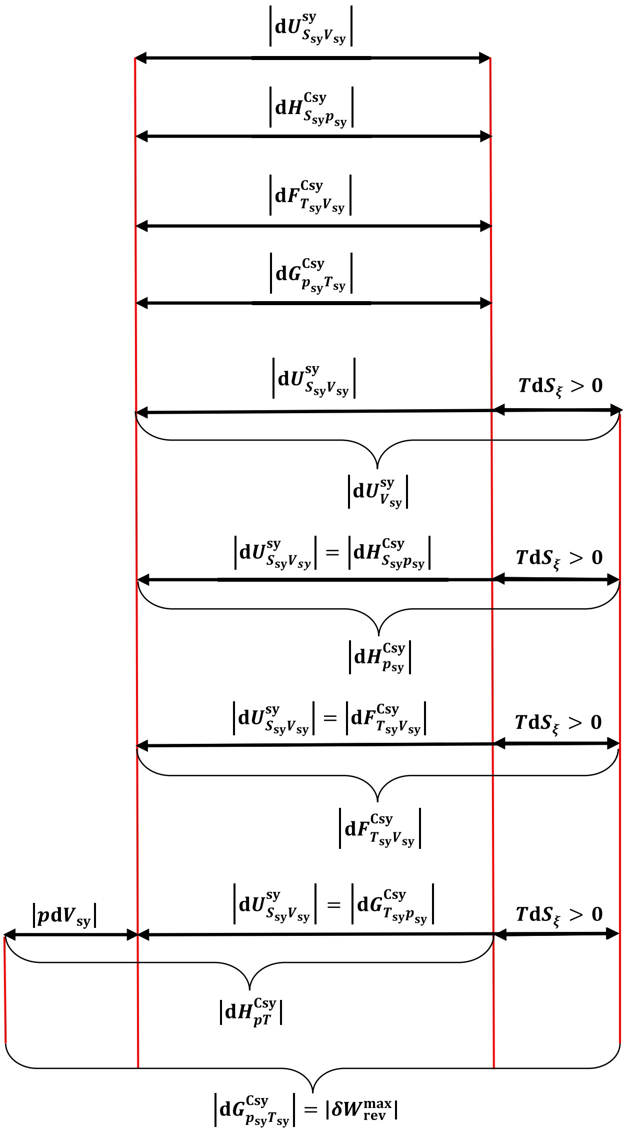

Figure 10: Absolute values of differential changes of thermodynamic potentials.

$$\mathrm{d}H^{\mathrm{Csy}}_{S_{\mathrm{sy}}p_{\mathrm{sy}}} \neq \mathrm{d}H^{\mathrm{Csy}}_{p_{\mathrm{sy}}} \neq \mathrm{d}H^{\mathrm{Csy}}_{pT}. \tag{40}$$

Based on the expression (39), it can be concluded that the global environment of the composite system from **Csy** receives the differential useful work partly from the system (-$A\mathrm{d}\xi_{\mathrm{sy}}$) and partly from the p,T-reservoir (-$T\mathrm{d}S_{\xi}+p\mathrm{d}V_{\mathrm{sy}}$) (Figure 9). If it is $\mathrm{d}U^{\mathrm{sy}}_{S_{\mathrm{sy}}V_{\mathrm{sy}}} = (\partial U/\partial\xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}}\mathrm{d}\xi_{\mathrm{sy}} = -A\mathrm{d}\xi_{\mathrm{sy}} < 0$; $\mathrm{d}S_{\xi}>0$; $\mathrm{d}V_{\mathrm{sy}}<0$ and $\mathrm{d}S_{\mathrm{T}} = 0$, then in relation to the other isochoric composite systems discussed so far (**Csy** where **R** is a thermal reservoir or a pressure reservoir and **Csy** = **sy**–isochoric system without **R**, Figure 10), from the composite system with the p,T-reservoir, the highest value of useful (non-pressure-volume) work is obtained by absolute value. Therefore, this work is also called maximum non-expansion work ($\delta W^{\max}_{\mathrm{rev}}$), and it is valid (Figure 10):

$$\mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}} = \delta W^{\max}_{\mathrm{rev}} \neq \delta W_{\mathrm{rev}} = \mathrm{d}F^{\mathrm{Csy}}_{T_{\mathrm{sy}}V_{\mathrm{sy}}} = \mathrm{d}H^{\mathrm{Csy}}_{p_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{Csy}}_{V_{\mathrm{Csy}}}\bigg| : \mathrm{d}S_{\mathrm{T}} = 0, \tag{41}$$

and

$$\left|\delta W^{\max}_{\mathrm{rev}}\right| > |\delta W_{\mathrm{rev}}|. \tag{42}$$

Let the goal be the carry-out of a non-spontaneous chemical reaction in the isentropic and quasi-static regime, and let the differential changes be: $\mathrm{d}H^{\mathrm{Csy}}_{pT} > 0$, $\mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}} > 0$ and $\mathrm{d}S_{\xi}>0$. Then, according to equation (39), the differential change of enthalpy in some infinitesimal step of the progress of a non-spontaneous reaction is:[17]

$$\mathrm{d}H^{\mathrm{Csy}}_{pT} = \mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}} + T\mathrm{d}S_{\xi} = \delta W^{\min}_{\mathrm{rev}} + T\mathrm{d}S_{\xi}. \tag{43}$$

The differential change in Gibbs free energy represents the minimum work ($\delta W^{\min}_{\mathrm{rev}}$) that must be provided to the system for the infinitesimal progression of non-spontaneous reactions. Because the system is isentropic, the value of the infinitesimal change in enthalpy is compensated by the differential amount of heat from the reservoir (surroundings): $T\mathrm{d}S_{\xi} = -T\mathrm{d}S_{\mathrm{R}}$.

2.5 Reaction entropy

One more comment remains. Sometimes, during lectures, students ask what precisely the entropy change of a reaction is. It is clear to the students that in exothermic reactions, chemical bonds of different energies are broken and created, and the excess energy can be used as useful work or dissipated in the environment in the form of heat. However, the entropy change during the reaction is quite mysterious for them. In the teaching of physical chemistry and thermodynamics, there is a direction that tends to explain thermodynamic functions (i.e., their changes), if possible (or at least to try) at the molecular (microscopic) level,[22,23] which we will also try. Let the entropy change in the system (where the reaction occurs) with p,T-reservoir be followed, and for simplicity, let the reaction mixture in the system (**sy**) behave as an ideal gas (IG). The partial molar entropy of some components in the IG mixture at pressure p and temperature T and composition $\mathbf{x} = (x_1 \ldots x_i \ldots)$ - the vector of mole fractions in **sy**–is[24,25]

$$\overline{S}_{\mathrm{i}}(p,T,\mathbf{x}) = \underline{S}_{\mathrm{i}}(p,T) - R\ln x_{\mathrm{i}}, \tag{44}$$

where $S_{\mathrm{i}}(p,T)$ corresponds to the molar entropy of the observed component in its pure state at a pressure and temperature identical to the **sy** mixture's pressure and temperature; at p,T = *const.* conditions, the entropy of a mixture containing C components is (n = amount of components):

$$S(p,T,\mathbf{x}) = \sum_{i}^{C} n_{\mathrm{i}}\overline{S}_{\mathrm{i}}(p,T,\mathbf{x}). \tag{45}$$

Since the system contains a reactive mixture, the vector **x** changes as the reaction progresses. Every component in the system is either a reactant or a product of the studied reaction, and no inert components are present. If the amount (mol) of each component from the reactive mixture is expressed using the stoichiometric coefficient and the degree of progress of the reaction, then taking into account expression (44), equation (45) is ($x_i(\xi) \equiv x_i = f(\xi)$):

$$S(p, T, \mathbf{x} = f(\xi)) = \sum_i^C (n_i^0 + \nu_i \xi)(S_i(p, T) - R \ln x_i(\xi)), \tag{46}$$

$$S(p, T, \mathbf{x} = f(\xi)) = \sum_i^C n_i^0 S_i(p, T) + \sum_i^C \nu_i S_i(p, T)\xi - R \sum_i^C (n_i^0 + \nu_i \xi) \ln x_i(\xi). \tag{46a}$$

The last term in the above equation represents the entropy of mixing depending on the degree of progress of the reaction. As the values of the mole fractions in the mixture are less than unity, $\ln x_i(\xi) < 0$ follows; therefore, it is:

$$\Delta S_{\mathrm{mix}}(p, T, \mathbf{x} = f(\xi)) = -R \sum_i^C (n_i^0 + \nu_i \xi) \ln x_i(\xi) > 0 \tag{47}$$

The second term ($\sum_i^C \nu_i S_i(p, T)\xi$) in equation (46a) represents the entropy change at $\xi = 1$ when the reactants and products are in a pure state, i.e., a hypothetical reaction without mixing. If the constant pressure of the reaction mixture is equal to the standard pressure, then the second term of the equation is the standard change of reaction entropy:

$$\Delta S_\xi^0(T) = \sum_i^C \nu_i S_i(p^0, T), \tag{48}$$

or more generally at some constant pressure:

$$\Delta S_\xi(p, T) = \sum_i^C \nu_i S_i(p, T). \tag{48a}$$

The first term ($\sum_i^C n_i^0 S_i(p, T)$) from equation (46a) represents the entropy of the reactants of the observed reaction in its pure state when it is $\xi = 0$. The change in entropy during the progress of the reaction at a particular value ξ relative to the entropy of the state $\xi = 0$ is (Figure 11):

$$\Delta S_\xi(p, T, \mathbf{x} = f(\xi)) = \sum_i^C n_i^0 S_i(p, T) + \sum_i^C \nu_i S_i(p, T)\xi - R \sum_i^C (n_i^0 + \nu_i \xi) \ln x_i(\xi) - \sum_i^C n_i^0 S_i(p, T),$$

$$\Delta S_\xi(p, T, \mathbf{x} = f(\xi)) = \sum_i^C \nu_i S_i(p, T)\xi - R \sum_i^C (n_i^0 + \nu_i \xi) \ln x_i(\xi), \tag{49}$$

that is, taking into account expressions (47) and (48a):

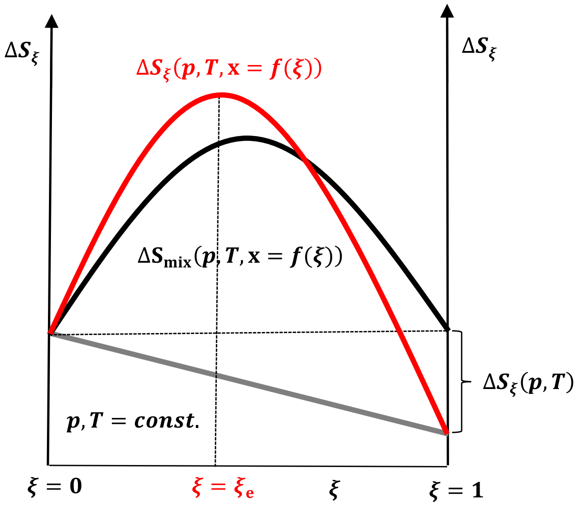

Figure 11: The change in entropy of the system during the reaction progress in case $\Delta S_\xi(p,T) < 0$; reactants at time $t = 0$ are in stoichiometric amount.

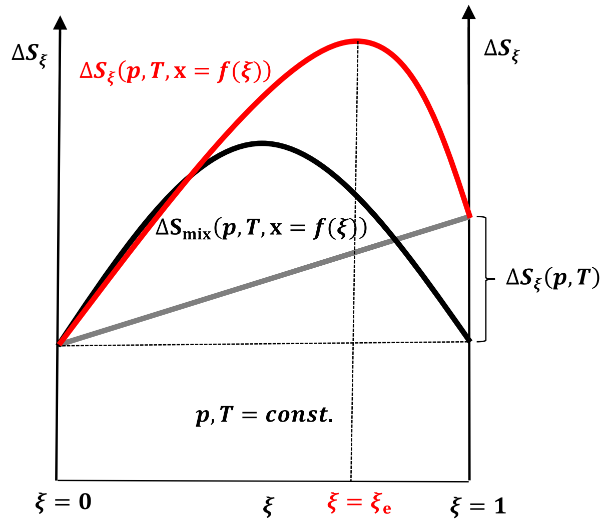

Figure 12: The change in entropy of the system during the reaction progress in case $\Delta S_\xi(p,T) > 0$; reactants at time $t = 0$ are in stoichiometric amount.

$$\Delta S_\xi\left(p,T,\mathbf{x}=f(\xi)\right) = \Delta S_\xi\left(p,T\right) - \Delta \mathrm{S}_{\mathrm{mix}}\left(p,T,\mathbf{x}=f(\xi)\right). \tag{50}$$

If the first term in equation (50) is zero ($\Delta S_\xi(p,T) = 0$) or $|\Delta S_\xi(p,T)<0|<\Delta \mathrm{S}_{\mathrm{mix}}(p,T,\mathbf{x} = f(\xi))$, then the increase in entropy to the equilibrium state ($\xi = \xi_\mathrm{e}$) in the chemical reaction through a series of quasi-static changes of state between $\xi = 0$ and $\xi = \xi_\mathrm{e}$ (Figure 11) is a consequence of the entropy of mixing ($\Delta \mathrm{S}_{\mathrm{mix}}(p,T,\mathbf{x} = f(\xi))>0$), which is compensated by the departure of heat from the composite system–an isentropic process–into the global environment as useful work that is superimposed on the useful work that originates from the change in the internal energy of the exothermic reaction (Figure 9). During the quasi-static change of the system's state during the reaction progress to the equilibrium state,[6] in each infinitesimal step of the progress of the exothermic reaction, the infinitesimal change in the system's internal energy enters the differential useful work–isentropic process. Of course, if $\Delta S_\xi(p,T)>0$ and this is the case when the energy is distributed over a more significant number of the product's quantum states than there are reactant's quantum state numbers–the partition function of the product increases concerning the partition functions of the reactants–or by in classical mechanics, energy is distributed over a more significant number of product's degrees of freedom, then $\Delta S_\xi(p,T)$ is superimposed on $\Delta \mathrm{S}_{\mathrm{mix}}(p,T,\mathbf{x} = f(\xi))$ and the entropy of the reaction increases to $\xi = \xi_\mathrm{e}>\xi = 0.5\xi = \xi_\mathrm{e}>\xi = 0.5$ (Figure 12).[21,26]

3 Conclusions

Here, differential changes of internal energy and other thermodynamic potentials in a system in which an exothermic reaction takes place are discussed with the aim of obtaining differential useful work. Equations and symbols are derivated for SL students, who, when mastering the material, can follow and analyze in detail every step of a given teaching unit.

What is necessary for every student to take away from this teaching unit is that the differential changes in thermodynamic potentials refer to the differential change in the internal energy of the composite system (system + reservoir). If the composite system is adiabatic and isochoric and the thermodynamic process in the system is isentropic, then the reaction's progress does not accompany the system's entropy (reaction entropy) change. The composite system's differential change in internal energy is equivalent to an adiabatic and isochoric system's (without a reservoir) differential change in internal energy: $\delta W_{\mathrm{rev}} = (\partial U/\partial \xi)_{S_{\mathrm{sy}},V_{\mathrm{sy}}} \mathrm{d}\xi_{\mathrm{sy}} = (\partial H/\partial \xi)_{S_{\mathrm{sy}},p_{\mathrm{sy}}} \mathrm{d}\xi_{\mathrm{sy}} = (\partial F/\partial \xi)_{T_{\mathrm{sy}},V_{\mathrm{sy}}} \mathrm{d}\xi_{\mathrm{sy}} = (\partial G/\partial \xi)_{T_{\mathrm{sy}},p_{\mathrm{sy}}} \mathrm{d}\xi_{\mathrm{sy}} = \mathrm{d}U^{\mathrm{Csy}}_{S_{\mathrm{Csy}}V_{\mathrm{Csy}}}$ (Figure 10).

Suppose the entropy of the system increases during the reaction progress. In that case, in order for the thermodynamic process to be isentropic, the reaction entropy must be compensated by the departure of heat from the composite system to the global environment where it contributes to useful work so that the composite system is only isochoric (not adiabatic). The differential change in the internal energy of an isochoric composite system (due to the infinitesimal progress of the reaction from the system) with a pressure reservoir or a thermoreservoir is equal to the differential change in the internal energy of an isochoric reactive system (without a reservoir) $\delta W_{\mathrm{rev}} = \mathrm{d}F^{\mathrm{Csy}}_{T_{\mathrm{sy}}V_{\mathrm{sy}}} = \mathrm{d}\,H^{\mathrm{Csy}}_{p_{\mathrm{sy}}} = \mathrm{d}\,U^{\mathrm{sy}}_{V_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{Csy}}_{V_{\mathrm{Csy}}}\Big| : \mathrm{d}S_{\mathrm{T}} = 0$.

The isochoric composite system, in which the reactive system is simultaneously in contact with a pressure reservoir and a thermoreservoir, deserves special attention. Namely, in this case, the most significant differential change in internal energy in absolute value (isentropic conditions) is obtained from the composite system, i.e., the highest absolute value of the differential useful work (maximum non-expansion work) if the entropy of the system increases during the progress of the exothermic reaction, and the volume of the system decreases at the same time $\mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{Csy}}_{V_{\mathrm{Csy}}} = \delta W^{\max}_{\mathrm{rev}} \neq \delta W_{\mathrm{rev}} = \mathrm{d}F^{\mathrm{Csy}}_{T_{\mathrm{sy}}V_{\mathrm{sy}}} = \mathrm{d}H^{\mathrm{Csy}}_{p_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}}$ (Figure 10). In this case, the differential change in the internal energy of the isochoric composite system ($\mathrm{d}G^{\mathrm{Csy}}_{p_{\mathrm{sy}}T_{\mathrm{sy}}} = \mathrm{d}U^{\mathrm{Csy}}_{V_{\mathrm{Csy}}}$) is not equal to the differential change in the internal energy of the isochoric system, i.e. system without p,T-reservoir ($\mathrm{d}U^{\mathrm{sy}}_{V_{\mathrm{sy}}}$). For students, Figure 10 can show the importance of setting (i.e., choosing) conditions in the composite system (in which **sy** the observed reaction takes place) to obtain maximum non-expansion work.

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Appendix A

The extent of reaction ξ, considering the reaction equation as it is written, may be calculated by dividing the number of times the chemical transformation occurs by the Avogadro constant, which means that it has the dimension of mol (sometimes denoted by mol-rxn).[9] The extent of a chemical reaction is an extensive variable whose value ranges from zero to the theoretical maximum value. The amount of some reactant r and some product p belonging to the same reaction in time t if the extent of reaction has the value $\xi(t)$ is:

$$n_{\mathrm{r}}(t) = n_{\mathrm{r}}(t = 0) - |\nu_{\mathrm{r}}|\xi(t) \tag{A1}$$

$$n_{\mathrm{p}}(t) = \nu_{\mathrm{p}}\xi(t) \tag{A2}$$

In the above equations, ν_{r}<0 and ν_{p}>0 are the stoichiometric coefficients of the selected reactant and product in the observed reaction. Before the start of the reaction, the amount of reactant r is $n_{\mathrm{r}}(t = 0)$; this amount of the observed reactant decreases with the progress of time during the reaction. Equations (A1) and (A3) follow the definition of the extent of reaction:

$$\xi(t) = (n_{\mathrm{r}}(t = 0) - n_{\mathrm{r}}(t))/|\nu_{\mathrm{r}}| = \tag{A3}$$

$$\xi(t) = n_{\mathrm{p}}(t)/\nu_{\mathrm{p}} \tag{A4}$$

If the initial amount of each reactant is equal to the stoichiometric coefficient, then the extent of the chemical reaction if the total stoichiometric amount of reactants is converted into the stoichiometric amount of products (i.e., one mole of the observed reaction takes place), according to equations (A3) and (A4), is:

$$\xi(t) = \xi_{\max} = (|\nu_{\mathrm{r}}| - 0)/|\nu_{\mathrm{r}}| = 1 \,\text{and}\, \xi(t) = \xi_{max} = \nu_{\mathrm{p}}/\nu_{\mathrm{p}} = 1$$

Suppose the reactants are in a non-stoichiometric relationship. In that case, a normalized extent of reaction can be introduced (normalization to a value of 1), which is explained in detail in the literature references.[9,10]

The change in Gibbs free energy of a reaction at constant temperature and pressure is:

$$dG = \sum \mu_i dn_i = \sum \mu_i \nu_i d\xi \tag{A5}$$

$$(\partial G/\partial \xi)_{T,p} = \Delta_r G = \Delta_r \mu = \sum \mu_i \nu_i \tag{A6}$$

The slope of the Gibbs free energy function from the extent of the chemical reaction according to De Donder's equation (2) is:

$$(\partial G/\partial \xi)_{T,p} = \Delta_r G = \Delta_r \mu = -A \tag{A7}$$

Appendix B

$$\begin{aligned}(\partial U/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}} &= \left(\partial\left(C_V^{\mathrm{sy}}\mathrm{d}T + \pi_T^{\mathrm{sy}}\mathrm{d}V\right)/\partial S\right)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}} = C_V^{\mathrm{sy}}\left(\partial T/\partial S\right)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}} + \pi_T^{\mathrm{sy}}\left(\partial V/\partial S\right)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}} \\ &= TC_V^{\mathrm{sy}}\Big/C_p^{\mathrm{sy}} + \pi_T^{\mathrm{sy}}\left(\partial V/\partial T\right)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\Big/\left(\partial S/\partial T\right)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}} = TC_V^{\mathrm{sy}}\Big/C_p^{\mathrm{sy}} + T\pi_T^{\mathrm{sy}}V\alpha_T^{\mathrm{sy}}\Big/C_p^{\mathrm{sy}}\end{aligned}$$

Multiplying the above equation by $\mathrm{d}S_{\mathrm{sy}}$ gives:

$$\begin{aligned}(\partial U/\partial S)_{p_{\mathrm{sy}},\xi_{\mathrm{sy}}}\mathrm{d}S_{\mathrm{sy}} &= \delta q = \left(C_V^{\mathrm{sy}}/C_p^{\mathrm{sy}}\right)T\mathrm{d}S_{\mathrm{sy}} + \left(\pi_T^{\mathrm{sy}}V\alpha_T^{\mathrm{sy}}/C_p^{\mathrm{sy}}\right)T\mathrm{d}S_{\mathrm{sy}} = C_V^{\mathrm{sy}}\left(\delta q/C_p^{\mathrm{sy}}\right) + \pi_T^{\mathrm{sy}}V\alpha_T^{\mathrm{sy}}\left(\delta q/C_p^{\mathrm{sy}}\right) \\ &= C_V^{\mathrm{sy}}\mathrm{d}T + \pi_T^{\mathrm{sy}}V\alpha_T^{\mathrm{sy}}\mathrm{d}T.\end{aligned}$$

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