Work Done During Reversible and Irreversible Isothermal Expansion of an Ideal Gas

by

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Abstract

This exercise examines how the work associated with stepwise irreversible isothermal expansions and compressions of an ideal gas changes as the number of steps is increased. It uses the graphing power of Mathcad to lead the user to discover that the work approaches an asymptote as the number of steps becomes very large and that that asymptote is the work for the reversible expansion or compression. It then challenges the user to recognize that the work for the reversible expansion or compression represents a limiting value for the work for the corresponding irreversible processes.

Goals

The goals of this exercise are to help the user to discover in a clear, visual, concrete way

1. that, when an ideal gas is expanded or compressed isothermally in a series of steps in which P_{ex} is decreased or increased instantaneously and then held constant while the system returns to equilibrium, as the number of steps increases and the size of each step decreases the work for the expansion or compression approaches that for the corresponding reversible process, and by implication that the irreversible process approaches reversibility;

2. that the work for the reversible expansion or compression represents a limiting value of the work for the corresponding irreversible processes.

Performance Objectives

After completing this exercise the user should

1. be able to describe how the work for stepwise isothermal expansions and compressions of an ideal gas change as the number of steps increases, including sketching graphs of the work vs. the number of steps and relating that graph to the work for the corresponding reversible expansion or compression;
2. recognize that the work for the reversible expansion or compression is the limiting value of the work for the corresponding irreversible expansions or compressions.

References and Suggestions for Further Reading

1. Sibley, Robert J.; Alberty, Robert A *Physical Chemistry*, 3rd ed.; John Wiley & Sons: New York, 2001; Section 2.5

2. Joshi, Bhairav D. *J. Chem. Educ.* **1986,** 63, 24-25

Introduction

The work resulting from the expansion or compression of a gas is PV work, for which the equation is

$$w = -\int_{V_{initial}}^{V_{final}} P_{ex}\,dV \qquad (1)$$

where P_{ex} is the pressure exerted by the surroundings on the system. By the definition of a reversible process, a reversible expansion is one that occurs so slowly that the system always remains in equilibrium, both internally and with the surroundings. When the system and surrounding are in equilibrium, P_{ex} = P of the system. Therefore, for a reversible expansion

$$w = -\int_{V_{initial}}^{V_{final}} P\,dV \qquad (2)$$

For an irreversible expansion P_{ex} has to be used in the calculation of w. The irreversible expansions we will look at will involve a series of steps in which the gas starts out at equilibrium, P_{ex} is dropped instantaneously from one value to a new lower one and is held constant at the new value while the gas expands until a new equilibrium is reached. Then P_{ex} is instantaneously dropped again to start the next step. For example, the expansion of a gas from a pressure of 10 atm to a pressure of 1 atm might happen in a series of 1-atm steps, with P_{ex} first dropping instantaneously from 10 atm to 9 atm and holding there until the gas has expanded enough to come into equilibrium with it, then dropping to 8 atm, etc. (The sudden drop in pressure at the beginning of each step destroys the equilibrium attained at the end of the last step, and it is this destruction of equilibrium that makes the expansion irreversible.) Since P_{ex} is constant during each of these steps, the value of w for each step as calculated from Equation 1 is simply $-P_{ex}\Delta V$, where P_{ex} is the value of P_{ex} for that step and ΔV is the change in volume during that step. The total work for the expansion is the sum of the values of w for the individual steps.

In this exercise we will examine how the work for an irreversible stepwise expansion of 1 mole of an ideal gas at 300 K from a pressure of 10 atm to a pressure of 1 atm changes as the number of steps is increased and will compare the work for the irreversible expansions to the work for a reversible expansion of the same gas between the same two pressures.

Setting Up Parameters That Apply to All of the Expansions

$P_{initial} := 10 \cdot atm \quad P_{final} := 1 \cdot atm \quad T := 300 \cdot K \quad R := .08205 \cdot \frac{liter \cdot atm}{K}$ (1 mole assumed)

$V_{initial} := \frac{R \cdot T}{P_{initial}} \qquad V_{final} := \frac{R \cdot T}{P_{final}}$

Establishing Arrays for P_{ex}, V, and w

Our approach will be to set up arrays for P_{ex}, V and w. Each element of P_{ex} will be the external pressure during a step in the expansion and will be smaller than the previous one by an amount **int** gotten by dividing the range between $P_{initial}$ and P_{final} by the number of steps the expansion will take. Each element of V will be the volume of the gas at the end of a step, when it is in equilibrium with the corresponding value of P_{ex}. Each value of w will be the work for a step, which is equal to $-P_{ex}$ for the step times the change in volume during the step, calculated as the difference between the volume at the end of the step and the volume at the end of the previous step. The total work will be the sum of the elements of the w array. Note that the values of the 0th elements of the P_{ex} and V arrays are set manually and that the range value **i** starts at 1 rather than the more customary 0 used in Mathcad.

$Steps := 1$

$P_{ex_0} := P_{initial}$ $\quad V_0 := V_{initial}$ $\quad int := \dfrac{P_{initial} - P_{final}}{Steps}$

$i := 1 .. Steps$

$P_{ex_i} := P_{ex_{i-1}} - int$ $\quad V_i := \dfrac{R \cdot T}{P_{ex_i}}$ $\quad w_i := -P_{ex_i} \cdot \left(V_i - V_{i-1}\right)$

$w_{total} := \sum_i w_i$ $\quad w_{total} = -2.245 \times 10^3 \, J$

Exercise 1

Before you start, use the **Enter** key to create a big chunk of blank space to work in below this text box. (Click on any text in this box to see the outlines of the box and where it ends.) Then create two vectors, **x** and **y**, each with 10 elements. To create **x** type **x:** and then **Ctrl-m** (or click on the matrix symbol on the Matrix palette on the Math toolbar) to insert a matrix. From the dialog box select 10 rows and 1 column. Do the same to create **y**. You may have to move the vector regions down to keep them from overlapping text or equations. **x** and **y** will both be shown with 10 empty place holders.

Make sure that the variable Steps given above equals 1, then replace the first place holder in **x** with 1 and the first place holder in **y** with the value of w_{total} that is given above. (Remember that to express the power of 10 in a number in scientific notation you have to use *10^power.) Change the value of Steps, enter the new value of Steps in place of the second place holder in **x** and the new value of w_{total} for the second place holder in **y**. Repeat 8 more times until you have completed the vectors **x** and **y**. **Make sure that your values of Steps cover a large range, with the largest value being at least 5000.** (The values 1, 2, 10, 25, 50, 100, 500, 1000, 5000, 10000 work well, but you may want to experiment with other values as well.)

In a space below your **x** and **y** vectors create a 2-dimensional graph (type the @ symbol or select x-y plot from the graph palette in the Math toolbar) of y as a function of x.

Answer each of the questions in this exercise in the space below the text box containing the question. Use the Enter key to clear space for your answer.

a. What does the graph you created above look like? Does it look very useful?

Click on the graph, select Format-Graph-XY Plot from the main toolbar, and check Log Scale for the x-axis.

b. Does this make the graph look better? Explain.

c. Describe the graph.

d. What happens to w_{total} as the number of steps gets larger?

e. What happens to the size of each step as the number of steps gets larger?

f. Is there a correlation between w_{total} and the size of the steps?

g. What happens to the graph, and the value of w_{total}, as the number of steps gets very large?

Calculate the work for the reversible expansion of 1 mole of an ideal gas between the same two pressures. The easiest way to do this is to copy Equation 2, substitute the assignment operator (:) for the equal sign, and make the appropriate substitution for P. Then on a separate line type w=. (Notice how quickly and easily Mathcad evaluates the integral.)

h. Compare the values of w_{total} for the irreversible expansions with the value of w for the reversible expansion. Are the values of w_{total} for the irreversible expansions larger or smaller than the value of w for the reversible expansion? Take the sign into account in giving your answer

i. What happens to the difference between the values of w_{total} for the irreversible expansions and the value of w for the reversible expansion as the number of steps gets larger?

j. Does the value of w_{total} ever "pass" the value of w for the reversible expansion (switch from being larger to being smaller or vice versa)?

k. Can you think of a mathematical term that describes the relationship between w for the reversible expansion and the values of w_{total} for the irreversible expansions?

Exercise 2

Repeat Exercise 1 for the compression, rather than the expansion, of the gas. This can be done very easily by simply reversing the values of $P_{initial}$ and P_{final}, recalculating the value of w_{total} for each value of Steps in the **x** vector, and replacing each element in the **y** vector with the new value of w_{total} for the corresponding value of Steps. Actually, in order to facilitate comparison between the data for the expansion and the compression, you may want to create new vector **yy** to contain the w_{total} values for the compression and create a new graph of **yy** as a function of **x**. **yy** can be created the same way that **y** was. **Answer the questions in Exercise 1 for the compression.**

l. Can you think of an expression of the relationship between the values of w for the reversible and irreversible processes that applies to both the expansion and the compression?

m. Compare the values of w for the reversible expansion and the reversible compression of the gas. Are they related? If so, how?

Using the **Enter** key create a create a sufficiently large section of blank space below and c opy your graph of **y** as a function of **x** into it. Add **-yy** as a variable on the vertical axis of the graph.

m. What does this graph tell you about the relationship between w_{total} for the irreversible expansions and the irreversible compressions as the number of steps becomes very large?