

PHY 341/641 Thermodynamics and Statistical Mechanics

MWF: Online at 12 PM & FTF at 2 PM

Plan for Lecture 3:

Reading: Chapters 1.5-1.6

- 1. Evaluation of work for various processes on an ideal gas**
- 2. Evaluation of heat for various processes on an ideal gas**
- 3. Internal energy and enthalpy**

Your questions

From Michael --How is the concept of enthalpy not a violation of the concept of conservation of matter? "To create a rabbit out of nothing" like the book states seems like this would be a violation of this law.

From Parker --How slow is considered "slow" in change of volume that is quasistatic for compression work?

From Kristen --I would like to discuss how the book arrived at equation 1.39 where the volume times the temperature to the $f/2$ power is constant. Also I am confused about the part of the book which discusses the heat capacity at constant pressure where there is additional heat added to compensate for the energy lost as work. If we could discuss that in more detail to clarify that would be great!

From Annelise --Can a compression be both quasistatic and adiabatic? I am confused about the difference between isothermal and quasistatic compressions? I am also confused on the concept of enthalpy. What is the significance of knowing the total energy needed to create a system out of nothing- what does that mean?

From Chao --While expressing the work done to the system, why is there a negative sign before the formula?

From Nick --can you go over again how the specific heat ratio, γ , is related to degrees of freedom, f ? I think my issue is still with the degrees of freedom bit, like why C_P and C_V have different degrees of freedom.

From Leon --Can you go over again how the specific heat ratio, γ , is related to degrees of freedom, f ? I think my issue is still with the degrees of freedom bit, like why C_P and C_V have different degrees of freedom.

From Rich -- If, as we discussed before, the equipartition theorem does not hold, are the derivations for the isothermal and adiabatic compression inaccurate as well? In the book's equation 1.54 for the first law of thermodynamics, where does the $(-PV)$ come from?

From Zezhong -- For the equation 1.30, during a phase transformation, what happens on molecules that makes the concept of heat capacity does not make sense(to infinitely large).

One-on-one meetings

Tue 1 PM – Kristen (4:30 PM this week)

Office hours

Tue 10 AM

PHY 341/641 Thermodynamics and Statistical Mechanics

MWF 12 and 2 Online and face-to-face <http://www.wfu.edu/~natalie/s21phy341/>

Instructor: [Natalie Holzwarth](#) Office: 300 OPL e-mail: natalie@wfu.edu

Course schedule for Spring 2021

(Preliminary schedule -- subject to frequent adjustment.) Reading assignments are for the **An Introduction to Thermal Physics** by Daniel V. Schroeder. The HW assignment numbers refer to problems in that text.

| | Lecture date | Reading | Topic | HW | Due date |
|---|-----------------|---------------|--------------------------------------|------|------------|
| 1 | Wed: 01/27/2021 | Chap. 1.1-1.3 | Introduction and ideal gas equations | 1.21 | 01/29/2021 |
| 2 | Fri: 01/29/2021 | Chap. 1.2-1.4 | First law of thermodynamics | 1.17 | 02/03/2021 |
| 3 | Mon: 02/01/2021 | Chap. 1.5-1.6 | Work and heat for an ideal gas | | |
| 4 | Wed: 02/03/2021 | | | | |

Note – on Wed. it is likely that we will review Chap. 1 (skipping 1.7 and notions of phase transformations for now)

Basic equations

General principle – expected of all systems
Follows from notion that we can/should
account for all energy

First "law" of thermodynamics

$$\Delta U = Q + W$$

Special for an ideal gas system –

Equation of state

$$PV = Nk_B T$$

Internal energy

$$U = \frac{1}{\gamma - 1} Nk_B T$$

Questions on “equipartition theorem” and what happen to degrees of freedom.

Comments --

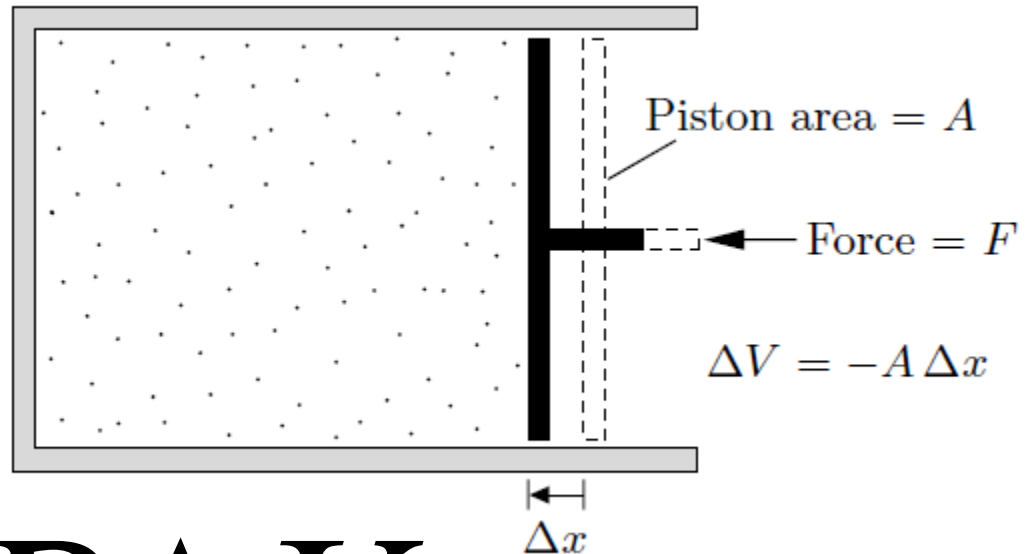
General formula for internal energy of an ideal gas

$$U = \frac{f}{2} N k_B T = \frac{1}{\gamma - 1} N k_B T$$

Here f denotes the degrees of freedom for the N particles of the system. In my opinion f is often hard to estimate directly and prefer to use the experimentally accessible parameter γ in the equivalent relationship given on the RHS of the equation above. Note that both f and γ have slight temperature dependences.

Calculation of work for various processes

Figure 1.8. When the piston moves inward, the volume of the gas changes by ΔV (a negative amount) and the work done on the gas (assuming quasistatic compression) is $-P\Delta V$. Copyright ©2000, Addison-Wesley.



$$W = -P\Delta V$$

Note that with our definition, work is positive when the system contracts.

Comment – the sign of work is just a convention, but it is essential to be consistent.

Work for various processes for an ideal gas

$$W = -P\Delta V \quad PV = Nk_B T$$

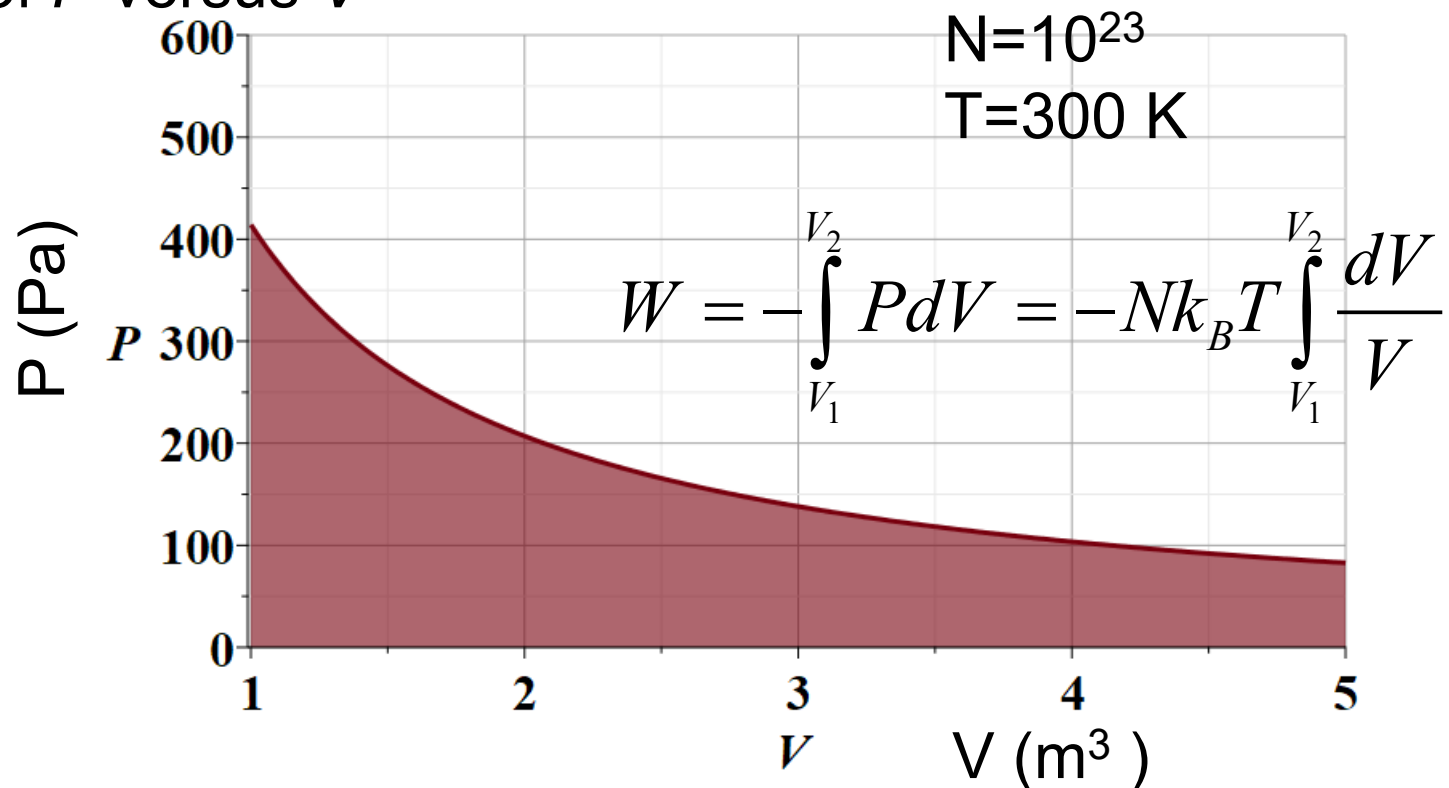
| | Initial | Final | W |
|--------------|-----------------|-----------------|-------------------|
| Constant V | $P_1 \quad V_1$ | $P_2 \quad V_1$ | 0 |
| Constant P | $P_1 \quad V_1$ | $P_1 \quad V_2$ | $-P_1(V_2 - V_1)$ |

Work for various processes for an ideal gas

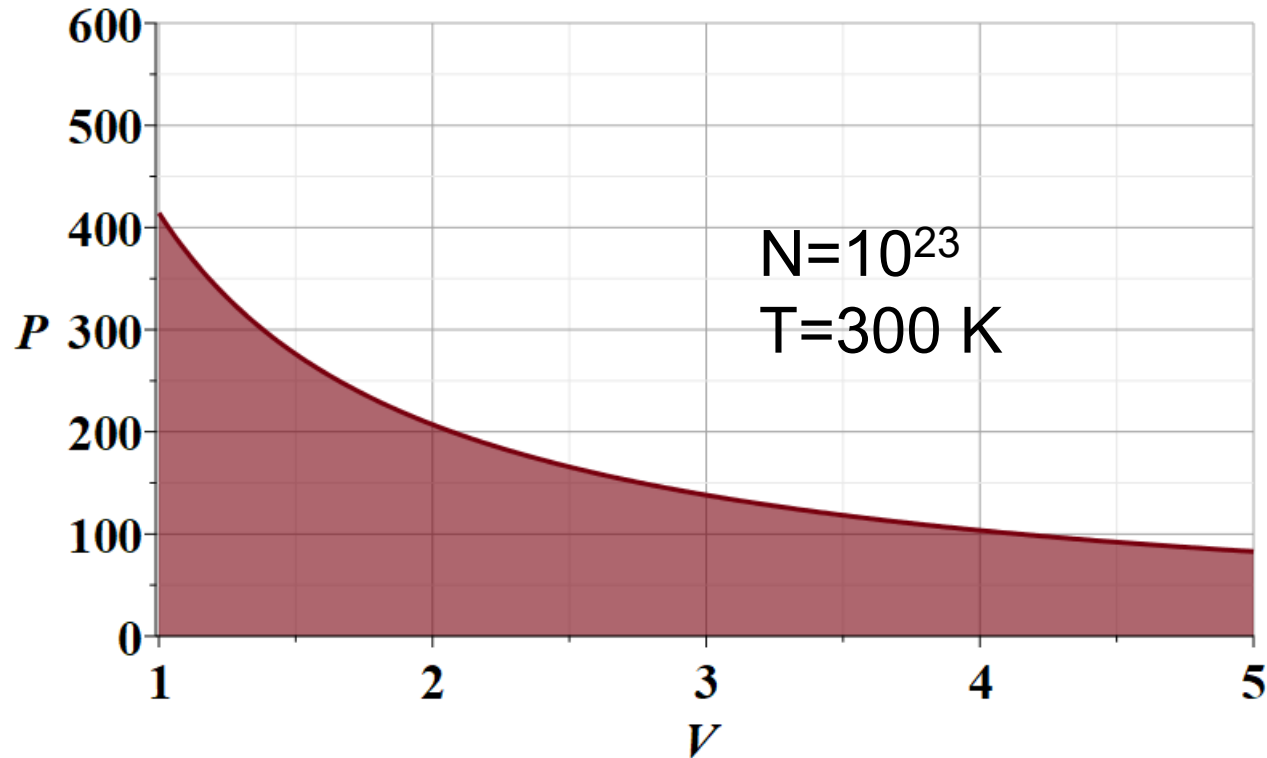
$$W = -P\Delta V \quad PV = Nk_B T$$

Now consider an isothermal process

In order to evaluate W , it is useful to consider a plot of P versus V



Work for an isothermal process in an ideal gas



$$W = -\int_{V_1}^{V_2} P dV = -Nk_B T \int_{V_1}^{V_2} \frac{dV}{V} = -Nk_B T \ln \left(\frac{V_2}{V_1} \right)$$

Summary of results

| | Initial | Final | W |
|--------------|-----------------|---------------------------|---------------------------|
| Constant V | $P_1 \quad V_1$ | $P_2 \quad V_1$ | 0 |
| Constant P | $P_1 \quad V_1$ | $P_1 \quad V_2$ | $-P_1(V_2 - V_1)$ |
| Constant T | $P_1 \quad V_1$ | $P_1 V_1 / V_2 \quad V_2$ | $-P_1 V_1 \ln(V_2 / V_1)$ |

Now consider the effects of heat on the system

First "law" of thermodynamics

$$\Delta U = Q + W$$

Special for an ideal gas system –

Equation of state

$$PV = Nk_B T$$

Internal energy

$$U = \frac{1}{\gamma - 1} Nk_B T$$

Consider the ideal gas processes that we have just discussed:

First "law" of thermodynamics

$$\Delta U = Q + W$$

| Con. | Initial | Final | W | ΔU | Q |
|------|-----------------|---------------------------|---------------------------|-------------------------------------|----------------|
| V | $P_1 \quad V_1$ | $P_2 \quad V_1$ | 0 | $\frac{V_1(P_2 - P_1)}{\gamma - 1}$ | ΔU |
| P | $P_1 \quad V_1$ | $P_1 \quad V_2$ | $-P_1(V_2 - V_1)$ | $\frac{P_1(V_2 - V_1)}{\gamma - 1}$ | $\Delta U - W$ |
| T | $P_1 \quad V_1$ | $P_1 V_1 / V_2 \quad V_2$ | $-P_1 V_1 \ln(V_2 / V_1)$ | 0 | $-W$ |

Now consider the case where $Q=0$, termed an “adiabatic” process for a system described by an ideal gas equation of state.

$$PV = Nk_B T$$

$$U = \frac{Nk_B T}{\gamma - 1} = \frac{PV}{\gamma - 1}$$

$$\Delta U = Q + W \Rightarrow \Delta U = W = -P\Delta V$$

$$\Delta U = \frac{\Delta PV + P\Delta V}{\gamma - 1} = -P\Delta V$$

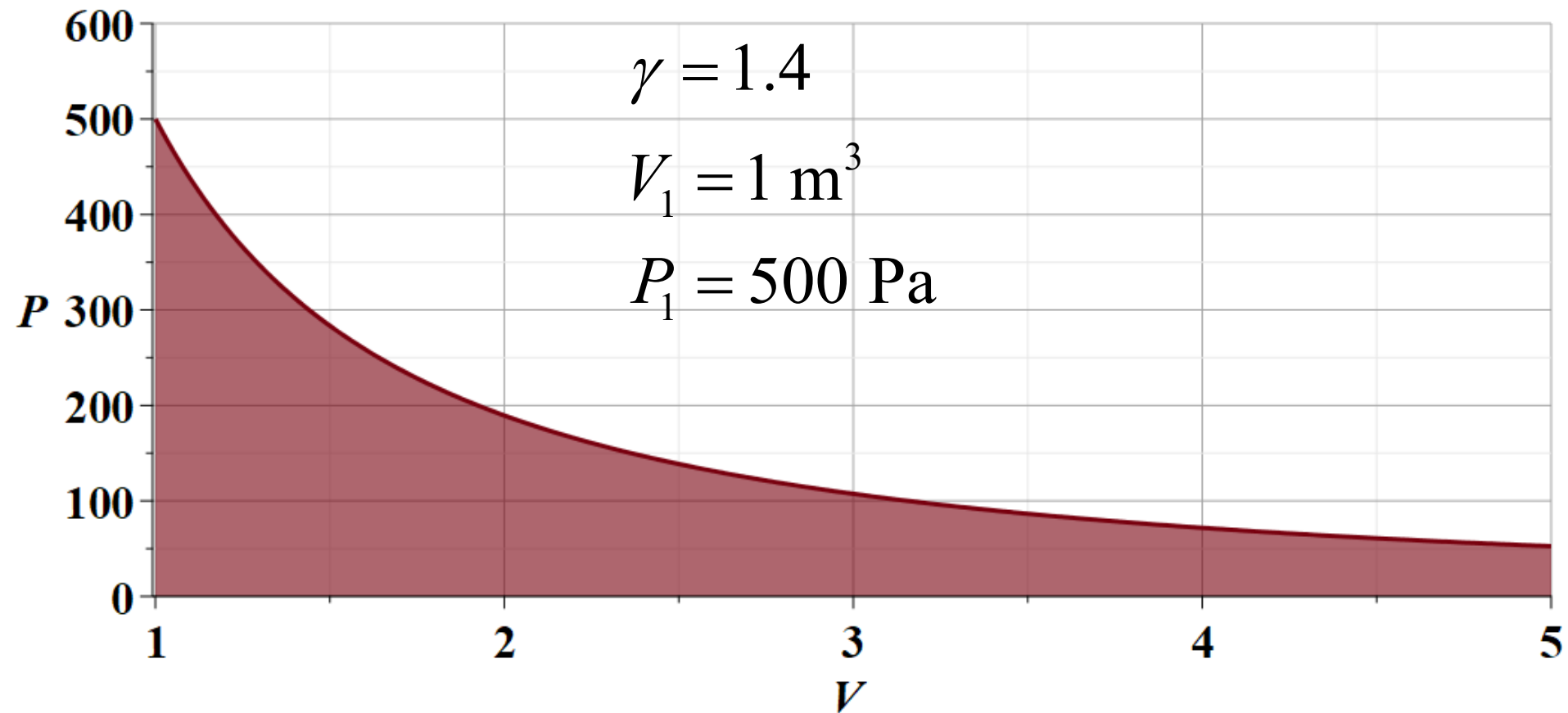
$$\Rightarrow \Delta PV = -\gamma P\Delta V \quad \text{Infinitesimal form} \quad \frac{dP}{P} = -\gamma \frac{dV}{V}$$

$$\Rightarrow d \ln P = -\gamma d \ln V = -d \ln V^\gamma \quad d \ln(PV^\gamma) = 0$$

$$PV^\gamma = \text{constant} \quad \text{Also} \quad VT^{1/(\gamma-1)} = \text{constant}$$

Work during an adiabatic process

$$W = -P_1 V_1^\gamma \int_{V_1}^{V_2} \frac{dV}{V^\gamma} = -\frac{P_1 V_1}{\gamma - 1} \left(1 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} \right)$$



The notion of heat capacity

The rate of heat increment per increment of temperature

$$C = \frac{dQ}{dT} \text{ depends on the process}$$

Constant volume process

$$C_V = \left. \frac{dQ}{dT} \right|_V = \frac{d}{dT} \left(\frac{Nk_B T}{\gamma - 1} \right) = \frac{Nk_B}{\gamma - 1}$$

Note that γ is temperature dependent, but its contribution is generally a small correction.

Constant pressure process

$$\begin{aligned} C_P &= \left. \frac{dQ}{dT} \right|_P = \frac{d}{dT} \left(\frac{Nk_B T}{\gamma - 1} + PV \right) \\ &= \frac{Nk_B}{\gamma - 1} + Nk_B = \frac{\gamma Nk_B}{\gamma - 1} \end{aligned}$$

Note that, as previously suggested --

$$\frac{C_P}{C_V} = \frac{\gamma Nk_B / (\gamma - 1)}{Nk_B / (\gamma - 1)} = \gamma$$

Comment on your textbook's discussion of enthalpy --

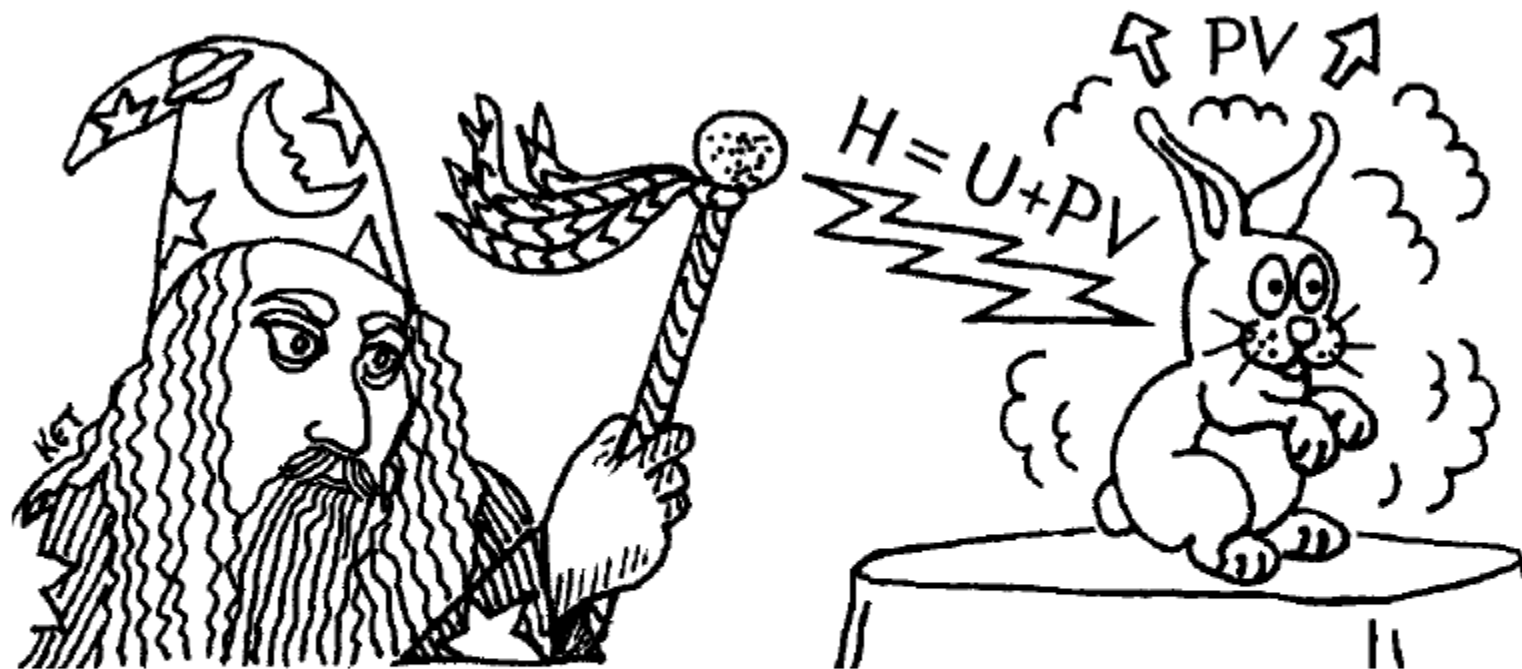


Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV , to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$. Drawing by Karen Thurber. Copyright ©2000, Addison-Wesley.

Another approach is to recognize that the internal energy and the enthalpy are two types of energy among several others that we will want to study. The key to sorting these out is to recognize that the parameters of this field – N, V, T, P, U, H, \dots are interdependent. We can use mathematical constructs (Legendre transformations) to help.

Example of specific heat for a constant pressure process

First "law" of thermodynamics

$$\Delta U = Q + W$$

Special for an ideal gas system –

$$\text{Equation of state } PV = Nk_B T$$

$$\text{Internal energy } U = \frac{Nk_B T}{\gamma - 1} = \frac{PV}{\gamma - 1}$$

For constant pressure process

$$Q = \Delta U - W = \frac{P_1(V_2 - V_1)}{\gamma - 1} + P_1(V_2 - V_1)$$

$$\text{with } P_1 V_1 = Nk_B T_1 \quad \text{and} \quad P_1 V_2 = Nk_B T_2$$

$$\Rightarrow Q(T_2) = Nk_B \left(\frac{T_2 - T_1}{\gamma - 1} + T_2 - T_1 \right)$$

$$C_P = \frac{dQ(T_2)}{dT_2} = Nk_B \left(\frac{1}{\gamma - 1} + 1 \right) = \frac{\gamma Nk_B}{\gamma - 1}$$

Now consider the enthalpy function

$$H \equiv U + PV$$

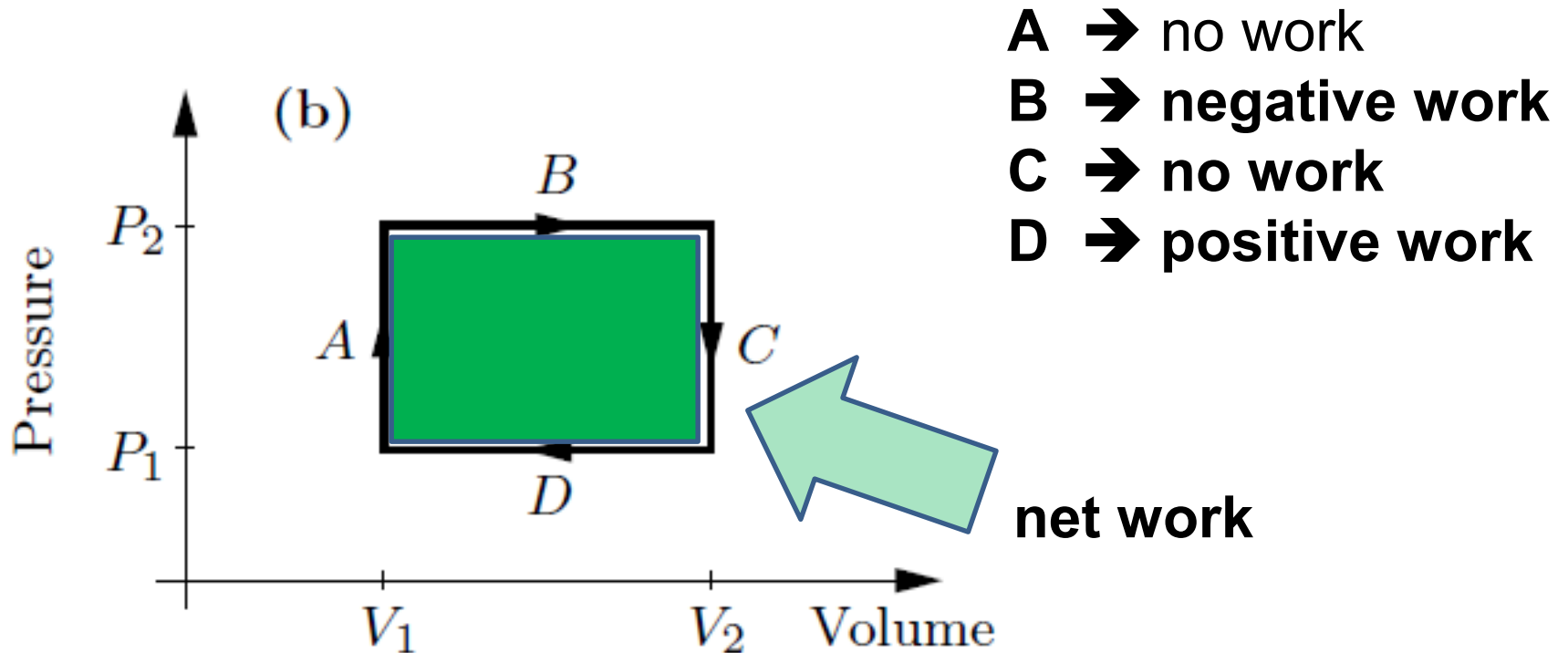
$$H = \frac{Nk_B T}{\gamma - 1} + PV = \frac{PV}{\gamma - 1} + PV = \frac{\gamma PV}{\gamma - 1} = \frac{\gamma Nk_B T}{\gamma - 1}$$

Notice that $\left. \frac{dH}{dT} \right|_P = \frac{\gamma Nk_B}{\gamma - 1}$

More precisely, we need to use the notion of partial derivatives.

Net work done in a cyclic process

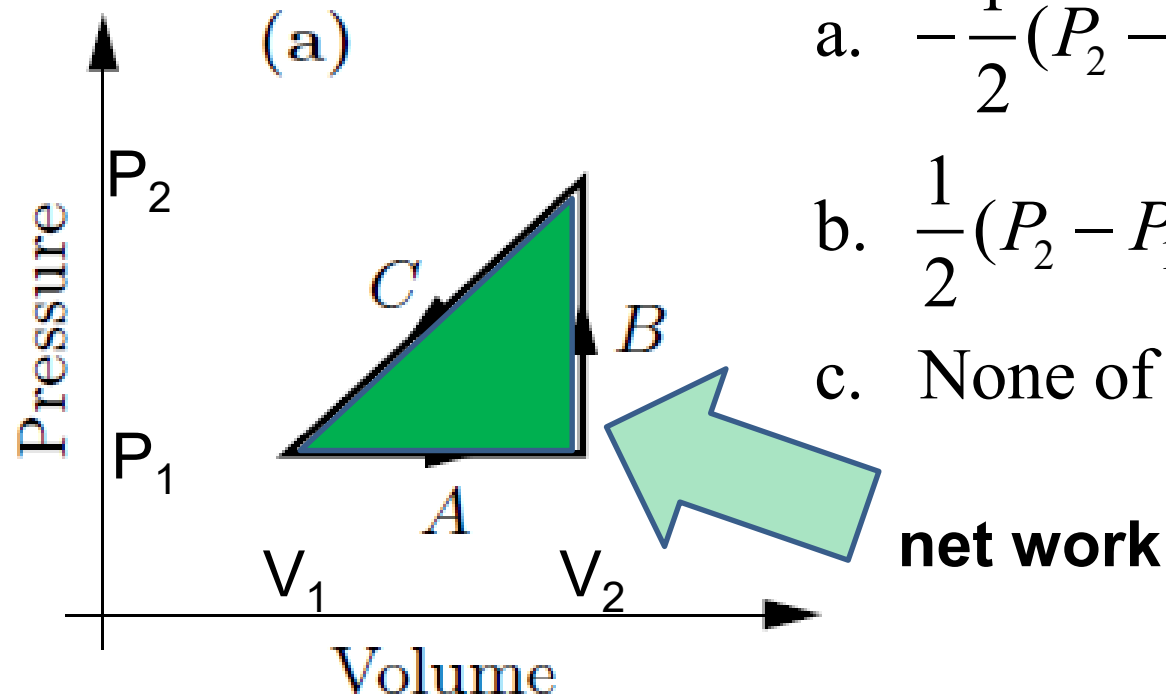
Consider the following 4 step cycle



$$W_{ABCD} = -(P_2 - P_1)(V_2 - V_1)$$

Net work done in a cyclic process -- continued
Consider the following 3 step cycle:

Which of the following represent
the net work W_{ABC} ?



- a. $-\frac{1}{2}(P_2 - P_1)(V_2 - V_1)$
- b. $\frac{1}{2}(P_2 - P_1)(V_2 - V_1)$
- c. None of these

Question – What is ΔU for full cycle process?