

# Chapter 3: Gas Processes

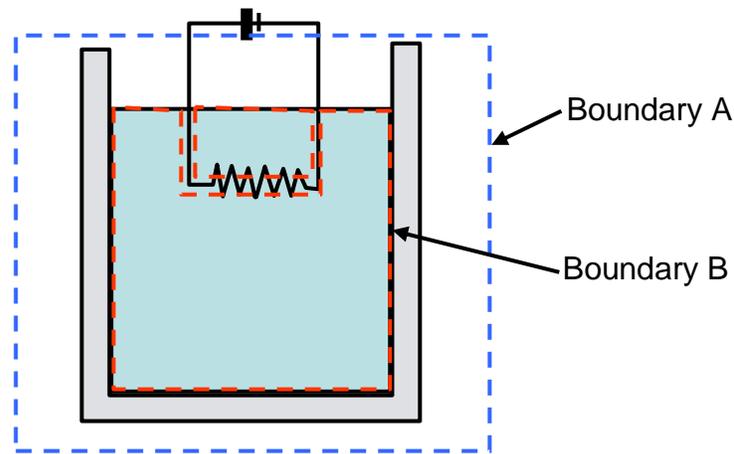
- In this chapter we want to continue to discuss gases.
  - We developed the ideal gas law in chapter 2  $PV = Nk_B T$
  - Now we want to understand some of the processes that occur as we change the P, V or T of a gas
  - We will also be interested in what happens as we add or subtract thermal (internal) energy from the system.
- Once again it is important to establish rigorous definitions before we start to consider the physical phenomena.
  - In this case we need to make sure we have strict definitions of **work** and **heat**.
- **Heat:** “This is the flow of energy across a boundary between to systems (objects) that are in thermal contact and a temperature difference exists between them”
  - **KEY POINT:**
  - **KEY POINT:**
- **Work:** “Any other flow of energy across a boundary that is not considered heat”
  - Example:
  - **Important:**

# Q (heat) or W (work) or k-W??

- This is exercise T3X.1 and T3X.2 in Moore:
- Using a Q to label heat and W to label W, classify each of the case below:
  - Soup (B) in a pan on an electric stove (A) gets hot
  - You (A) compress air (B) in a bike pump, making it warm.
  - Your hands (A) are warmed when they face a fire (B).
  - The atmosphere (A) warms a reentering spacecraft (B).
  - A hot pie (A) becomes cooler while sitting in the kitchen (B).
  - Your chair (B) becomes warmer after you (A) sit in it for a while.
  - A drill bit (B) becomes hot after being spun by a drill (A)
- Using a W for thermal work and a K for “k-work”, classify each case below:
  - The total Kinetic Energy of the molecules in a gas bottle increase as the bottle falls in a gravitational field.
  - The total Kinetic Energy of the molecules in a gas bottle increase as the gas is stirred with a fan in the bottle.
  - Air drag on a falling meteorite causes the meteorite’s temperature to increase.
  - Air drag on a falling meteorite causes it to slow down (lose kinetic energy)
  - Gas in a bottle gains energy from a spark.
  - A small pellet is vaporized by a laser beam.

# Q vs W

- We must be a little bit careful when classifying Q and W.
  - The distinction between the two is a little bit artificial and depends on how we are defining the boundary of our system.
- Moore has a good example with an electrical circuit through water as shown below.



- Case A: We define the water, the container, and the resistor as the system.
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  - Case B: We define the water alone to be the system.
    -
- Be careful how you label an energy transfer across a boundary...it may depend critically on where you define that boundary.

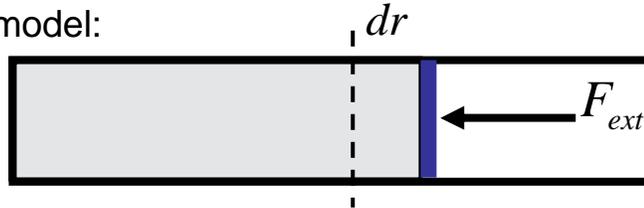
# Q, W and U

- Both heat and work represent ways of transferring energy into a system.
  - U, represents the total internal energy of a system.
  - Q, W represent an amount of energy that is being added (or taken away) from the system across its boundary.
  - By conservation of energy we get:

## First Law of Thermodynamics

- Important feature:
  - ❑  $Q > 0$  if energy is flowing **into** the system
  - ❑  $W > 0$  if energy is flowing **into** the system
- Let's consider a way that we might perform work on a gas.
  - One way that is of interest is to compress the gas.
  - Here is our model:

Sign definition is not universal.



- We want to think about performing this compression in a very specific way:
  - ❑ We move the piston a small distance  $dr$  by pushing on the piston with an external force  $F_{ext}$ .
  - ❑ We move it slowly enough that the piston does not gain significant kinetic energy.
- These two points imply something very important.
  - ❑ The gas must be extracting energy from the piston at the very same rate that we are performing work on the piston.

See Page 44  
for a  
explanation  
of how piston  
adds energy  
to molecules  
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$$[dK]_{piston} = \vec{F}_{ext} \cdot d\vec{r} = F_{ext} dr$$

$$dW = F_{ext} dr$$

$dK$  is the work done on the piston by the external force.  $dW$  is the work done by the piston on the gas...the total work done on the piston is zero.

# Compression, W

- Now since the piston is not gaining any kinetic energy, the total force on it must be zero. Therefore the force exerted by the gas must be equal to the force exerted by the external force.

$$F_{ext} = F_{gas} \quad (\text{but pointed in opp. dir.})$$

- Now if we substitute this back into our earlier equation we find.

- Where we have noted that the force of the gas is just the pressure times the area and that  $\Delta r$  equals a small (negative) change in the volume  $-dV$ .
- This gives us an important relationship for how work can be performed on a gas by compressing it.

$$dW = -PdV$$

- Notes:



# Macrostate of a Gas

- Let's make a connection back to some ideas of quantum mechanics. In QM we talked about “state vectors” which contained information regarding the particle.
  - In the case of hydrogen we defined the state in terms of a small number of variables  $n, l, m, m_s$
- Can we define the “state of a gas”?
  - The answer is yes, but we must be careful to distinguish between “macrostate” and “microstate”.
  - The macrostate is described in terms of the macroscopic variables (in addition you need to know chemical comp.)
    - ❑ Pressure (P)
    - ❑ Temperature (T)
    - ❑ Volume (V)
    - ❑ Total Internal Energy (U)
    - ❑ Number of Molecules (N)
    - ❑ Total Mass (M)
- But we have discovered that many of these quantities are related

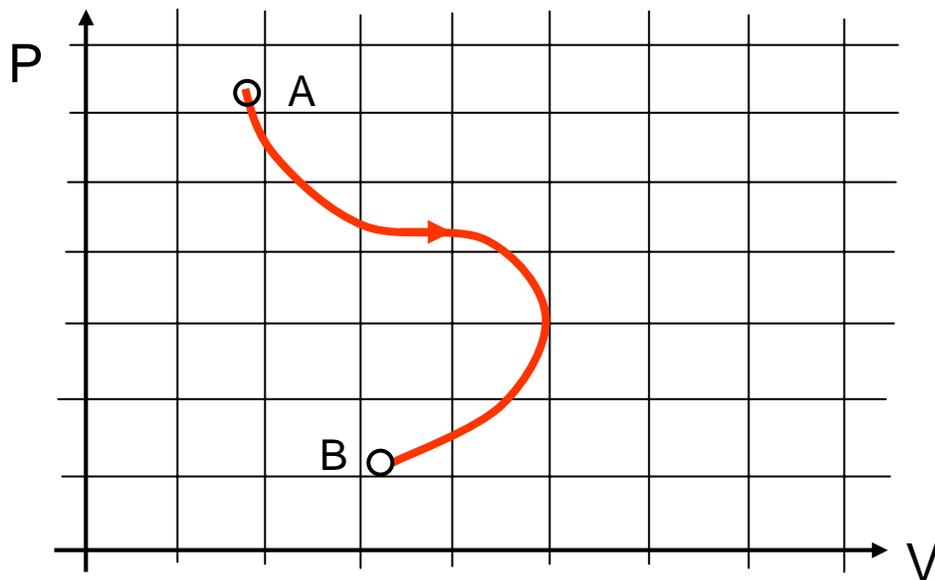
Properties of the **whole** object versus individual pieces.

$$N = \frac{M}{M_A} N_A \quad PV = Nk_B T \quad U = \frac{f}{2} Nk_B T$$

- It turns out that if you know a triplet of these (**almost** any triplet, see T3X.4), the other variables can be calculated. For example, if you know P, V and T:

# P-V Diagrams

- In many cases, the amount of gas ( $N$ ) is not changing and known. Therefore, we can pick two of the other macroscopic quantities to define the macroscopic state of the gas. It is very common to pick Pressure ( $P$ ) and Volume ( $V$ ).
- $P$  and  $V$  are independent in the sense that for any volume all values of pressure are allowed.
- We can make a plot of  $P$  versus  $V$  and every point on the graph represents a specific **macroscopic** state of the gas (for known  $N$ ).



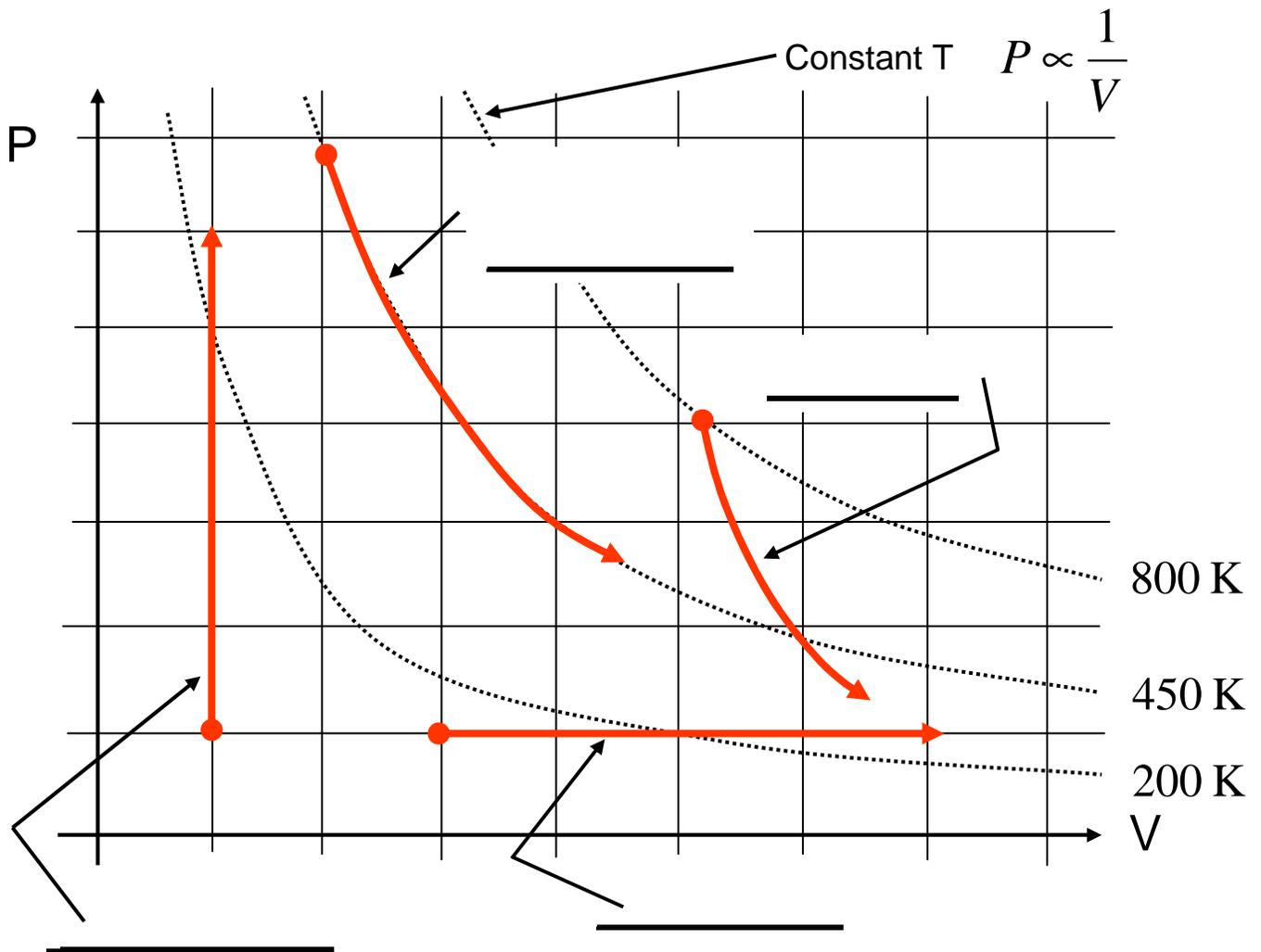
- As the gas undergoes changes it will map out a curve or path in the P-V space. Above is an example of a general process.
  - The gas started at macrostate A and moved through some process to macrostate B.

# Processes

- Although in general the path from A to B can be quite general, there are some special processes or paths that of interest for our study of thermal dynamics.
- Definition: **Quasistatic**: This means that the change the state of the gas occurs slow enough that all parts of the gas remain in equilibrium.
- **Four Special Processes:**
- (1) **Isochoric**: The gas is changed in such a way that the volume of the gas remains fixed.
  - 
  -
- (2) **Isobaric**: The gas is changed in such a way that the pressure of the gas remains fixed
  - 
  -
- (3) **Isothermal**: The gas is changed in such a way that the temperature of the gas remains fixed.
  - 
  -

# Gas Processes

- (4) **Adiabatic:** In this process the gas changes state but no heat is allowed to flow into or out of the gas.



# Calculating Work

- One of the advantages of a P-V diagram is that it is easy to calculate the amount of work done on (or by) the gas.

- Recall the expression that we derive earlier

$$dW = -PdV$$

- This was for a *infinitesimal* amount of work. To determine the work done when moving between two separate states we must integrate the above equation.

$$W = - \int_{V_1}^{V_2} P(V) dV$$

Work done **on** the gas.

- Notice that P can be a function of volume. With our four specific processes we can perform this integral.

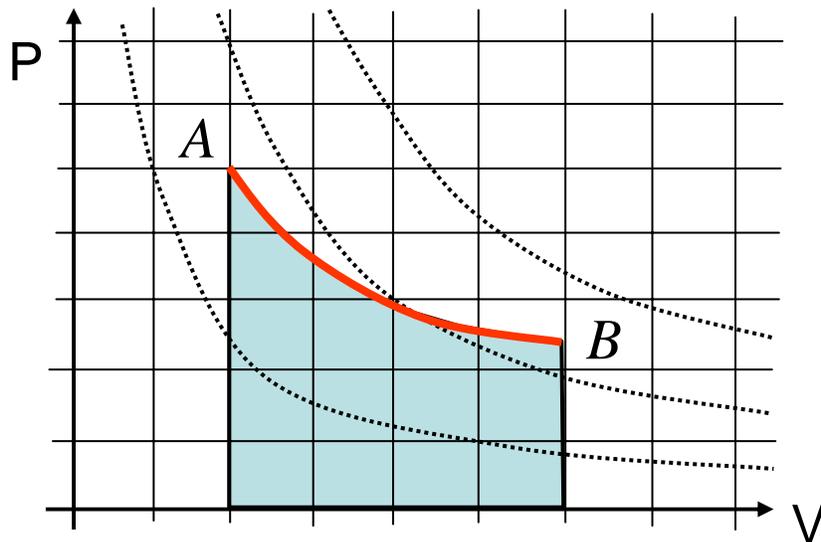
➤ **Isochoric:**

➤ **Isobaric:**

➤ **Isothermal:**

# Work

- We will deal with the adiabatic process in a moment. But first let's make a general observation about the value of the work.
  - The magnitude of the work is simply the area under the curve on the P-V diagram

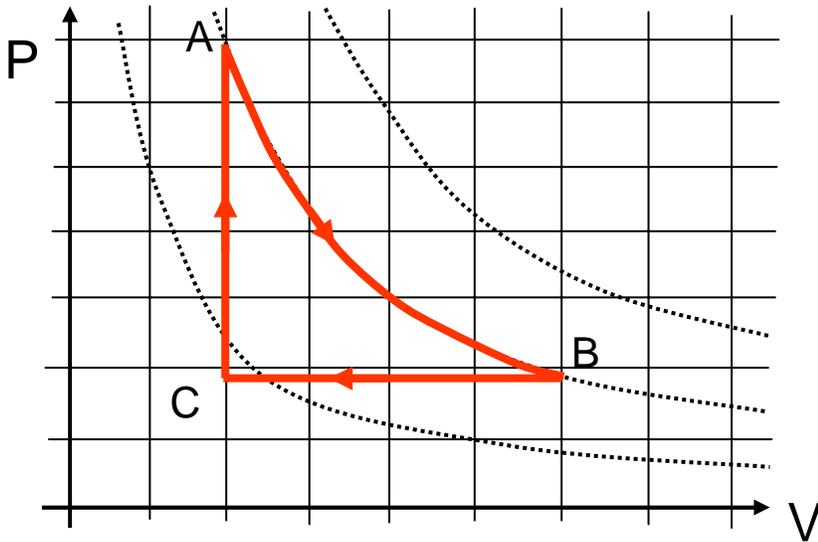


- One of the features that we need to pay attention to is whether the work is positive or negative. This depends on the “direction” of the process.
  - Going from A→B:
  - Going from B→A:
- When analyzing a change on the P-V diagram we can make a useful table

|     | Q | W | $\Delta U$ |
|-----|---|---|------------|
| A→B |   |   |            |

# Example

- Let's consider analyzing the following example.



|                   | Q | W | $\Delta U$ |
|-------------------|---|---|------------|
| A $\rightarrow$ B |   |   |            |
| B $\rightarrow$ C |   |   |            |
| C $\rightarrow$ A |   |   |            |

- Going from A to B:
- Going from B to C:
- Going from C to A:

# Example

- The three processes that took place in this last example represent a **cycle**...the last state was the same as the first state...it got back to the starting point.
  - However, the work done is NOT zero.
  - The net work is equal to the area *enclosed* by the cycle.
    - ❑ Is it positive or negative?
    - ❑ In general if we go “clock-wise” around a cycle the net work will be \_\_\_\_\_
    - ❑ If we go “counter-clockwise” around a cycle the net work will be \_\_\_\_\_
  - The internal energy must be back to its original value.
$$\Delta U_{TOT} = 0$$
  - But since there is a net work, there must be a net amount of heat (Q) which is opposite the net work.
- In this case we can actually calculate the amount of work

$$W_{TOT} = W_{A \rightarrow B} + W_{B \rightarrow C} = -P_A V_A \ln \frac{V_B}{V_A} - P_B (V_A - V_B)$$

- It doesn't seem to simplify any but we can certainly calculate this with all the values.

# Adiabatic Process

- Recall the definition of an adiabatic process: The macrostate of the gas changes without the addition or subtraction of heat from the gas.  $Q = 0$ .
- In this case we would like to know how  $P$ ,  $V$  and  $T$  change for an adiabatic process.
- Observations:
  - 
  -
- Moore has a derivation of the condition on adiabatic process. I do not find it very satisfying since it does a number of things which are not obviously motivated and it never clearly makes use of the condition above.
- Let's start by stating what the condition is and then we will show a derivation of it:

$$PV^\gamma = \text{constant} \quad \Rightarrow \quad TV^{\gamma-1} = \text{constant}$$

- Where  $\gamma$  is  $5/3$  for a monatomic gas,  $7/5$  for diatomic and between  $1$  and  $4/3$  for a polyatomic gas.
- This is only true for ideal gas.
- This is a good approximation if the expansion or compression occurs very rapidly so that the heat flow into or out of the gas is negligible.
- But the speed is still slower than thermal speed of molecule.

# Derivation of Adiabatic Process

- If we think about making a small adiabatic change we should have

$$dU = dW = -PdV$$

$$dU = \frac{f}{2} Nk_B dT \Rightarrow -PdV = \frac{f}{2} Nk_B dT$$

$$PV = Nk_B T \Rightarrow PdV + VdP = Nk_B dT$$

$$PdV + VdP = -\frac{2}{f} PdV$$

$$P\left(1 + \frac{2}{f}\right)dV + VdP = 0 \quad \text{define } \gamma = \left(1 + \frac{2}{f}\right)$$

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0$$

Divide by PV

- Now integrating both side we find:

$$\gamma \ln V + \ln P = \text{constant}$$

$$\ln(PV^\gamma) = \text{constant} \Rightarrow PV^\gamma = \text{constant}$$

- Using the ideal gas law we can rewrite this relationship as

$$PV = Nk_B T \Rightarrow P = \frac{Nk_B T}{V}$$

$$\left(\frac{Nk_B T}{V}\right)V^\gamma = \text{constant} \Rightarrow TV^{\gamma-1} = \text{constant}$$

# Example

- T3R.1: Imagine the pressure at the top of a tall mountain is about  $0.65P_{\text{bottom}}$ . If a stiff breeze is flowing up the mountain and it is  $30\text{ }^{\circ}\text{C}$  ( $86\text{ }^{\circ}\text{F}$ ) at the bottom. Assuming the air travels up the mountain so rapidly that the air expands adiabatically, what is the temperature at the top?