

Isobars and isochores as simple examples of quasi-static processes that are neither reversible nor irreversible

Kamal Bhattacharyya

Department of Chemistry, RKMVCC, Kolkata 700 118, India

ARTICLE INFO

Keywords:

Thermodynamics
Reversible process
Irreversible process
Quasi-static process
Indicator diagram

ABSTRACT

There exist several ways to define a reversible process and distinguish it from an irreversible one. From the need of practically explaining a reversible process, the concept of a quasi-static transformation is primarily introduced; otherwise, no special significance is attached to such a process. We consider here all these three processes and scrutinize their relative merits in the light of prevalent definitions of reversibility. Two simple processes, viz., the isochoric and isobaric ones, are then put forward that are found to be independently quasi-static on their own right, but not strictly reversible; they are not irreversible either. The importance of these two specific processes in the p - V diagrams and of reversible processes in the T - S diagrams are separately delineated. One mol of an ideal gas is chosen as the working substance everywhere to keep all calculations at the simplest level.

1. Introduction

A thermodynamic process is characterized by changes of state functions. The p - V diagram is particularly useful for gases. If $\Delta p = 0$ and $\Delta V = 0$, we conclude that a state has remained unchanged. However, a more general viewpoint, valid *not just* for gases, exists. From the first and second laws, we obtain U and S as two such functions. So, naturally, we are led to conclude that if both ΔU and ΔS are zero, a state has not changed. Auxiliary functions like ΔA and ΔG do not qualify in this regard because they are useful *only* for *isothermal* processes. The case of ΔH is not independently important either; it requires knowledge of ΔU .

Once we consider a process, it is imperative to judge if it is reversible or not. For a reversible process (RP), variations are continuous and calculations of changes in thermodynamic functions are simple. Practical implementation of an RP is conceived in terms of a quasi-static process (QSP), requiring an infinite number of heat reservoirs at intermediate points to keep the system *infinitesimally close* to equilibrium at each point during the entire transition. Indeed, this is how a QSP is introduced in a thermodynamic context [1]. It's more a concept than reality. One may notice a close correspondence of RP-QSP with the notion of 'integration as the limit of a sum'. On the other hand, an irreversible process (IP) is associated usually with *sudden* changes,

may well be in *finite steps*, to move from one equilibrium state to another in a *discontinuous* fashion. At any intermediate stage, the system is in a non-equilibrium state. This is why, for any IP, we look for 'equivalent reversible paths' to calculate changes in thermodynamic functions.

The above discussion makes one point quite clear. An IP is often distinctly different from an RP or a QSP. But, a few other queries are left open. Specifically, the following questions arise immediately. (i) Does *any* QSP qualify as RP? (ii) Is the converse true? (iii) What does an RP strictly mean? Are all the definitions of reversibility pristine? (iv) Are there situations where a QSP can have an identity of its own, and it is neither an RP nor an IP?

Several attempts were made from time to time to understand questions like whether a QSP may also be an IP [2], how a QSP differs from an RP [3], how ΔS calculations [4] or entropy productions [5] are linked with RP. Usually, we associate a QSP with a *slow* process [6]. But, *slow* processes are not *necessarily* reversible [7]. In addition, dissipation, if there is any, may be a reason behind an IP [1, 7]. In the particular case of non-isothermal heat transfer processes, we have earlier analyzed point (i) in great detail [8] and arrived at a negative conclusion. Primarily, this is due to the work involved in the on-off switches connected to an infinite number of heat reservoirs with which the system has to thermally equilibrate at different instants, and such work term is left outside the scope of thermodynamics. Here, however,

*Corresponding author: E-mail address: pchemkb@gmail.com (K. Bhattacharyya)

we shall choose a few much simpler examples, without going deeper into the inner mechanisms, to decipher how a QSP may visibly differ from an RP. As regards point (i), the same negative conclusion follows here too. We intend to also establish that the answer to point (ii) is always in the affirmative. Various existing definitions of an RP will be taken up to ascertain the status of each one separately in course of discussions on point (iii). Finally, we explore cases where a QSP *does* have an independent status, in the context of point (iv), highlighting *isochoric* and *isobaric* processes in particular.

Our organization is as follows. In Sec. 2, we point out various standard definitions of reversibility with brief explanations. Sec. 3 is devoted to studies on isochoric and isobaric QSP in relation to RP and IP. Work, ΔS (system) and ΔS (universe) calculations are given primary importance here. The bearing of such data on the characterization of an RP is noted. Necessary amendments are made. That the isobar-isochore pair of QSP, mutually perpendicular in the p - V plane, can act independently to easily calculate ΔS for any transformation is confirmed in Sec. 4. Finally, Sec. 5 summarizes the major conclusions of the whole endeavor.

2. Criterion of a reversible process

We shall throughout follow the *older convention* [9] and stick to the prevalent definitions (D) of an RP as the one that satisfies either (or all!) of the following:

D-I. Work done by (on) the system is maximum (minimum).

D-II. Heat (Q) and work (W) terms remain same in magnitude but opposite in sign if the process is reversed, and the reverse process is also acceptable or practicable.

D-III. ΔS (system) = $\int dQ / T$.

D-IV. ΔS (universe) = ΔS (system) + ΔS (surroundings) = 0.

Keeping aside the fact that all natural processes are irreversible, we do not wish to invoke any dissipation anywhere as well. The latter will ensure simplicity in the whole endeavor. Also, henceforth, we shall choose here *one-step* IP only. Now, turning attention to the definitions, we note that D-I has been elaborated at length elsewhere [9] and needs no further clarification. D-II plainly means that ΔU changes sign when a process is reversed, where $\Delta U = Q - W$. But, this does not preclude the possibility that $\Delta U = Q' - W'$ ($Q' = Q + \alpha$, $W' = W + \alpha$). Only if $\alpha = 0$, the phrase 'same in magnitude but opposite in sign' would be obeyed; it's true for an RP, but not for an IP. So, cases with $\alpha \neq 0$ usually account for (but see below) alternative paths, and are important in IP. In addition, there is something else in D-II. Consider a non-

Carnot engine that takes up Q_1 heat from a source at temperature T_1 , performs work W and transfers Q_2 heat to a sink kept at temperature T_2 . By merely changing signs of the work and heat terms, we do not get an *acceptable* pump. This is taken care of in the *extra clause*. The definition D-III follows from the definition of entropy [10] as

$$dS = dQ_{rev} / T. \quad (1)$$

For an RP, therefore, the subscript is unnecessary; for a finite change, we need additionally an integration step. Hence, an RP should obey D-III:

$$\Delta S = \int dQ / T. \quad (2)$$

On the other hand, definition D-IV forms another part of the second law relevant to an RP. It actually goes as

$$\Delta S (\text{universe}) = \Delta S (\text{system}) + \Delta S (\text{surroundings}) \geq 0, \quad (3)$$

where the equality refers to an RP, the other to an IP.

3. Selected examples

We like to choose two examples here. For a closed system, the first one sought an answer to the question of 'reversible work' for a process with $\Delta V = 0$ (see Levine [10]). Indeed, the idea behind this whole article has arisen from this particular problem. An extension to the case of $\Delta p = 0$ is subsequently treated here. In course of the analysis on QSP, we have found it more convenient to consider isochoric ($dV = 0$) and isobaric ($dp = 0$) processes respectively, replacing just $\Delta V = 0$ and $\Delta p = 0$ that are characteristic of IP. Our choices are thus restrictive, but certainly appropriate in the QSP context.

3.1. Two specific processes

Let us consider the *isochoric* process from A to B_1 in Fig. 1. Since $\Delta V = 0$, no work is done. No *straight line* in the p - V diagram will ever correspond to any RP for a gas; we have only reversible isotherms and adiabats, both well-defined *curves*. As the final state has a higher pressure, it will have a higher temperature too. Therefore, we choose a reversible adiabatic compression path (A to C) and next a reversible isothermal expansion path (C to B_1) to calculate the overall 'reversible work'. Here, area (S) under ACB_1A [$S(ACB_1A)$] accounts for the same, and it is *positive*. C is an intermediate point where the two reversible paths intersect.

We next choose the *isobaric* process from A to B_2 in Fig. 1. Since $\Delta V \neq 0$, some work is done. This irreversible work (one-step) is defined by $S(AB_2O_3O_2A)$. As usual, being a *straight line* in the p - V diagram, it cannot represent the 'reversible work'. Here

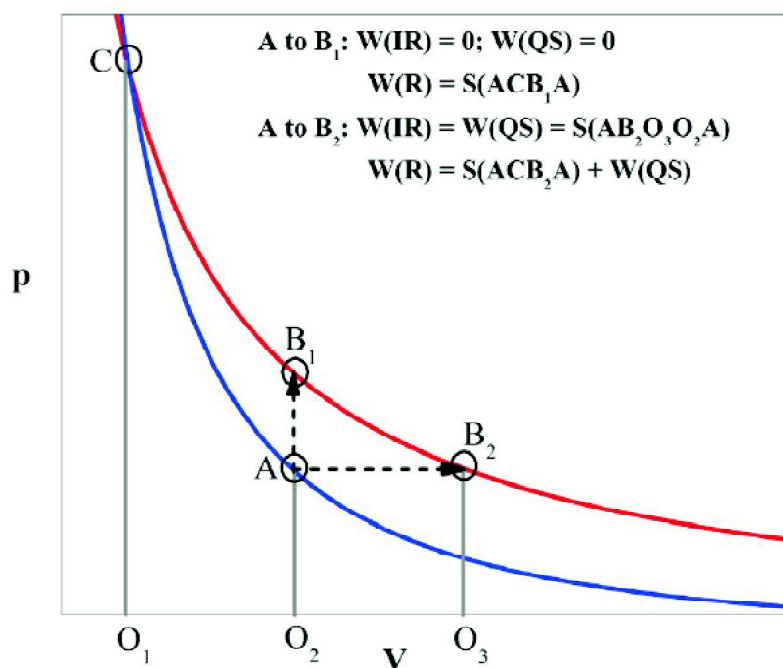


Fig. 1. Isochoric (A to B_1) and isobaric (A to B_2) processes are shown in the p-V diagram. The red line refers to a reversible isothermal process and the blue one to a reversible adiabatic process. The work done W by the system via irreversible [$W(\text{IR})$], quasi-static [$W(\text{QS})$] and reversible [$W(\text{R})$] paths in each case are pointed out in the figure. $S(\text{XYZX})$ symbolically represents the area under the curve XYZX .

too, the final state has a higher volume, and so it will have a higher temperature. Therefore, we choose a reversible adiabatic compression path (A to C) and subsequently a reversible isothermal expansion path (C to B_2) to calculate the 'reversible work'. Note that, point C in this case may not refer to the earlier one. It is only a symbolic representation. Here, area ACB_2A [$S(\text{ACB}_2\text{A})$] denotes the *extra* work due to reversibility and it is again *positive*.

In both the above cases, therefore, D-I is satisfied, *i.e.*, $W(\text{R}) > W(\text{QS}) = W(\text{IR})$ [cf. Fig. 1].

3.2. A few characteristics

Certain features, common to both the above two processes, are now worth mentioning. Clearly, these are not RP; in terms of work, they may be called either IP or QSP (dotted line). However, there is a subtle difference (see below) in respect of certain other properties. When we only impose $\Delta V = 0$ or $\Delta p = 0$, it does not follow that the process is isochoric ($dV = 0$) or isobaric ($dp = 0$). The latter is more restrictive, proceeds *infinitesimally*, and hence certainly means a QSP, but *not* an IP. However, the work term alone *cannot* distinguish such a QSP from a one-step IP. On the other hand, ΔU has to remain same if initial and final points are fixed. This means, $Q(\text{R}) > Q(\text{QS}) = Q(\text{IR})$ is true in either example.

Consider now the reverse process (B_1 to A or B_2 to A). The

W term changes sign in either case, so does ΔU . Hence, Q has to change its sign. This is important for two reasons. (i) It implies that definition D-II should *also apply* to a QSP. (ii) There is yet another issue. If we *trace back the reversible path* in Fig. 1, one notes that D-I is in trouble; *minimum work is not done* on the system. Rather, it is *maximum* in each situation. This calls for a fresh investigation.

To circumvent the above problem, we need indeed another *alternative* reversible path. Fortunately such a path is available for each problem. Fig. 2 shows such paths. The isotherm and adiabat meet now at the intermediate point D. Corresponding work terms are presented in the figure. Here we do find that a positive (and maximum) work is done by *the system*, in accordance with D-I.

The choice of the *proper* RP route to be followed depends on the temperatures of the states under consideration. If we go from a lower T to a higher T point, an adiabatic compression with a subsequent isothermal expansion would be appropriate. In case of the converse transformation, an adiabatic expansion followed by an isothermal compression would work desirably. To be wise after the events, the above simple *rules of thumb* may be kept in mind.

3.3. Preliminary remarks on reversibility

The discussion so far has made two points quite clear. Defi-

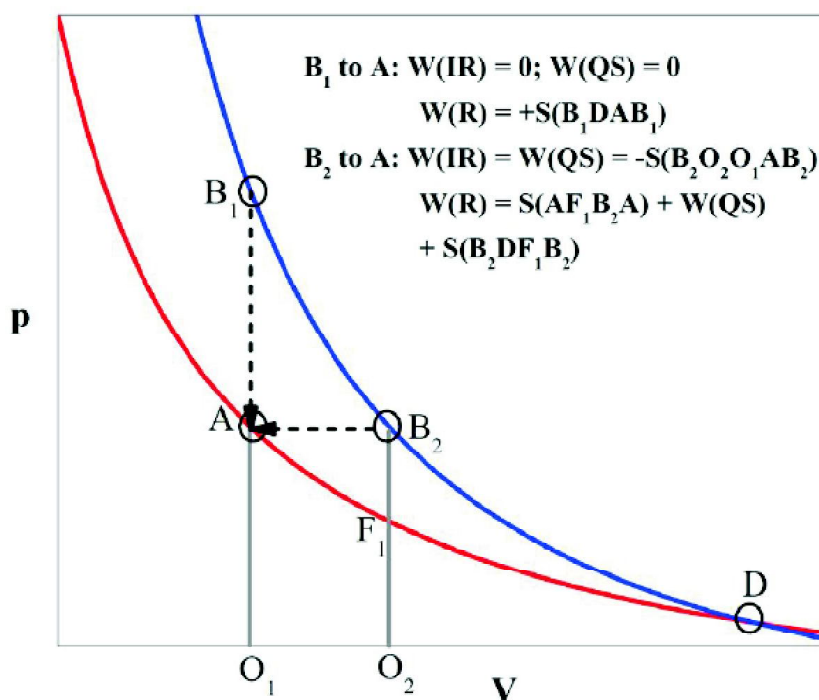


Fig. 2. Reverse processes of those depicted in Fig. 1 are presented in relation to reversible isotherm (red line) and reversible adiabat (blue line). Here, B_1 to A is isochoric and B_2 to A is isobaric. The work done W by the system via irreversible [$W(\text{IR})$], quasi-static [$W(\text{QS})$] and reversible [$W(\text{R})$] paths in each case are pointed out in the figure. The significance of S remains same as that in Fig. 1.

nitions D-I and D-II need some amendments. First, if there is one intermediate point (C or D), there exist *two* reversible paths; along one path, D-I is obeyed (e.g., A to B_1 or B_2 , see Fig. 1) along the other, D-I is also obeyed (e.g., B_1 or B_2 to A, see Fig. 2). Thus, wherever *multiple reversible paths* are available, we should choose the *specific one* that respects D-I, and such a path can always be found. Second, we need to improve D-II in two respects: (i) As it stands, D-II applies equally well to QSP beyond doubt. Both isochoric and isobaric processes lend credence in this issue. Therefore D-II cannot differentiate a QSP from an RP. (ii) If a process is reversed, the difference ΔU of Q and W terms remains same. We have already seen, W terms differ via paths ACB (Fig. 1) and BDA (Fig. 2), where B stands either for B_1 or B_2 . The major point here is that, path BCA is surely reversible, but with regard to the B to A transition, we should choose route BDA that *satisfies* D-I. Otherwise, no doubt should be cast on the viability or acceptability of either process. It is just that *we lose the identity* of a reversible path as the *only one* that can be *traced back to undo* the course. But, isochoric and isobaric QSP do not support any alternative paths.

The next natural query is the following: If multiple reversible paths exist, how many of them should we need to consider? Here, the associated figures reveal that there are *two routes* with *one* intermediate point (C or D). That these are all, and

nothing is left out of consideration, may be appreciated once we look at Fig. 3. This T - S plot tells us that, given two states at A and B (again, B means either B_1 or B_2), one has really *two options*, and *no more*, to reach reversibly from one of them to the other, provided there is just *one intermediate point*. The area under this curve signifies the heat Q involved in the process. Path ACB, first adiabatic (blue) and then isothermal (red), is akin to Fig. 1; kinship of the other route BDA with Fig. 2 is obvious. If we compare paths ACB and ADB, the heat absorbed by the system, and hence the work done, is greater in the former case by an amount $\Delta T \Delta S$, which is here the rectangular area ADBC. It also shows, a *single RP* (no intermediate point) necessitates either $\Delta T = 0$ (an isotherm), or $\Delta S = 0$ (an adiabat). The conclusion corresponds to that in the p - V diagram as well.

3.4. Entropy changes

Let us note that, two other definitions of reversibility [*viz.*, D-III and D-IV] rest solely on entropy changes. Therefore, we now concentrate on this aspect. Indeed, the use of QSP is most rewarding in ΔS calculations for the system, to be outlined below. Traditionally, the change of any thermodynamic property is normally calculated via 'equivalent reversible paths'. So, as per prescription, we should employ the RP route (see Fig. 1).

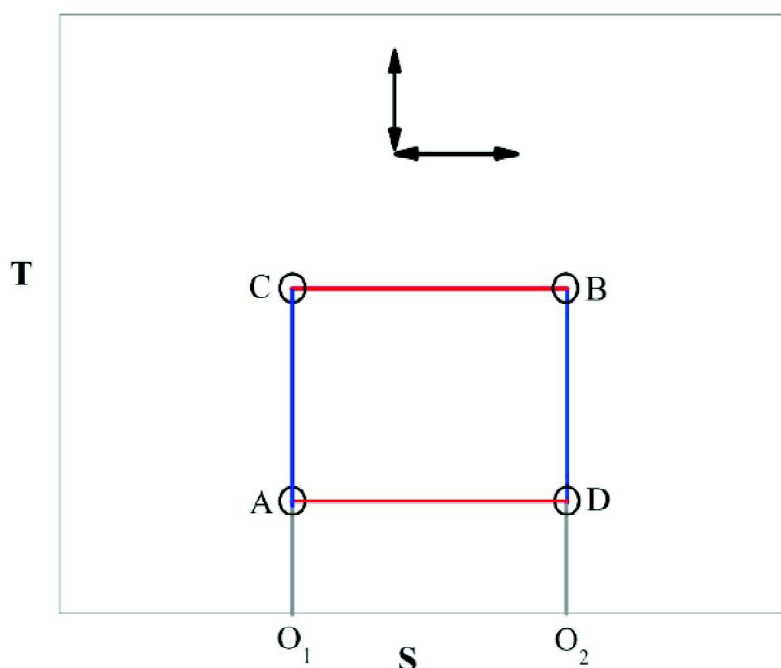


Fig. 3. Transitions A to B, where B formally represents either B_1 or B_2 of Figs. 1 and 2, are shown in the T - S diagram. Two reversible routes exist, one via ACB and the other via ADB. In either case, only one intermediate point (C or D) is considered.

$$\Delta S(A \rightarrow B_1) = \Delta S(A \rightarrow C) + \Delta S(C \rightarrow B_1) \quad (4)$$

and calculate the changes for the overall *isochoric* process. Likewise, the net change of entropy for the *isobaric* process A to B_2 (see Fig. 1) has to be evaluated on the basis of (5), where

$$\Delta S(A \rightarrow B_2) = \Delta S(A \rightarrow C) + \Delta S(C \rightarrow B_2) \quad (5)$$

Thus, one isotherm and one adiabat are involved in the RP-based approach. Further, we know that $\Delta S = 0$ for the adiabatic path $A \rightarrow C$.

The situations become much simpler via straightforward QSP. Let us choose the isochoric A to B_1 transformation. Since $dV = 0$ throughout, here $dQ \equiv dU$ and, U being a state function, the question of reversibility during heat transfer becomes redundant. Hence, we plainly write

$$\begin{aligned} \Delta S &= \int_A^{B_1} \frac{dQ_{rev}}{T} \\ &= \int_A^{B_1} \frac{dU}{T} = C_V \ln(T_{B_1}/T_A) = C_V \ln(P_{B_1}/P_A) \quad (6) \end{aligned}$$

On the other hand, the isobaric A to B_2 transformation takes advantage of $dp = 0$, and hence $V dp = 0$, throughout. The identification $dQ \equiv dH$ thus follows. Again, H being a state function, the question of whether $dQ \equiv dQ_{rev}$ becomes superfluous. Consequently, we are allowed to proceed as

$$\begin{aligned} \Delta S &= \int_A^{B_2} \frac{dQ_{rev}}{T} \\ &= \int_A^{B_2} \frac{dH}{T} = C_P \ln(T_{B_2}/T_A) = C_P \ln(V_{B_2}/V_A) \quad (7) \end{aligned}$$

It is imperative now to check if the calculations of ΔS on the basis of (4) and (6), or (5) and (7), agree. The following subsection will be devoted to this task. Let us note in passing that (6) or (7) does not apply to an IP where, by definition, we are not permitted to impose $dV = 0$, or $dp = 0$, respectively. In this respect, such a QSP differs from the corresponding IP.

3.5. Preliminary calculations

We start with point A in Fig. 1 with (p, V, T) coordinates as $(1, 1, R^{-1})$ where R is the universal gas constant in unit commensurate with the same of p and V . Suppose the *isochoric* process to B_1 changes coordinates to $(3, 1, 3R^{-1})$. Then, it is pretty easy to check that point C in Fig. 1 will have the correct coordinates $(3^{\gamma/(\gamma-1)}, 3^{-1/(\gamma-1)}, 3R^{-1})$. Now, from (4), we find

$$\begin{aligned} \Delta S(A \rightarrow B_1) &= \Delta S(A \rightarrow C) + \Delta S(C \rightarrow B_1) \\ &= 0 + R \ln(3^{\frac{1}{\gamma-1}}) = \frac{R}{\gamma-1} \ln 3. \quad (8) \end{aligned}$$

This is the RP result. Proceeding via QSP, from (6), we obtain straightforwardly

$$\Delta S = C_V \ln 3. \quad (9)$$

One may now use the definition of γ , along with the known ideal-gas relation, viz.,

$$\gamma = C_P/C_V, \quad R = C_P - C_V. \quad (10)$$

Putting (10) in (8), the equivalence of (8) with (9) is immediately established.

Similarly, starting from the same point A at $(1, 1, R^{-1})$, suppose the *isobaric process* to B_2 changes coordinates to $(1, 3, 3R^{-1})$. This will keep C at the same place as before in the p - V diagram. In this case, therefore, we find from (5) that

$$\begin{aligned} \Delta S(A \rightarrow B_2) &= \Delta S(A \rightarrow C) + \Delta S(C \rightarrow B_2) \\ &= 0 + R \ln 3^{\gamma/(\gamma-1)} = \frac{\gamma R}{\gamma-1} \ln 3. \end{aligned} \quad (11)$$

This RP result should be compared now with the QSP outcome in (7). The latter yields directly

$$\Delta S = C_P \ln 3. \quad (12)$$

Employing (10), one can easily check that (11) agrees with (12).

It is thus clear that *isochoric and isobaric processes are neat examples* of QSP that are *not* RP (and neither IP), and they provide simpler routes to calculate ΔS (system) *exactly*. In both the cases, we have employed D-III to our advantage. Hence, D-III is obeyed in at least *two* situations for QSP that are distinctly *not* RP. We now need to explore how far these two independent QSP fare in respect of D-IV. To achieve this end, one requires ΔS (surroundings), and so we proceed as follows.

Consider the RP along $A \rightarrow C \rightarrow B_1$ [cf. Fig. 1]. The quantities of interest emerge as

$$\begin{aligned} W(A \rightarrow C) &= \frac{1-3}{\gamma-1} = \frac{-2}{\gamma-1}; \quad \Delta U(A \rightarrow C \rightarrow B_1) \\ &= \Delta U(A \rightarrow C) + 0 = -W(A \rightarrow C). \end{aligned} \quad (13)$$

Further, we get

$$\begin{aligned} W_{rev}(A \rightarrow C \rightarrow B_1) &= \frac{-2}{\gamma-1} + \frac{3}{\gamma-1} \ln 3; \\ Q_{rev}(A \rightarrow C \rightarrow B_1) &= \frac{3}{\gamma-1} \ln 3. \end{aligned} \quad (14)$$

The expression for ΔS (system) is already found in (8). We shall now use these findings in (13) and (14) to obtain the value of Q

(QSP). For the QSP $A \rightarrow B_1$, $W = 0$. So, it follows that

$$\begin{aligned} \Delta U(A \rightarrow B_1) &= \Delta U(A \rightarrow C) \\ &= W_{rev}(A \rightarrow C) = \frac{2}{\gamma-1} = Q(\text{QSP}). \end{aligned} \quad (15)$$

It may be emphasized here that the RP route has been chosen because QSP *alone* cannot estimate Q or ΔU for the direct path $A \rightarrow B_1$. Anyway, by energy conservation, this heat Q (QSP) in (15) is taken *from* the surroundings. But, unlike the RP where heat is taken from a single reservoir at a fixed temperature via the C to B_1 path, *lesser* amount of *total* heat Q (QSP) is abstracted by the system from an infinite number of reservoirs at varying temperatures along $A \rightarrow B_1$. Therefore, in applying (1) to evaluate ΔS (surroundings), we need some kind of averaging for the T -part. One particular way that we have found useful reads as

$$\begin{aligned} \Delta S(\text{surroundings}) &= \int_A^{B_1} \frac{dQ}{T} \\ &= -Q(\text{QSP}) \frac{1}{3R^{-1} - R^{-1}} \int_{R^{-1}}^{3R^{-1}} \frac{1}{T} dT \\ &= \frac{-R}{\gamma-1} \ln 3 \end{aligned} \quad (16)$$

Notably, a *uniform averaging* of the ' $1/T$ -term' has been used in arriving at (16). As a result, we see that (16) is exactly the same as (9) in magnitude, but opposite in sign. This *specific* averaging scheme has thus the advantage of revealing that D-IV *can be true also* for an *isochoric* QSP.

Consider next the RP [cf. Fig. 1] along the route $A \rightarrow C \rightarrow B_2$. The quantities W and ΔU now turn out as

$$\begin{aligned} W(A \rightarrow C) &= \frac{1-3}{\gamma-1} = \frac{-2}{\gamma-1}; \quad \Delta U(A \rightarrow C \rightarrow B_2) \\ &= \Delta U(A \rightarrow C) + 0 = -W(A \rightarrow C). \end{aligned} \quad (17)$$

Results in (17) are same as those in (13). In addition, we find

$$\begin{aligned} W_{rev}(A \rightarrow C \rightarrow B_2) &= \frac{-2}{\gamma-1} + \frac{3\gamma}{\gamma-1} \ln 3; \\ Q_{rev}(A \rightarrow C \rightarrow B_2) &= \frac{3\gamma}{\gamma-1} \ln 3. \end{aligned} \quad (18)$$

The expression for ΔS (system) is already known [see (11)]. As before, let us now use the estimates in (17) and (18) to get Q (QSP) for the process $A \rightarrow B_2$. Here, one obtains directly $W = 2$

from the embedded area. So,

$$\begin{aligned}\Delta U(A \rightarrow B_2) &= \Delta U(A \rightarrow C) + 0 \\ &= -W_{rev}(A \rightarrow C) = \frac{2}{\gamma - 1} \\ Q(\text{QSP}) = \Delta U + W &= \frac{2}{\gamma - 1} + 2 = \frac{2\gamma}{\gamma - 1}.\end{aligned}\quad (19)$$

Once more, assistance of the RP is required since QSP alone cannot estimate Q or ΔU for the direct path $A \rightarrow B_2$. This net heat $Q(\text{QSP})$ in (19) is taken from an infinite number of reservoirs at varying temperatures along $A \rightarrow B_2$. Therefore, in applying (1) to evaluate ΔS (surroundings), we need some kind of averaging, as done above for the isochoric change. Again, we choose the *uniform averaging* scheme for the same '1/T-term'. This leads to

$$\begin{aligned}\Delta S(\text{surroundings}) &= \int_A^{B_2} \frac{\delta Q}{T} \\ &= -Q(\text{QSP}) \frac{1}{3R^{-1} - R^{-1}} \int_{R^{-1}}^{3R^{-1}} \frac{1}{T} dT \\ &= \frac{-\gamma R}{\gamma - 1} \ln 3\end{aligned}\quad (20)$$

For a second time, we note that (20) and (11) are same in magnitude, but opposite in sign. Hence, D-IV is true also for the *isobaric* QSP.

Let us note that we have taken advantage of an averaging with a uniform distribution in both examples. For some variable x with finite upper and lower limits set at x_1 and x_0 respectively, such an average of a function $G(x)$ is generally given by

$$\langle G(x) \rangle = \frac{1}{x_1 - x_0} \int_{x_0}^{x_1} G(x) dx.\quad (21)$$

In case of the direct path $A \rightarrow B_1$, total heat $Q = \Delta U(A \rightarrow B_1)$ is abstracted from source via the intermediate-temperature reservoirs placed along the line $A \rightarrow B_1$ at varying T -values. During this transition, p increases *uniformly* and, at any point above A , the rise in pressure *alone* dictates the increase in T . The uniform averaging scheme is thus justified. Justification for the uniform distribution for the isobaric case $A \rightarrow B_2$ rests on a similar reasoning. Here, V rises *uniformly* and, at any point at the right of A , the expansion in volume *alone* dictates the growth in T . Hence, T rises uniformly in either situation.

3.6. Additional remarks on reversibility

Results of the last two subsections show that D-III applies to both the isochoric and isobaric QSP beyond doubt. Besides, a *specific averaging* in the variable-temperature cases ensures the validity of D-IV as well in these two situations. Coupled with our observations in Sec. 3.3, it can be safely said that *all the definitions of reversibility* [cf. Sec. 2] are put forward to distinguish an RP from an IP *only*; the case of a QSP is *different*, and the more so for the two special QSP chosen here.

4. Independent quasi-static processes

The discussion so far has probably made it clear that processes like $A \rightarrow B_1$ and $A \rightarrow B_2$ in Fig. 1, or those like $B_1 \rightarrow A$ and $B_2 \rightarrow A$ in Fig. 2 are QSP proper. They have *not* been imported to *practically justify* some RP. It is also now transparent that these two QSP are quite handy in calculating entropy changes for the system, though they are unable to provide ΔU . So, we assert that ΔS (system) calculations for any change of coordinates in the p - V diagram could be performed via *equivalent quasi-static paths*, instead of the traditional 'equivalent reversible paths' idea. Here, a few changes are considered to estimate ΔS (system) via both the above routes to justify our assertion.

4.1. Isotherms and adiabats

Let us start with Fig. 4 where a pure isotherm $A \rightarrow B_1$ and another pure adiabat $A \rightarrow B_2$ are chosen as two independent RP. Point A is taken at $(3, 1, 3R^{-1})$. Coordinates of points B_1 and B_2 are chosen respectively at $(2, 3/2, 3R^{-1})$ and $(1, 3^{1/\gamma}, 3^{1/\gamma}R^{-1})$. Then, the following answers are found for the RP:

$$\Delta S(A \rightarrow B_1) = R \ln(3/2); \quad \Delta S(A \rightarrow B_2) = 0.\quad (22)$$

Consider now the QSP route $A \rightarrow C_1 \rightarrow B_1$ in place of the reversible isotherm. Point C_1 stays at $(2, 1, 2R^{-1})$. It's an *isochore-isobar* combination that yields

$$\begin{aligned}\Delta S(A \rightarrow B_1) &= \Delta S(A \rightarrow C_1) + \Delta S(C_1 \rightarrow B_1) \\ &= C_V \ln(2/3) + C_P \ln(3/2) \\ &= (C_P - C_V) \ln(3/2) = R \ln(3/2).\end{aligned}\quad (23)$$

The agreement of this estimate with (22) is evident. Similarly, by means of another such combination, *viz.*, the QSP route $A \rightarrow C_2 \rightarrow B_2$, we can replace the reversible adiabat. Using C_2 at $(1, 1, R^{-1})$, which is fairly easy to obtain, results emerge as

$$\begin{aligned}\Delta S(A \rightarrow B_2) &= \Delta S(A \rightarrow C_2) + \Delta S(C_2 \rightarrow B_2) \\ &= C_V \ln(1/3) + C_P \ln(3^{1/\gamma}) \\ &= (C_P/\gamma - C_V) \ln 3 = 0.\end{aligned}\quad (24)$$

change is calculated as

$$\begin{aligned}\Delta S(A \rightarrow B) &= \Delta S(A \rightarrow C) + \Delta S(C \rightarrow B) \\ &= 0 + R \ln 2^{(2\gamma-1)/(\gamma-1)} = \frac{(2\gamma-1)}{(\gamma-1)} R \ln 2 \\ &= (2C_P - C_V) \ln 2.\end{aligned}\quad (25)$$

However, there also exists another QSP route to reach B, viz., $A \rightarrow E \rightarrow B$, which is an *isochore-isobar* combination. The point E stays at $(1, 1, R^{-1})$. Therefore, one should be able to arrive at the same result for ΔS (system) as found in (24). We check it below [see (9) and (12)]:

$$\begin{aligned}\Delta S(A \rightarrow B) &= \Delta S(A \rightarrow E) + \Delta S(E \rightarrow B) \\ &= -C_V \ln 2 + C_P \ln 4 = (2C_P - C_V) \ln 2.\end{aligned}\quad (26)$$

The matching is, once again, *precise*.

4.3. Equivalent quasi-static paths

The adequacy of *equivalent quasi-static paths* should now be transparent, as long as we are interested in evaluating only ΔS (system). In case of an RP, Fig. 3 shows how two mutually perpendicular lines in the T - S diagram allow us to join any two given points, the initial and final states of a system. They are very similar to unit vectors (\vec{i}, \vec{j}) on a plane. In the p - V diagram, one should likewise choose an isotherm and an adiabat, but they are non-linear. In Fig. 5, with mutually perpendicular *dotted* lines corresponding to isochore-isobar combination, we indicate how any two points (states) in the p - V diagram may be linked via QSP in order that ΔS evaluations are simplified. The idea is akin to the use of unit vectors (\vec{i}, \vec{j}) on a plane, as mentioned above in the RP context.

5. Conclusions

To summarize, the present work is intended to highlight the *status* of QSP in elementary thermodynamics. While it is known that any RP needs a QSP at the conceptual level, our analysis has established that a QSP can play a bigger role. Particularly, isochoric and isobaric QSP do possess *independent* significance. They are neither RP nor IP.

We have further noted that the definitions D-I to D-IV are meant to differentiate an RP from an IP only. Status of the QSP is different. Specifically, it has turned out that both D-I and D-II

need some modifications for a composite RP, e.g., in presence of one intermediate point. The case is discussed at length in Sec. 3.3, supported by Figs. 1–3. Later, in Sec. 3.6, it has been found that D-III is also unable to distinguish a QSP from an RP, and so is D-IV, at least when we stick to a particular (uniform) averaging scheme. Incompleteness and non-uniqueness in each definition is thus brought to light.

It emerged from our analysis that two different states can always be connected by using two mutually perpendicular QSP lines in the p - V diagram. The spirit is very much the same that one maintains for RP in the T - S diagram. Moreover, we can make profitable use of these mutually perpendicular isochore-isobar QSP lines in calculating entropy changes for a system, as Figs. 4 and 5 reveal. Indeed, this idea of employing 'equivalent quasi-static paths' in ΔS (system) calculations may count as the greatest advantage of such *independent* QSP, as sketched in Sec. 4. Admittedly, however, the notion of 'equivalent reversible paths' has a wider appeal because it offers both ΔS (system) and ΔU .

Finally, our demonstrative calculations have involved only the *ideal* gas. While one may argue that such a choice is quite restrictive, the cases worked out here should *at least* act as proper counter-examples to denounce the *uniqueness* of certain definitions and paradigms.

Dedication

This write-up is dedicated to the memory of my esteemed senior colleague, Dr. S. S. Z. Adnan, of the Department of Chemistry, University of Calcutta.

References

- [1] Zemansky MW, Dittman RH. Heat and Thermodynamics: An Intermediate Textbook (McGraw-Hill, New York, 1997), 7th ed.
- [2] Thomsen JS. Am. J. Phys. 1960;28,119.
- [3] Thomsen JS. Am. J. Phys. 1960;28,564.
- [4] Calkin MG, Kiang D. Am. J. Phys. 1983;51,78.
- [5] Thomsen JS, Bers HC. Am. J. Phys. 1996;64,580.
- [6] Callen HB. Thermodynamics and an Introduction to Thermostatistics (John Wiley and Sons, New York, 1985), 2nd ed.
- [7] Bridgman PW. Rev. Mod. Phys. 1950;22,56.
- [8] Mukhopadhyay D, Bhattacharyya K. arXiv 0911.5010, 2009.
- [9] Castellan GW. Physical Chemistry (Addison-Wesley, Reading, Mass., 1983), 3rd ed.
- [10] Levine IN, Physical Chemistry (McGraw-Hill, New York, 1995), 4th ed.



Prof. Kamal Bhattacharyya has currently (since 2020) been associated with the Department of Chemistry, RKMVCC, as an Emeritus Professor. He did his B.Sc. (Presidency College) in 1975, M.Sc. (Rajabazar Science College) in 1977 and Ph.D. (IACS) in 1985, all from the University of Calcutta. He had served the University of Burdwan during 1985-2005 and then joined the University of Calcutta as Sir Tarak Nath Palit Professor of Chemistry. After his retirement in 2017, he also acted as an Adjunct Faculty in HRI, Prayagraj, during 2018-20. Broadly, his area of research is theoretical physical chemistry.