

Carnot Knowledge

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Abstract

The Carnot cycle is illustrated with numerical calculations on an ideal, monatomic gas. An elementary exercise is to investigate the consequences on the net work and the thermodynamic efficiency of changing variables such as the pressure to which expansion occurs, and the working temperatures of the process. $p dV$ is integrated using the trapezoid rule, and the area under p vs v is illustrated for each of the four steps of the process.

A much more challenging problem is to repeat the process, except for a real gas equation of state. The van der Waals model of methane is thoroughly illustrated as an example; the instructor can decide how much of this help would be provided to students. Student groups might be assigned different gases or different equations of state, with as much of the van der Waals development provided as is appropriate for the course and the students.

Objectives

After completing this assignment, all students should be able to identify the variables that affect the efficiency of the Carnot cycle (and some that do not). Those who complete the non-trivial challenge of computing the cycle for a non-ideal gas will be able to convert given pressure-temperature conditions into the corresponding volume, or the inverse, for gases that do not obey the simplest equation.

Goals

1. To gain an understanding of the four steps of the Carnot cycle for a monatomic ideal gas through their graphical depiction.
2. To investigate the effect on the efficiency of the process of changing the volume to which the gas is expanded.
3. To investigate the effect on the efficiency of the process of changing the high and low temperatures of the cycle.
4. To observe how using a van der Waals model of methane as the working fluid changes the manner in which the cycle must be calculated.
5. To investigate the consequences of using the van der Waals parameters of a gas other than methane.
...and for the advanced, ambitious and/or foolhardy student or group of students:
6. To create a new worksheet, using as a template as much as necessary of the van der Waals example, that computes the Carnot cycle for a different equation of state.

Introduction

The Carnot cycle is an idealized heat engine that converts into work a fraction of the heat flowing from a high temperature reservoir to a lower temperature sink. In this tutorial-exercise, you will be able to investigate what happens when the temperature and pressures of the cycle are changed. The calculations shown assume that the monoatomic gas sample (one mole) behaves ideally. A challenge to the ambitious student is to modify this worksheet so that it calculates the same steps, except for a nonideal gas.

A Carnot cycle consists of four steps:

- Starting at some initial temperature and volume, a sample of gas undergoes reversible expansion isothermally to a new volume. This occurs while the gas is in contact with the hot reservoir, so heat flows into the gas.
- The gas is insulated from its surroundings while it undergoes reversible adiabatic expansion. The temperature falls to a lower value, that of the low-temperature sink.
- While in contact with the low-temperature heat sink, it is reversibly and isothermally compressed to a smaller volume. Heat flows into the cold sink. The volume to which it is compressed is that which will allow the fourth step to complete the cycle.
- Again isolated from its surroundings, the gas is reversibly and adiabatically compressed back to the original volume, while the temperature increases back to its original value.

$$\text{bar} \equiv 10^5 \cdot \text{Pa}$$

$$R \equiv 0.08314 \cdot \frac{\text{L} \cdot \text{bar}}{\text{K}}$$

In step a, the work done on the gas is given by $-RT \ln V_2/V_1$, where V_2 is the new volume and V_1 is the original volume. This is the same as the area under the graph of pressure versus volume, as is the case in each of the other steps of the cycle.

Let $P_1 = 20 \text{ bar}$ and $T_{\text{hot}} = 400 \text{ K}$, and the first expansion be until the pressure is 4 bar.

$$P_1 := 20 \cdot \text{bar}$$

$$P_2 := 4 \cdot \text{bar}$$

$$T_{\text{hot}} := 400 \cdot \text{K}$$

$$i := 0..100$$

$$V_1 := \frac{R \cdot T_{\text{hot}}}{P_1}$$

$$V_2 := \frac{R \cdot T_{\text{hot}}}{P_2}$$

$$V_1 = 1.663 \times 10^{-3} \text{ m}^3$$

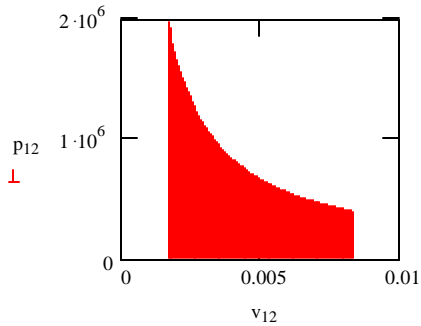
$$V_2 = 8.314 \text{ liter}$$

The initial and final volume are computed from the ideal gas equation. The work involved in each step is computed by a trapezoidal approximation of the area under the P-V curve. We divide the pressure change into 100 steps and sum $P \times \Delta V$ for each of them. v_{12_i} is the volume at each step, i , from V_1 to V_2 . In SI units, volume is measured in cubic meters and the pressure in bars. One liter = 10^{-3} m^3 .

$$v_{12_i} := V_1 + i \cdot \left(\frac{V_2 - V_1}{100} \right)$$

$$P_{12_i} := \frac{R \cdot T_{\text{hot}}}{v_{12_i}}$$

The red area represents the work done on the gas during expansion. It is calculated numerically below using "the trapezoid rule". The first term in the sum is the average pressure during the step, and the second is the change in volume. Their product is summed to get the integral.



$$w_{12} := - \sum_{i=0}^{99} \left(\frac{P_{12_i} + P_{12_{i+1}}}{2} \right) \cdot (V_{12_{i+1}} - V_{12_i})$$

$$w_{12} = -5.353 \times 10^3 \text{ J}$$

Of course, this is the same thing as the negative of the integral of PdV from V_1 to V_2 , and $P = RT/V$ for an ideal gas.

$$w_{12} := - \int_{V_1}^{V_2} \frac{R \cdot T_{\text{hot}}}{v} dv$$

$$w_{12} = -5.352 \times 10^3 \text{ J}$$

The small difference between the work calculated from the sum and from the integral represents the error in using the the trapezoidal approximation, instead of an infinite number of infinitesimal steps.

In step b, reversible adiabatic expansion occurs while the temperature falls to T_{cold} . Let's let the final temperature be 300 K.

The work done on the gas during this expansion is obtained by summing the product of P and ΔV for many points between V_2 and V_3 , the initial and final volumes during this step. It is also the blue area in the graph below:

$$T_{\text{cold}} := 300 \text{ K}$$

$$j := 0..100$$

$$V_3 := V_2 \cdot \left(\frac{T_{\text{hot}}}{T_{\text{cold}}} \right)^{\frac{3}{2}}$$

$$V_3 = 12.8 \text{ liter}$$

For the adiabatic expansion of an ideal gas, when the temperature range is small enough so that the heat capacity does not change too much, $T_2/T_1 = (V_1/V_2)^{\gamma-1}$, where γ is the ratio of heat capacities C_p/C_v . In the present calculation, where we are dealing with an ideal monatomic gas, the heat capacities are independent of temperature and we can forget about the question of whether the range is small enough.

$$v_{23_j} := V_2 + j \cdot \frac{(V_3 - V_2)}{100}$$

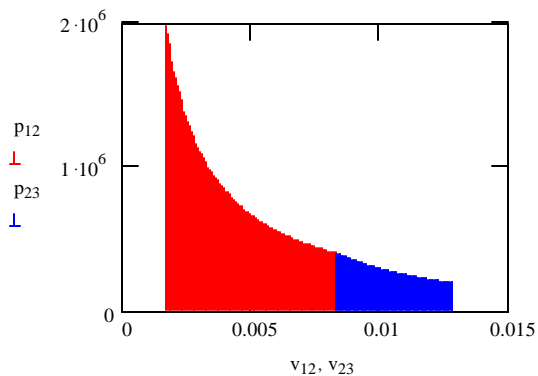
$$T_{23_j} := T_{\text{hot}} \left(\frac{V_2}{v_{23_j}} \right)^{\frac{2}{3}}$$

Unlike the previous isothermal expansion, the temperature constantly decreases during this step, which is why the heat capacities come into the calculation.

$$p_{23_j} := \frac{R \cdot T_{23_j}}{v_{23_j}}$$

Notice the small change in the derivative of p vs v when the expansion changes from isothermal to adiabatic.

$$w_{23} := - \sum_{j=0}^{99} \left(\frac{p_{23_j} + p_{23_{j+1}}}{2} \right) \cdot (v_{23_{j+1}} - v_{23_j})$$



$$w_{23} = -1.247 \times 10^3 \text{ J}$$

In step c, we compress the gas reversibly and isothermally at T_{cold} back to a volume that will allow us to adiabatically compress it further (in step d) back to its original T, P, and V.

A way to figure out what the pressure and volume will be after the step c compression is to start back at the original point and calculate what conditions result from reversible adiabatic expansion from there to T_{cold} . Since the process is reversible, the end points will be the same, no matter which way you calculate them.

Adiabatic expansion from P_1 , V_1 , and T_{hot} to T_{cold} would give

$$V_4 := V_1 \cdot \left(\frac{T_{\text{hot}}}{T_{\text{cold}}} \right)^{\frac{3}{2}} \quad (\text{which would also be the end point of the compression in step c})$$

$$V_4 = 2.56 \text{ liter}$$

Isothermal compression from V_3 to V_4 :

$$j := 0..200$$

$$v_{34_j} := V_3 - j \cdot \frac{(V_3 - V_4)}{200}$$

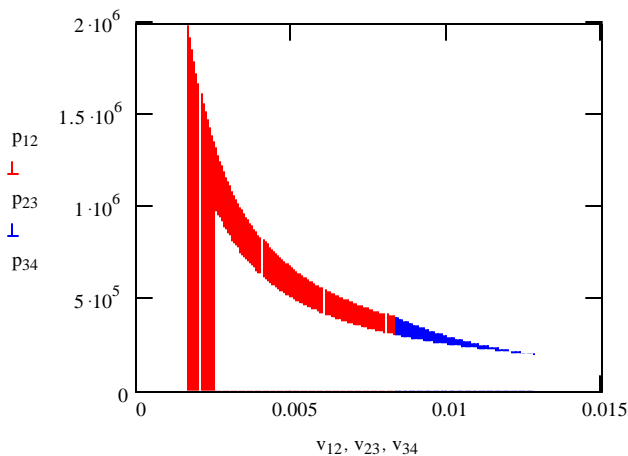
$$p_{34_j} := \frac{R \cdot T_{\text{cold}}}{v_{34_j}}$$

We use 200 steps here so that the graphical representation of the work will have enough data points in it to make the area in the graph completely white. Had we used 100 points as we did before, some of color would have "shown through" because the change in volume in this compression step is larger than that in the previous adiabatic expansion.

If your monitor/computer does not show the area all white, you can either make the graph width a bit smaller, further increase the number of integration steps, or just forget about the aesthetics.

$$w_{34} := - \sum_{j=0}^{199} \left(\frac{p_{34_j} + p_{34_{j+1}}}{2} \right) \cdot (v_{34_{j+1}} - v_{34_j})$$

$$w_{34} = 4.014 \times 10^3 \text{ J}$$



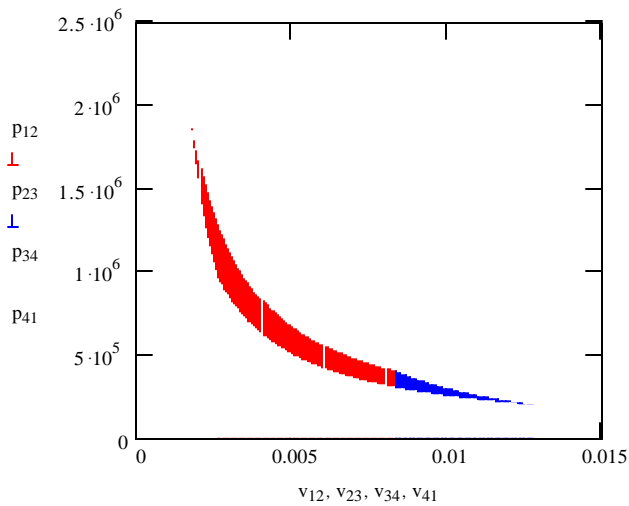
In the graph above, we represent the work done to compress the gas by the whitened area.

Finally, in step d, the gas is adiabatically compressed back to its original temperature, pressure, and volume.

$$v_{41_i} := V_4 - i \cdot \frac{(V_4 - V_1)}{99}$$

$$T_{41_i} := T_{\text{cold}} \cdot \left(\frac{V_4}{v_{41_i}} \right)^{\frac{2}{3}}$$

$$p_{41_i} := \frac{R \cdot T_{41_i}}{v_{41_i}}$$



The remaining little sliver of left-over work is the net work for this Carnot cycle.

$$w_{41} := - \sum_{i=0}^{98} \left(\frac{p_{41_i} + p_{41_{i+1}}}{2} \right) \cdot (v_{41_{i+1}} - v_{41_i})$$

$$w_{41} = 1.247 \times 10^3 \text{ J}$$

$$w_{12} = -5.352 \times 10^3 \text{ J}$$

$$w_{23} = -1.247 \times 10^3 \text{ J}$$

$$w_{\text{net}} := w_{12} + w_{23} + w_{34} + w_{41}$$

$$w_{34} = 4.014 \times 10^3 \text{ J}$$

$$w_{\text{net}} = -1.338 \times 10^3 \text{ J}$$

$$w_{41} = 1.247 \times 10^3 \text{ J}$$

By definition, the heat flow is zero during the two steps that are adiabatic (the gas is insulated from its surroundings during steps b and d). The heat q that is exchanged during the isothermal steps, a and c, is given by $RT \ln(V_{\text{final}}/V_{\text{initial}})$ for an ideal gas.

$$q_{12} := R \cdot T_{\text{hot}} \cdot \ln\left(\frac{V_2}{V_1}\right)$$

$$q_{12} = 5.352 \times 10^3 \text{ J}$$

$$q_{34} := R \cdot T_{\text{cold}} \cdot \ln\left(\frac{V_4}{V_3}\right)$$

$$q_{34} = -4.014 \times 10^3 \text{ J}$$

Exercises and a Challenge

Exercise 1: Make a note of the work involved in each of the steps as they appear above. Then change the initial pressure and the pressure to which the first (isothermal) expansion occurs. Can you increase the amount of net work in the cycle by changing these parameters? Does this also affect the efficiency of the process? The thermodynamic efficiency is the net work divided by the heat supplied from the hot reservoir.

$$q_{\text{h}} := R \cdot T_{\text{hot}} \cdot \ln\left(\frac{V_2}{V_1}\right)$$

$$\varepsilon := \frac{|w_{\text{net}}|}{q_{\text{h}}}$$

$$\varepsilon = 0.25$$

Exercise 2: Try changing the initial and/or the final temperatures of the cycle, leaving the pressures the same while you do so. Can you increase the net amount of work in the cycle by changing the temperatures? Does this also affect the efficiency of the process?

A Challenge: Would you expect a real gas to produce more work or less work than this ideal gas? Redo this worksheet, so that it corresponds to the behavior of a "real" gas, such as H_2 , N_2 , or CO_2 . You will have to decide which equation of state you want to try. Van der Waals and Redlich-Kwong parameters are readily available for many real gases in textbooks such as References 3-5 below. You will also need heat capacity values for the gas you choose (where do they come into the calculation?). Was your prediction realized?

References

1. A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge University Press, 1961)
2. Gilbert Newton Lewis and Merle Randall (revised by Kenneth S. Pitzer and Leo Brewer) *Thermodynamics, Second Edition* (Mc Graw-Hill, 1961)
3. Robert G. Mortimer *Physical Chemistry, Second Edition* (Harcourt Academic Press, 2000)
4. R. Stephen Berry, Stuart A. Rice, and John Ross *Physical Chemistry, Second Edition*, (Oxford University Press, 2000)
5. Peter Atkins *Physical Chemistry, Sixth Edition* (W. H. Freeman, 1998)
6. Walter Dannhauser, "PVT Behavior of Real Gases" *Journal of Chemical Education* **1970** 47 126.
7. J. L. Pauley and Elwyn H. Davis, "P-V-T Isotherms of Real Gases", *Journal of Chemical Education* **1986** 63 466.

Over here in the second column, we'll develop the Carnot cycle for methane, as a van der Waals gas, in a parallel development.

The vdW equation of state is:

$$P = \frac{R \cdot T}{V - b} - \frac{a}{V^2}$$

We will use the same variable names, except that the subscript labels will begin with VDW

These are the vdW constants for methane⁵:

$$a := 2.283 \text{ atm} \cdot \text{liter}^2 \quad \text{and its heat capacity}^5 \text{ at 298 K is } C_{p\text{VDW}} := 35.31 \frac{\text{J}}{\text{K}}$$

$$b := 4.278 \cdot 10^{-2} \cdot \text{liter}$$

Step a

In the first, isothermal step of the cycle, we need the initial and final volumes of the gas, as the pressure changes from P_1 to P_2 .

The vdW equation is not as convenient for calculating volume as it is pressure, since there is the possibility of three different roots.

We will write the equation of state in polynomial form, and find roots corresponding to P_1 and P_2 .

$$f(V) := -a \cdot b + a \cdot V - (R \cdot T_{\text{hot}} + P_1 \cdot b) \cdot V^2 + P_1 \cdot V^3$$

$$V := 1 \quad (\text{This is just an initial guess for the root function.})$$

$$V_{\text{VDW1}} := (\text{root}(f(V), V)) \cdot \text{m}^3$$

$$V_{\text{VDW1}} = 1.637 \text{ liter}$$

$$f(V) := -a \cdot b + a \cdot V - (R \cdot T_{\text{hot}} + P_2 \cdot b) \cdot V^2 + P_2 \cdot V^3$$

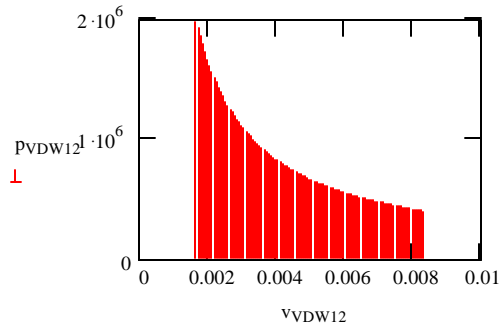
$$V_{\text{VDW2}} := \text{root}(f(V), V) \cdot \text{m}^3$$

$$V_{\text{VDW2}} = 8.287 \text{ liter}$$

$$V_{\text{VDW12}_i} := V_{\text{VDW1}} + i \cdot \left(\frac{V_{\text{VDW2}} - V_{\text{VDW1}}}{100} \right)$$

$$P_{VDW12_i} := \left[\frac{R \cdot T_{hot}}{v_{VDW12_i} - b} - \frac{a}{(v_{VDW12_i})^2} \right]$$

At each volume, we calculate the corresponding pressure.



$$w_{VDW12} := - \sum_{i=0}^{99} \left(\frac{P_{VDW12_i} + P_{VDW12_{i+1}}}{2} \right) \cdot (v_{VDW12_{i+1}} - v_{VDW12_i})$$

$$w_{VDW12} = -5.352 \times 10^3 \text{ J}$$

Step b

The exponent "3/2" in the equation for V_3 is the ratio C_v/R for a monatomic gas. For methane, $C_p = 35.31 \text{ J/K mol}$ at 298K;

$C_v = C_p - R$ (This is approximately true for real gases as well as ideal ones. See Reference 2, p. 107.)

$$C_v := C_{pVDW} - R$$

$$\frac{C_v}{R} = 3.247$$

The heat capacities are actually temperature-dependent, but we'll neglect that. (It would not be too difficult to incorporate.)

$$\frac{C_v}{R} \cdot \ln \left(\frac{T_{cold}}{T_{hot}} \right) = \ln \left(\frac{V_2}{V_3} \right)$$

$$V_{VDW3} := V_{VDW2} \cdot \left(\frac{T_{hot}}{T_{cold}} \right)^{\frac{Cv}{R}}$$

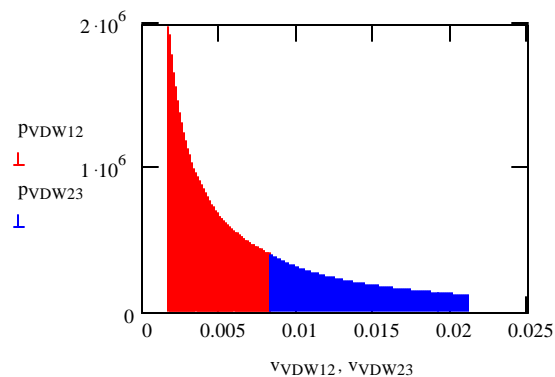
$$V_{VDW3} = 21.09 \text{ liter}$$

$$v_{VDW23_i} := V_{VDW2} + i \cdot \frac{(V_{VDW3} - V_{VDW2})}{100}$$

As the volume changes from v_{VDW2} to v_{VDW3} , the temperature and the pressure both change. The relationships needed are derived in the column at the right.

$$T_{VDW23_i} := \exp \left(\frac{-R}{Cv} \cdot \ln \left(\frac{v_{VDW23_i} - b}{V_{VDW2} - b} \right) \right) \cdot T_{hot}$$

$$P_{VDW23_i} := \left[\frac{R \cdot T_{VDW23_i}}{v_{VDW23_i} - b} - \frac{a}{(v_{VDW23_i})^2} \right]$$



$$w_{VDW23} := - \sum_{j=0}^{99} \left(\frac{P_{VDW23_j} + P_{VDW23_{j+1}}}{2} \right) \cdot (v_{VDW23_{j+1}} - v_{VDW23_j})$$

$$w_{VDW23} = -2.691 \times 10^3 \text{ J}$$

Step c

$$V_{VDW4} := V_{VDW1} \cdot \left(\frac{T_{hot}}{T_{cold}} \right)^{\frac{Cv}{R}}$$

$$V_{VDW4} = 4.166 \text{ liter}$$

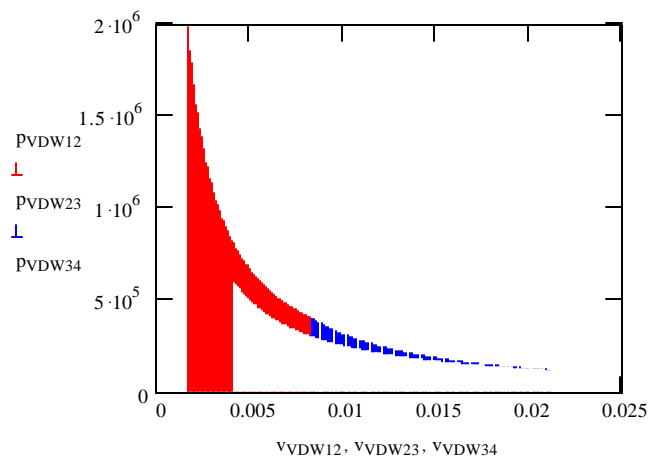
$$V_{VDW3} = 21.091 \text{ liter}$$

$$v_{VDW34_j} := V_{VDW3} - j \cdot \frac{(V_{VDW3} - V_{VDW4})}{200}$$

$$P_{VDW34_j} := \frac{R \cdot T_{cold}}{v_{VDW34_j} - b} - \frac{a}{(v_{VDW34_j})^2}$$

$$w_{VDW34} := - \sum_{j=0}^{199} \left(\frac{P_{VDW34_j} + P_{VDW34_{j+1}}}{2} \right) \cdot (v_{VDW34_{j+1}} - v_{VDW34_j})$$

$$w_{VDW34} = 4.022 \times 10^3 \text{ J}$$

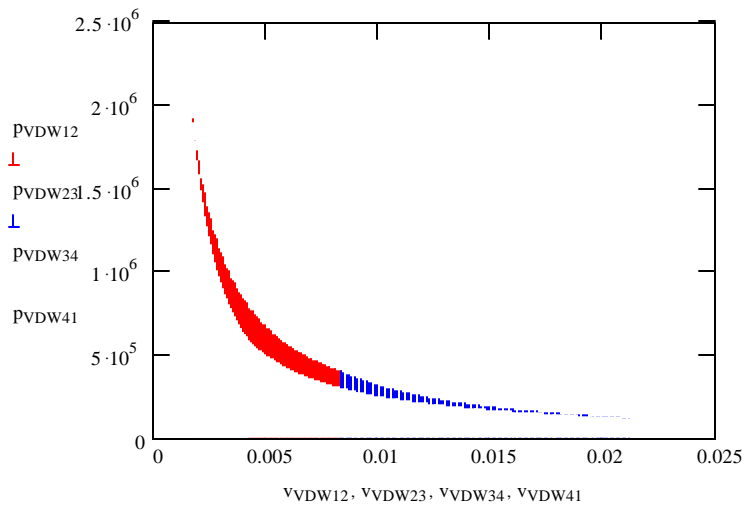


Step d

$$v_{VDW41_i} := V_{VDW4} - i \cdot \frac{(V_{VDW4} - V_1)}{99}$$

$$T_{VDW41_i} := \exp\left(\frac{-R}{C_v} \cdot \ln\left(\frac{v_{VDW41_i} - b}{V_{VDW4} - b}\right)\right) \cdot T_{cold}$$

$$P_{VDW41_i} := \frac{R \cdot T_{VDW41_i}}{v_{VDW41_i} - b} - \frac{a}{(v_{VDW41_i})^2}$$



$$w_{VDW41} := - \sum_{i=0}^{98} \left(\frac{P_{VDW41_i} + P_{VDW41_{i+1}}}{2} \right) (v_{VDW41_{i+1}} - v_{VDW41_i})$$

$$w_{VDWnet} := w_{VDW12} + w_{VDW23} + w_{VDW34} + w_{VDW41}$$

$$w_{VDWnet} = -1.405 \times 10^3 \text{ J}$$

$$w_{VDW12} = -5.352 \times 10^3 \text{ J}$$

$$w_{VDW23} = -2.691 \times 10^3 \text{ J}$$

$$w_{VDW34} = 4.022 \times 10^3 \text{ J}$$

$$w_{VDW41} = 2.616 \times 10^3 \text{ J}$$

$$q_{VDWh} := \int_{v_{VDW1}}^{v_{VDW2}} \left(\frac{R \cdot T_{hot}}{v - b} - \frac{a}{v^2} \right) dv$$

$$q_{VDWh} = 5.351 \times 10^3 \text{ J}$$

$$\epsilon_{VDW} := \frac{|w_{VDWnet}|}{q_{VDWh}}$$

$$\epsilon_{VDW} = 0.26$$

Because $q = -w$ for step a, we could use $-w_{VDW12}$. The calculation at left is an alternative evaluation.

$$w_{VDW12} = -5.352 \times 10^3 \text{ J}$$

The difference in efficiency between this and the monatomic ideal gas is presumably a reflection of numerical integration error, the approximations that the heat capacity is constant, and that $C_p - C_v = R$. Of course, both of them should be given by $\epsilon = 1 - T_{cold}/T_{hot} = 1 - 300/400 = 0.25$

One of the interesting aspects of the comparison between ideal and vdW gases is that, while the efficiency is determined by the temperatures and is equal for the two cases, both of the the adiabatic work terms are larger for the vdW gas. Which parameter of the model causes this to be so?

In this third column of the worksheet are derivations of equations that are needed for the calculations involving nonideal gases.

In order to find the relationship between P and V in a reversible adiabatic change, we need an expression for dP/dV at constant S in terms of the measured properties of the fluid. See Reference (1), pp. 61-2.

$$(dP/dV)_S / (dP/dV)_T = [(dS/dV)_P (dP/dS)_V] / [(dT/dV)_P (dP/dT)_V] = (dS/dT)_P / (dS/dT)_V = \gamma$$

where $\gamma = C_p/C_v$

[Here we used the mathematical relationships:

$$(dz/dx)_y (dx/dy)_z (dy/dz)_x = -1$$

$$\text{and } (dw/dx)_y / (dz/dx)_y = (dw/dz)_y]$$

Therefore, $(dP/dV)_S = \gamma (dP/dV)_T$

and this equation can be integrated step-by-step. For an ideal gas, $PV = RT$ and $(dP/dV)_S = -\gamma P/V$, whereas for a VdW gas,

$$P = \frac{R \cdot T}{v - b} - \frac{a}{v^2}$$

$$\frac{dP}{dv} = \frac{-R \cdot T}{(v - b)^2} + 2 \cdot \frac{a}{v^3} \quad \text{at constant T (isothermal)}$$

$$\frac{dP}{dv} = \frac{-R \cdot T \cdot \gamma}{(v-b)^2} + \frac{2 \cdot a \cdot \gamma}{v^3} \quad \text{at constant S (adiabatic)}$$

We also need $(dT/dV)_S$ so that we can integrate both T and P versus volume. From Reference (2), p. 108, $(dT/dP)_S = - (dS/dP)_T / (dS/dT)_P = T/C_p (dV/dT)_P$ and $(dT/dV)_S = - (dS/dV)_T / (dS/dT)_V = -T/C_v (dP/dT)_V$. For a vdW gas, $(dP/dT)_V = R / (V-b)$, so that $(dT/dV)_S = - RT/C_v(V-b)$.

$$\frac{dT}{dv} = \frac{-R \cdot T}{C_v \cdot (v-b)}$$

$$\int_{T_{\text{hot}}}^{T_{\text{cool}}} \frac{1}{T} dT = \frac{-R}{C_v} \int_{v_2}^{v_3} \frac{1}{v-b} dv$$

$$\ln \left(\frac{T_{\text{cool}}}{T_{\text{hot}}} \right) = \frac{-R}{C_v} \cdot \ln \left(\frac{v_3 - b}{v_2 - b} \right)$$

$$T_{\text{cool}} = \exp \left[\frac{-R}{C_v} \cdot \ln \left[\frac{(v_3 - b)}{(v_2 - b)} \right] \right] \cdot T_{\text{hot}}$$

This is the equation used to calculate the intermediate temperatures (T_{cool}) during the adiabatic steps for the vdW gas.