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Line Integrals and Work in Thermodynamics

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I. SYNOPSIS

Introductory thermodynamics for chemists usually involves starting with heat and work, and working one's way to energy, enthalpy, etc..

Work, for chemists, is so out of the common experience (sic!, smile) that it behooves us to spend some time differentiating between work of the common sort, i.e., studying, waiting on tables, earning a living, etc., and work as the physicist defines it, especially in the context of thermodynamics.

II. INTRODUCTION

Work is a path integral, and that in itself is daunting for some chemistry students. When we write that force moving through a distance constitutes work, we are employing the physicists definition of work. Anything else is colloquial nonsense as far as thermodynamics is concerned.

Moving a force through a distance, for simple forces (say constant) becomes

$$force \times distance$$

but if the force is varying as we move it along, we need to amend this to

$$\int force(x) \times dx$$

where force(x) is a spatially varying force, i.e., its value depends on where we are, and dx is a small (infinitesimal) step along the x-axis. This integral, from x_{start} to x_{finish}, is the total work along the path from start to finish, i.e.,

$$\int_{start}^{finish} f(x) \times dx \equiv \int dw$$

where we are equating a differential element of work, dw, with f(x)dx.

III. A NON-WORK LINE INTEGRAL

The ability to do line integrals is central to the study of the first part of thermodynamics. Consider the arbitrary invented function

$$w(x,y) = x^2 y - e^{xy}$$

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whose differential form would be

$$dw = (2xy - ye^{xy})\, dx + \left(x^2 - xe^{xy}\right) dy \tag{3.1}$$

We will do two line integrals involving this particular integrand.

A. I_1 and I_2

The first integral of dw will be along the straight line paths denoted as $path_1 \rightarrow$ (x,y) = (0,0) $\rightarrow$ (0,1) and then, second, from (0,1) $\rightarrow$ (1,1), as shown in Figure 1. For the first part of the path, we have

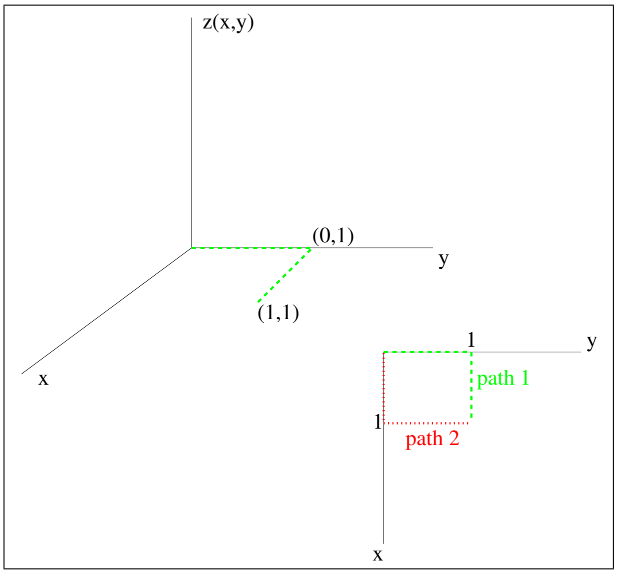

FIG. 1: The line integral's $path_1 \rightarrow (I_1$ and $I_2)$ from (0,0) to (0,1) to (1,1) and $path_2 \rightarrow$ (I_3 and I_4) from (0,0,) to (1,0) to (1,1)

$$I_1 = \int_{0,0}^{0,1} \left((2xy - ye^{xy})\, dx + \left(x^2 - xe^{xy}\right) dy \right) \tag{3.2}$$

Since dx is equal to zero if we are following a path of constant x, i.e.,

$$I_1 = \int_{0,0}^{0,1} \left(x^2 - xe^{xy}\right) dy$$

and with x = 0, and

$$I_1 = \int_{0,0}^{0,1} \left(0^2 - 0e^{0y}\right) dy \rightarrow 0$$

For the second part of the path we have

$$\int_{0,1}^{1,1} (2xy - ye^{xy})\, dx \rightarrow \int_{0,1}^{1,1} \left(2x1 - 1e^{x1}\right) dx \rightarrow$$

$$\left(2\frac{x^2}{2} - e^x\right)\Big|_0^1 \rightarrow 1 - e - (-1) \rightarrow 2 - e = I_2 \tag{3.3}$$

since $y = 1$ for this part and dy is zero. The total integral, the sum of the two parts, is just $2 - e$.

One needs to understand why dx is not included in the line integral of the first part (x isn't varying) and why dy is not included in the second part (y is not varying, just x). One needs to understand that on the first part of the path, $x = 0$ always, while on the second part of the path, $y = 1$ (always).

B. I_3 and I_4

We now re-perform the path integration, this time taking an alternative path which ends at the same point, (1,1). This time, we choose $path_2 \rightarrow$ (0,0) $\rightarrow$ (1,0) followed by (1,0) $\rightarrow$ (1,1). This is shown on Figure 1.

For the first part, we have

$$I_3 = \int_{0,0}^{1,0} \left((2xy - ye^{xy})\, dx + \left(x^2 - xe^{xy}\right) dy\right)$$

with $y = 0$, i.e.,

$$\int_{0,0}^{1,0} \left(2x0 - 0e^{x0}\right) dx$$

which is zero. For the second part, we have

$$I_4 = \int_{1,0}^{1,1} \left(1^2 - 1e^{1y}\right) dy$$

which gives

$$I_4 = y - e^y|_0^1$$

$$I_2 = 1 - e^1 - \left(0 - e^0\right)$$

or

$$path_2 = 1 - e^1 + 1 \rightarrow 2 - e \tag{3.4}$$

That equation 3.3 is the same as equation 3.4 is extraordinary, and we will see (*vide infra* that there is a general property here to be studied. But before we do that, let's attempt to destroy that property.

IV. CHANGING (DESTROYING) THINGS SLIGHTLY

Imagine we looked at equation 3.1 and for some odd reason, needed to perform the integral (using a differential work element slightly altered from before):

$$dw = (2x - ye^{xy})\, dx + \left(x^2 - xe^{xy}\right) dy \tag{4.1}$$

yielding an integral:

$$\int_{0,0}^{0,1} \left((2x - ye^{xy})\, dx + \left(x^2 - xe^{xy}\right) dy\right)$$

instead, where the term $2xy$ became $2x$ relative to equation 3.2 i.e.,

$$\int_{0,0}^{0,1} \left((2x - ye^{xy})\, dx + \left(x^2 - xe^{xy}\right) dy\right) \tag{4.2}$$

Again, we do the integral following two paths, although this time we'll skip some details.

We have, for the path (x,y) = (0,0) $\rightarrow$ (0,1) and then from (0,1) $\rightarrow$ (1,1), so for the first part, when x=0, we have

$$I_5 = \int_{0,0}^{0,1} \left(0^2 - 0e^{0y}\right) dy \rightarrow 0$$

and for the second part, when y=1 we have

$$I_6 = \int_{0,0}^{0,1} \left(2x - 1e^{x1}\right) dx = \left(2\frac{x^2}{2} - e^x\right)\Big|_0^1$$

$$I_5 = 1 - e - (-1) = 2 - e$$

The total value is then $2 - e$.

Finally

$$\int_{0,1}^{1,1} \left((2x - ye^{xy})\, dx + \left(x^2 - xe^{xy}\right) dy\right)$$

which has y fixed at 1. Therefore,

$$I_6 = \int_0^1 (2x - e^x)\, dx$$

which becomes

$$I_6 = (x - e^x)|_0^1$$

which is, finally

$$I_6 = 1 - e^1 - (1 - e^0)$$

so out final results is $-1 - e$ which is not equal to the value obtained using the other path!

We've destroyed something, and made the integral path dependent rather than path independent!

V. COMBINING THE TWO PATHS BY DOING A "CIRCULAR" INTEGRAL

If this is clear, then what is the integral of the same integrand about the path:

$$(x, y) = (0, 0) \rightarrow (0, 1)$$

and then from

$$(0, 1) \rightarrow (1, 1)$$

and then from

$$(1, 1) \rightarrow (1, 0)$$

and then from

$$(1, 0) \rightarrow (0, 0)$$

This is the path completely around the square, isn't it? Symbolically, one has

$$\oint \left(x(s)^2 y(s) - e^{x(s)y(s)} \right) ds$$

where s is the path.

It is possible to combine $path_1$ and the reverse of $path_2$ (see Equation 3.4)to get this "circular" path, "circular" only in the closed nature of the path, since the actual path is "square".

If we reverse $path_2$, we obtain $e - 2$ for its value, i.e., $1(2 - e)$, so that the sum of $path_1$ (see Equation 3.3)and reversed $path_2$ is zero.

Ah Hah!

Now we've gotten somewhere. For the kind of objects whose integral does not depend on path, an integral from $(a, b) = start$ to $(c, d) = finish$ gives a value regardless of the path we choose to employ, and the integral from (a, b) to (c, d) and then back again to (a, b) gives zero, since we've followed the topological equivalent of a circle back to where we started.

A. Pressure as an example

Consider the pressure of an ideal gas,

$$p = \frac{nRT}{V} = \frac{RT}{v}$$

where V is the actual volume and v is the molar volume, V/n.

We know that $p[v, T]$ is a function of v and T, which we indicate with square brackets (so as not to confuse arguments with multiplication). That means that we can plot $p[v, T]$ versus v and T in a three dimensional plot, and at constant v, we can observe the intersection of the constant v plane with the surface of $p[v, T]$ giving rise to a locus of intersection points which constitutes an isochore.

Equivalently, we can choose a plane of constant T, and plot $p[v, T]$ versus v giving rise to the familiar Boyle's law hyperbola.

For any gas we know that

$$dp = \left(\frac{\partial p}{\partial T} \right)_v dT + \left(\frac{\partial p}{\partial v} \right)_T dv$$

so we could ask, what is the change in pressure in going from p_1 to p_2 where (for an ideal gas)

$$p_1 = \frac{RT_1}{v_1}$$

and

$$p_2 = \frac{RT_2}{v_2}$$

Clearly, $\int_{v_1,T_1}^{v_2,T_2} dp = p_2 - p_1$. p is a property, and knowing v_1, T_1 we know p_1 and the same for condition 2. Therefore, the change in pressure is just that, $p_2 - p_1$.

What if we formally wished to actually do a path integral, say

$$\int_{v_1,T_1}^{v_2,T_2} dp = \int_{v_1,T_1}^{v_2,T_2} \left\{ \left(\frac{\partial p}{\partial T} \right)_v dT + \left(\frac{\partial p}{\partial v} \right)_T dv \right\}$$

and let's choose a path $(v_1, T_1) \rightarrow (v_1, T_2) \rightarrow (v_2, T_2)$ in analogy with what we've done before. Clearly, we need to do these two integrals the same as we did the opening integrals, i.e.,

$$II_1 = \int_{v_1,T_1}^{v_1,T_2} \left\{ \left(\frac{\partial p}{\partial T} \right)_v \right\} dT + \left\{ \left(\frac{\partial p}{\partial v} \right)_T \right\} dv$$

and

$$II_2 = \int_{v_1,T_2}^{v_2,T_2} \left(\frac{\partial p}{\partial T} \right)_v dT + \left(\frac{\partial p}{\partial v} \right)_T dv$$

II_1 is being done at constant v and II_2 is being done at constant T, and the sum of the two should be the answer we desire.

Let us do these integrals in turn. For II_1 we have

$$II_1 = \int_{v_1,T_1}^{v_1,T_2} \left(\frac{\partial p}{\partial T} \right)_v dT$$

since v is constant. Evaluating the partial derivative we have

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v}$$

so the integral becomes

$$II_1 = \int_{v_1,T_1}^{v_1,T_2} \frac{R}{v} dT = \frac{R}{v_1} \int_{v_1,T_1}^{v_1,T_2} dT = \frac{R}{v_1} (T_2 - T_1)$$

II_2 becomes, integrating at constant T and knowing that

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{v^2}$$

so that

$$II_2 = -\int_{v_1,T_2}^{v_2,T_2} \frac{RT_2}{v^2} dv = RT_2 \left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$

Now $II_1 + II_2$ becomes

$$\frac{RT_2}{v_1} - \frac{RT_1}{v_1} + \frac{RT_2}{v_2} - \frac{RT_2}{v_1}$$

which gives us the expected result!

B. Altering (destroying) the integral's path independence

We had

$$\int_{v_1,T_1}^{v_1,T_2} \frac{R}{v} dT + \int_{v_1,T_2}^{v_2,T_2} \frac{RT}{v^2} dv$$

for the sum of the two path integrals.

Now again, we surgically change one of these terms, attempting to destroy what we have. Now we posit

$$\int_{v_1,T_1}^{v_1,T_2} \frac{R}{v} dT + \int_{v_1,T_2}^{v_2,T_2} \frac{RT_2}{v} dv$$

where we've changed v^2 arbitrarily to v^1 in the second term. We obtain

$$\frac{R}{v_1}\left(T_2 - T_1\right) - RT_2 \ell n \frac{v_2}{v_1}$$

which is very, very different from the result we got before. So different in fact that we have to face the fact that when the integrand was derived from partial differentiation from a formula ($p = \frac{RT}{v}$) rather than arbitrary functions, something happened to make the path integrals ultimately independent of path and solely dependent of end points. for the sum of the two path integrals.

C. The point

So finally we conclude that there are two kinds of integrals we are interested in, those which depend on path, and those which don't. The ones that don't correspond to properties, such as the pressure, volume or temperature, and including the energy, enthalpy, entropy and various free energies. The ones that depend on path, corresponding to heat and work, need to have a path specified, because we *can not* condense them into a form

$$\int_{start}^{finish} d(something) = something_{finish} - something_{start}$$

such as

$$\int_{p_1}^{p_2} dp = p_2 - p_1$$

and

$$\int_{T_1}^{T_2} dT = T_2 - T_1$$

$$\int_{v_1}^{v_2} dv = v_2 - v_1$$

and finally

$$\int_{condition_1}^{condition_2} dE = E_2 - E_1$$

VI. WORK (AT LAST)

On the other hand, work, as defined by the physicists, is moving a force through a distance, which for us is the resisting force, expressed via a resisting pressure, i.e.,

$$f_{res} = p_{res} A$$

so

$$f_{res} dx = p_{res} A dx = p_{res} dv$$

since Adx is the infinitesimal change in volume. To add up all the infinitesimal dx's creates the overall work in going from the starting point, wherever that is, to the ending point, i.e.,

$$work = -\int_{condition_1}^{condition_2} p_{res} dv$$

where we have arbitrarily chosen to work with the molar expressions temporarily (v rather than V). Now, the trick in thermodynamics discussions is to understand how to evaluate this integral (which is a line line integral, being path dependent) given the specification of path. So now we explore these various paths. We start with irreversible paths, i.e., those in which the resisting pressure does not equal the actual pressure of the gas under consideration. Oh, did we forget to mention that we're dealing with gases, and that most of our examples will be ideal gases (with perhaps an occasional excursion to van der Waals gases)?

A. irreversible paths

The most famous irreversible path is the one in which a gas expands against a zero pressure, i.e., into a vacuum. We then have

$$work = -\int_{condition_1}^{condition_2} zero\ dv = 0$$

no matter where we started from and where we end up.

The second most famous irreversible path is the one in which a gas expands against a constant non-zero pressure. We picture the gas as existing in a vertical piston/cylinder arrangement with masses sitting on the top of the piston to establish the beginning equilibrium pressure. Next, we remove some part of the mass on the piston so that instantaneously, the resisting pressure is less than the starting equilibrium pressure. As a result, the piston will rise, coming to a stop when the internal pressure equals the external pressure created by the (reduced) mass on the top of the piston. The work then will be

$$work = -\int_{\frac{RT}{p_i}}^{\frac{RT}{p_f}} p_f dv$$

where p_i is the starting pressure, and p_f is the ending (final, reduced) pressure. Clearly, since p_f is constant, the integral is

$$work = -p_f \int_{\frac{RT}{p_i}}^{\frac{RT}{p_f}} dv$$

$$work = -p_f \left(\frac{RT}{p_f} - \frac{RT}{p_i} \right)$$

B. The passage from irreversible to reversible paths

To construct a reversible work path in which we will pass to the limit of an infinite number of irreversible paths appended together, we use an example of isothermal irreversible work, as illustrated in Figure 3. The four constant pressure expansions (against changing static pressures) are carried out irreversibly. The total work is the sum of the work associated with each of the four constant pressure steps, each chosen (in our example) to have one fourth of the pressure drop assigned in going from the initial to the final pressure.

We then have

$$\begin{aligned} w_{irrev} &= \\ &+p_2(v_2 - v_{initial}) \\ &+p_3(v_3 - v_2) \\ &+p_4(v_4 - v_3) \\ &+p_{final}(v_{final} - v_4) \end{aligned} \quad (6.1)$$

which becomes

$$\begin{aligned} w_{irrev} &= \\ &+p_2\left(\frac{nRT}{p_2} - \frac{nRT}{p_{initial}}\right) \\ &+p_3\left(\frac{nRT}{p_3} - \frac{nRT}{p_2}\right) \\ &+p_4\left(\frac{nRT}{p_4} - \frac{nRT}{p_3}\right) \\ &+p_{final}\left(\frac{nRT}{p_{final}} - \frac{nRT}{p_4}\right) \end{aligned} \quad (6.2)$$

or

$$\begin{aligned} w_{irrev} &= \\ +nRT\Bigg[&p_2\left(\frac{1}{p_2} - \frac{1}{p_{initial}}\right) \\ &+p_3\left(\frac{1}{p_3} - \frac{1}{p_2}\right) \\ &+p_4\left(\frac{1}{p_4} - \frac{1}{p_3}\right) \\ &+p_{final}\left(\frac{1}{p_{final}} - \frac{1}{p_4}\right)\Bigg] \end{aligned} \quad (6.3)$$

or

$$\begin{aligned} w_{irrev} &= \\ +nRT\Bigg[&\left(1 - \frac{p_2}{p_{initial}}\right) \\ &+\left(1 - \frac{p_3}{p_2}\right) \\ &+\left(1 - \frac{p_4}{p_3}\right) \\ &+\left(1 - \frac{p_{final}}{p_4}\right)\Bigg] \end{aligned} \quad (6.4)$$

or

$$\begin{aligned} w_{irrev} &= \\ +nRT\Bigg[&\left(1 - \frac{p_{initial} + \Delta p}{p_{initial}}\right) \\ &+\left(1 - \frac{p_2 + \Delta p}{p_2}\right) \\ &+\left(1 - \frac{p_3 + \Delta p}{p_3}\right) \\ &+\left(1 - \frac{p_4 + \Delta p}{p_4}\right)\Bigg] \end{aligned} \quad (6.5)$$

which becomes, finally,

$$\begin{aligned} w_{irrev} &= \\ -nRT\Bigg[& \\ \left(\frac{\Delta p}{p_{initial}}\right) + \left(\frac{\Delta p}{p_2}\right) &+ \left(\frac{\Delta p}{p_3}\right) + \left(\frac{\Delta p}{p_4}\right)\Bigg] \end{aligned} \quad (6.6)$$

Therefore, the total work is

$$w_{irrev} = -nRT \sum_{i=1}^{i=4} \frac{\Delta p}{p_i}$$

It is clear that this can be re-written, in the limit that Δp goes to zero, and the number of steps increases commensurately, to

$$w_{rev} = -nRT \int_{p_{start}}^{p_{end}} \frac{dp}{p}$$

which is the standard logarithmic result. Each infinitesimal irreversible step has the resisting pressure equal to the gas pressure, so the work is no long irreversible, but reversible.

Note that one can not easily treat the compression in the same terms, but the mathematical result is commensurate.

VII. A DIFFERENT PATH

If, instead of using equal Δp values at each step, we used equal ratios of pressures, we would have (possibly) a different result. Let's set the number of steps we will use as m, and set the ratio to

$$ratio = \left(\frac{p_f}{p_i}\right)^{\frac{1}{m}}$$

where p_f is the final pressure and p_i is the initial pressure.

We had

$$\begin{aligned} w_{irrev} &= \\ +nRT \Bigg[\left(1 - \frac{p_2}{p_{initial}}\right) \\ + \left(1 - \frac{p_3}{p_2}\right) \\ + \left(1 - \frac{p_4}{p_3}\right) \\ + \left(1 - \frac{p_{final}}{p_4}\right)\Bigg] \end{aligned} \quad (7.1)$$

as Equation 6.4, which we now rewrite under the current assumptions as

$$\begin{aligned} w_{irrev} &= \\ +nRT\,[(1 - ratio) \\ + (1 - ratio) \\ + (1 - ratio) \\ + (1 - ratio)] \end{aligned} \quad (7.2)$$

which, obviously, is

$$w_{irrev} = +nRTm\,(1 - ratio)$$

What then is w_{irrev} in the expression

$$\lim_{m\to\infty}\left(w_{irrev} = -nRTm\left(1 - \left(\frac{p_f}{p_i}\right)^{1/m}\right)\right) \to w_{rev} \quad (7.3)$$

in the limit that the number of steps is raised to larger and larger values, approaching infinity?

In elementary calculus, we learned about taking limits such as this, and were introduced to L'Hôpital's Rule as an isolated exercise which (usually) occurred on one examination paper as one question, and that was the end of it. It is therefore amusing that in our context, L'Hôpital's Rule plays the dominant role that it does.

Since L'Hôpital's Rule is taught almost exclusively in the form of a ratio, we recast the above in that form, ignoring the prefixed constant for the time being and obtaining:

$$ratio = \frac{\left(1 - \left(\frac{p_f}{p_i}\right)^{1/m}\right)}{\frac{1}{m}}$$

Now, we have the task according to L'Hôpital to take the derivatives of the numerator and denominator of this ratio (with respect to m), i.e., for the future numerator we have:

$$numerator = \frac{\partial\left(1 - \left(\frac{p_f}{p_i}\right)^{1/m}\right)}{\partial m}$$

We re-write this as

$$numerator = -\frac{\partial e^{\ell n\left(\frac{p_f}{p_i}\right)^{\frac{1}{m}}}}{\partial m}$$

and again:

$$numerator = -\frac{\partial e^{\frac{1}{m}\ell n\left(\frac{p_f}{p_i}\right)}}{\partial m}$$

which is

$$numerator = -e^{\frac{1}{m}\ell n\left(\frac{p_f}{p_i}\right)}\ell n\left(\frac{p_f}{p_i}\right)\frac{\partial\frac{1}{m}}{\partial m}$$

and one more time (into the fray):

$$numerator = +e^{\frac{1}{m}\ell n\left(\frac{p_f}{p_i}\right)}\ell n\left(\frac{p_f}{p_i}\right)\partial\frac{1}{m^2}$$

The emergent denominator becomes

$$denominator = \frac{\partial\frac{1}{m}}{\partial m}$$

which is elementary, yielding

$$denominator = -\frac{1}{m^2}$$

so the ratio we seek has the form

$$ratio = \frac{e^{\frac{1}{m}\ell n\left(\frac{p_f}{p_i}\right)}\ell n\left(\frac{p_f}{p_i}\right)\partial\frac{1}{m^2}}{-\frac{1}{m^2}}$$

Thus, the final result (i.e., the value of Equation 7.3 becomes

$$w = -nRT\ell n\left(\frac{p_f}{p_i}\right)$$

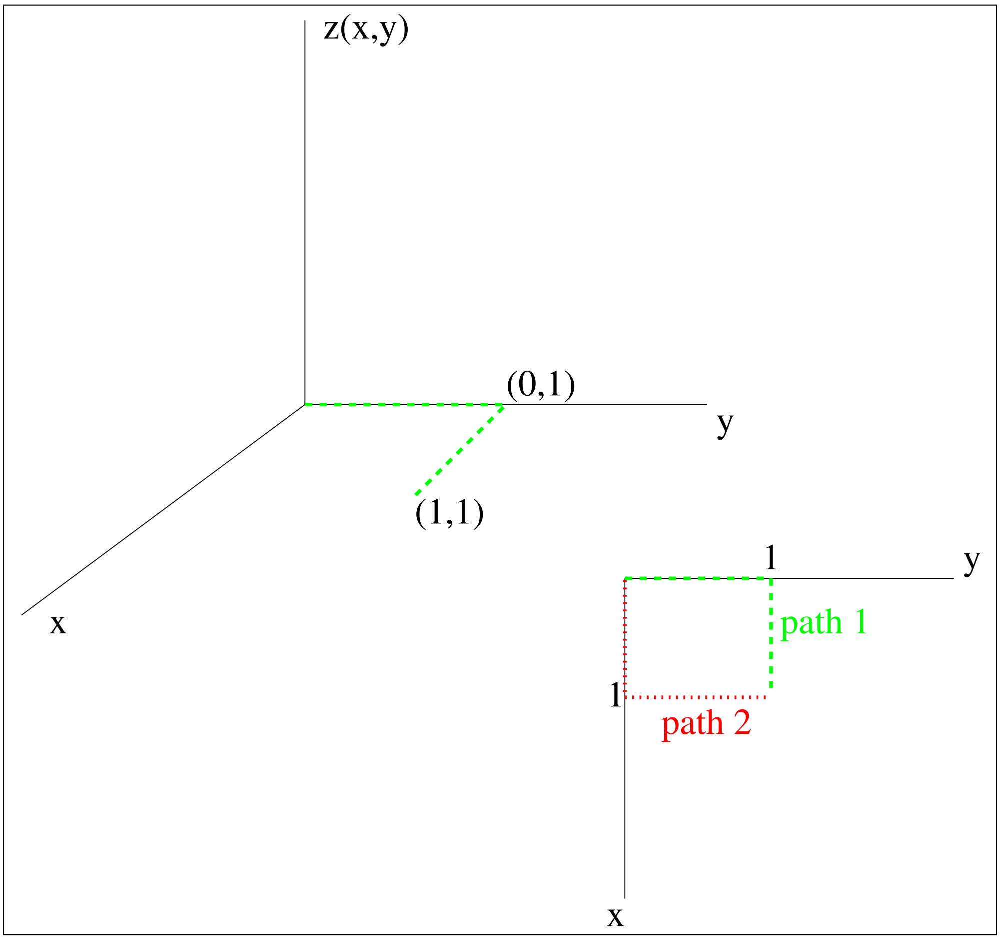

FIG. 2: The line integral's path from (0,0) to (0,1) to (1,1)

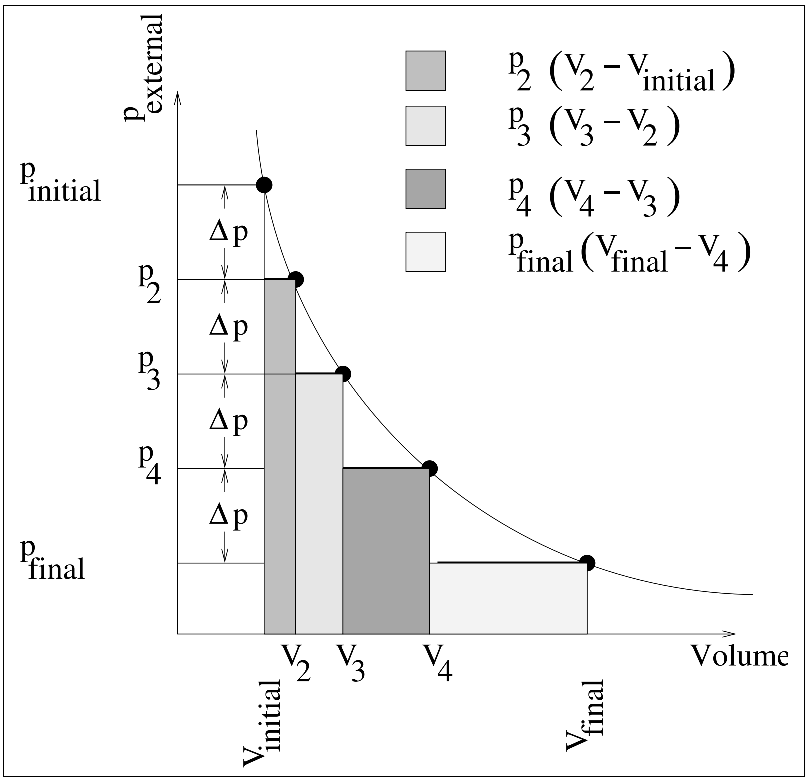

FIG. 3: Isothermal irreversible work with constant Δp steps

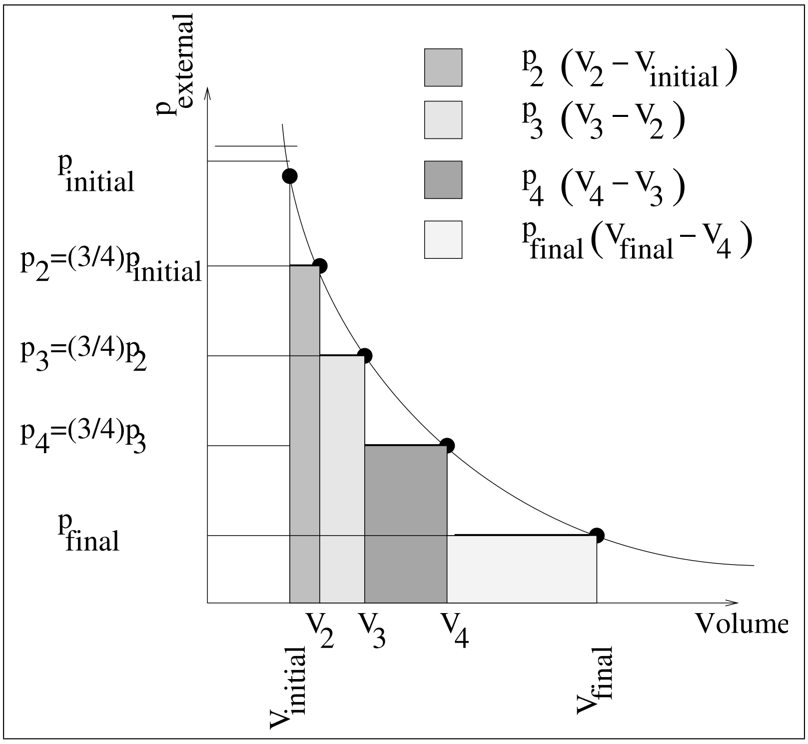

FIG. 4: Isothermal irreversible work with constant ratio of pressure steps