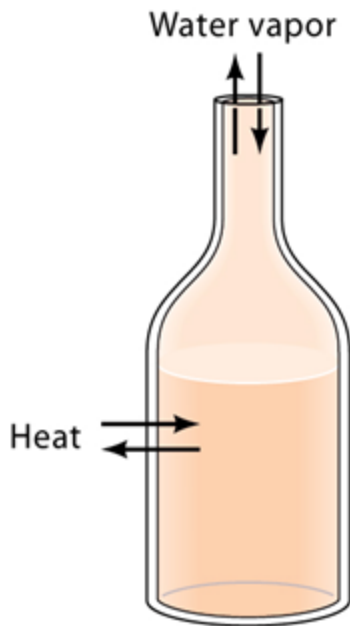


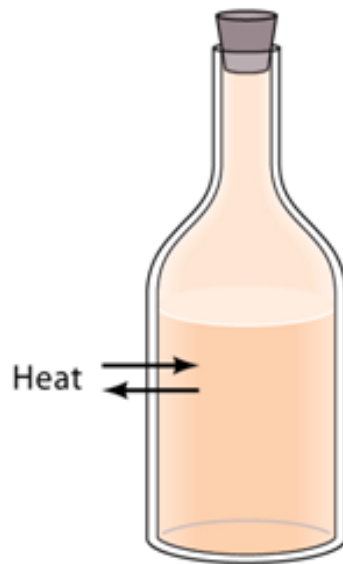
**Chem 123 (section 201)**  
**Lecture 2 (Jan. 7)**

# Open, closed and isolated system

- Open system: both mass and energy exchange with its surroundings
- Closed system: no mass exchange, only energy exchange
- Isolated system: no mass nor energy exchange



Open system



Closed system



Isolated system

# How can we describe the state of a system?

## ---Equation of state

The **state** of a system is defined by a particular set of **properties** (e. g.  $p$ ,  $V$  and  $T$ ,  $n$ ). These properties can be related by an algebraic expression called an **equation of state**. For ideal gas, the State Equation is:

$$pV = nRT$$

or

$$pV_m = RT$$

$p$ : pressure ( $N/m^2$ )

$V$ : volume ( $m^3$ )

$n$ : number of moles of substance

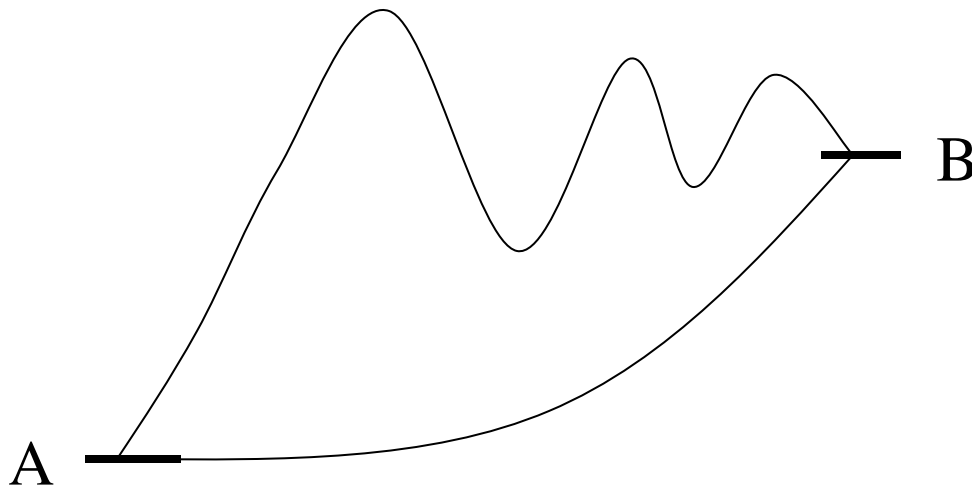
$T$ : temperature (Kelvin)

$R$ : gas constant ( $8.314 J K^{-1} mol^{-1}$ )

$V_m = V/n$ : molar volume

# State Variable

The state of a system is defined by a particular set of properties, State Variables. A state variable is a physical property that depends only on the present state of the system and is independent of the manner in which the state was prepared.

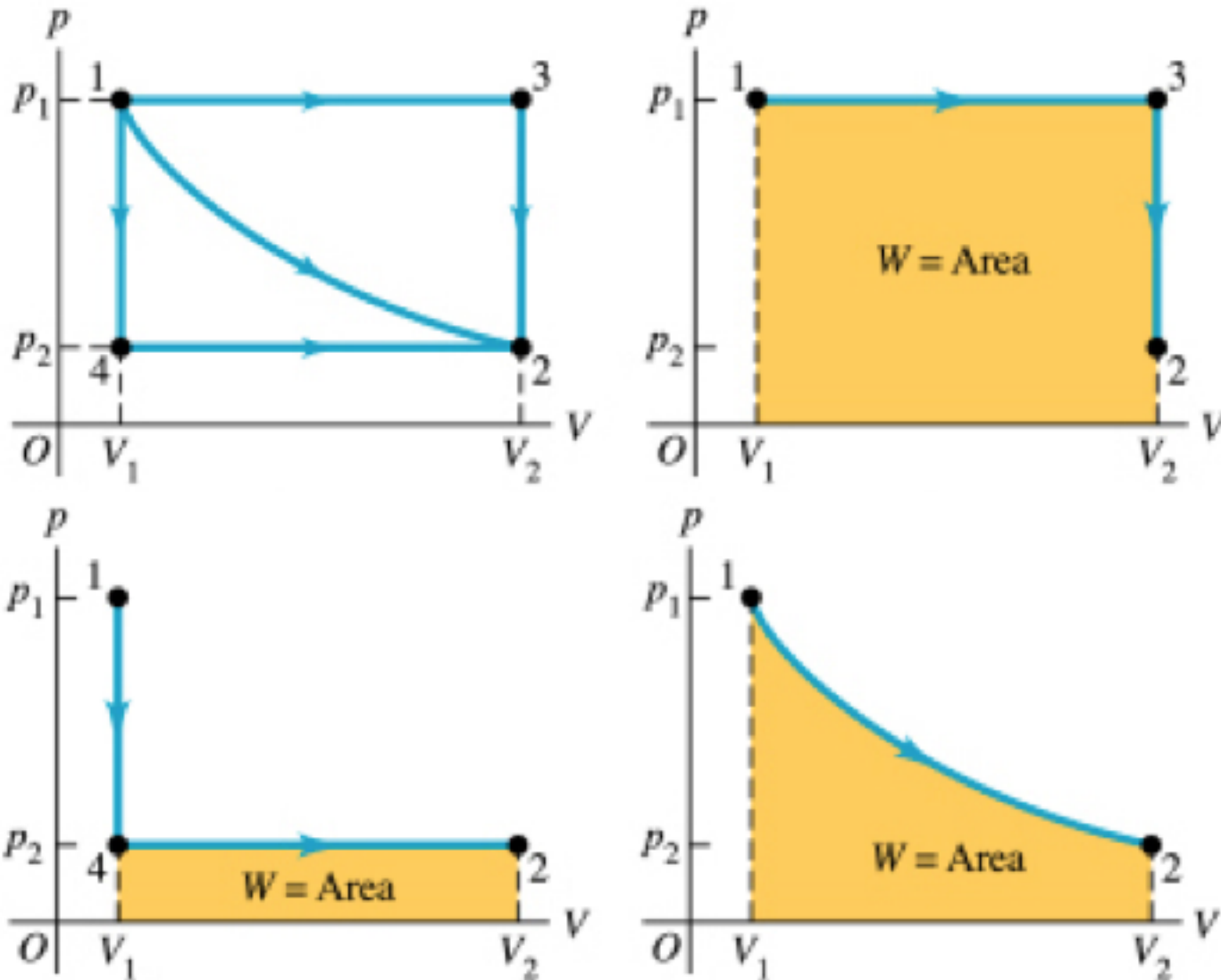


$Z$  is a state function if  $Z(B) - Z(A) = \text{constant}$ , independent of the path by which B is reached.

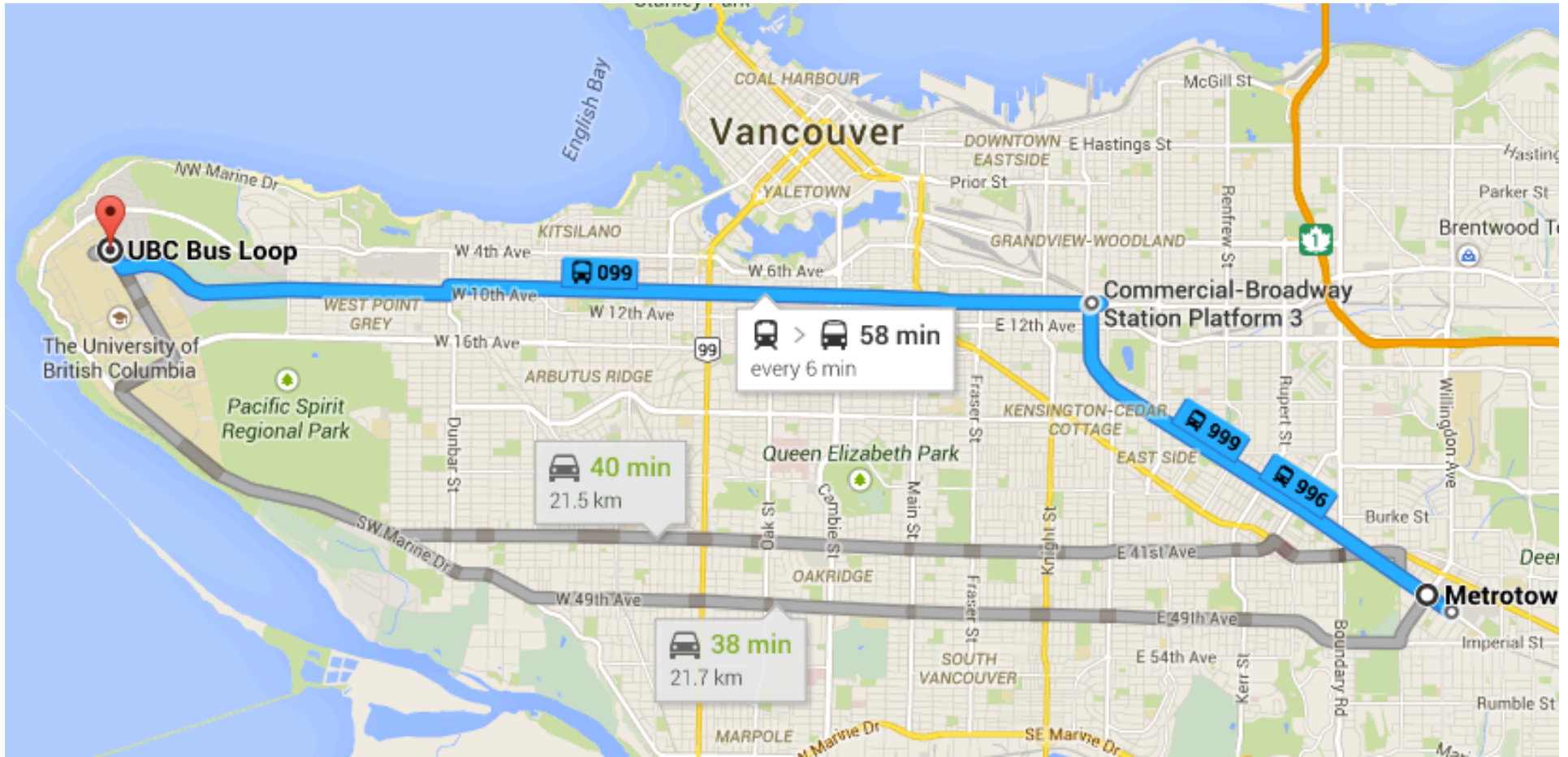
## State variables

- T - Temperature
- P - Pressure
- V - Volume
- E – Internal Energy (U)
- H - Enthalpy
- S - Entropy
- G – Gibb's Free Energy
  
- • •

# Paths Between Thermodynamic States



The path between two states is NOT unique



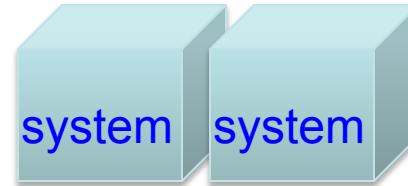
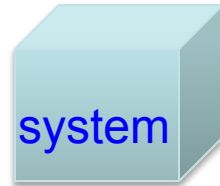
# State Variables

State variables can be divided into extensive and intensive properties.

- Extensive: scale with the amount of materials  
*Such as: mass, volume, energy...*
- Intensive: depends on the nature of materials  
(independent of the amount of materials)  
*Such as: density, temperature, pressure...*

# How to figure out whether a variable is extensive or intensive?

Double the system and see what effect that has on the parameter



Variable	System	Systemx2	Extensive or intensive?
Volume	V		
Temperature	T		
Pressure	P		
Concentration	C		

Note: the ratio of two extensive variables is intensive

## State variables are related to each other

- T - Temperature
- P - Pressure
- V - Volume
- E – Internal Energy (U)
- H - Enthalpy
- S - Entropy
- G – Gibb's Free Energy



**Equation of state**

• • •

For ideal gas, the State Equation is:

$$\boxed{pV = nRT} \quad \text{or} \quad \boxed{pV_m = RT}$$

*p: pressure (N/m<sup>2</sup>)*

*V: volume (m<sup>3</sup>)*

*n: number of moles of substance*

*T: temperature (Kelvin)*

*R: gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>)*

*V<sub>m</sub> = V/n: molar volume*

For an one-component closed system, if 2 of the state variables (P, V and T) are fixed, you can determine the third.

## Surroundings

### System

$P, T, V, n, m,$   
 $E, H, S, G...$

Inside the system: State variables

- Precisely define the state of the system
- Characterize changes in state
- Predict changes in state

The system has extensive properties, defined by state variables.

The system has intensive properties, defined by state variables.

## Surroundings

### System

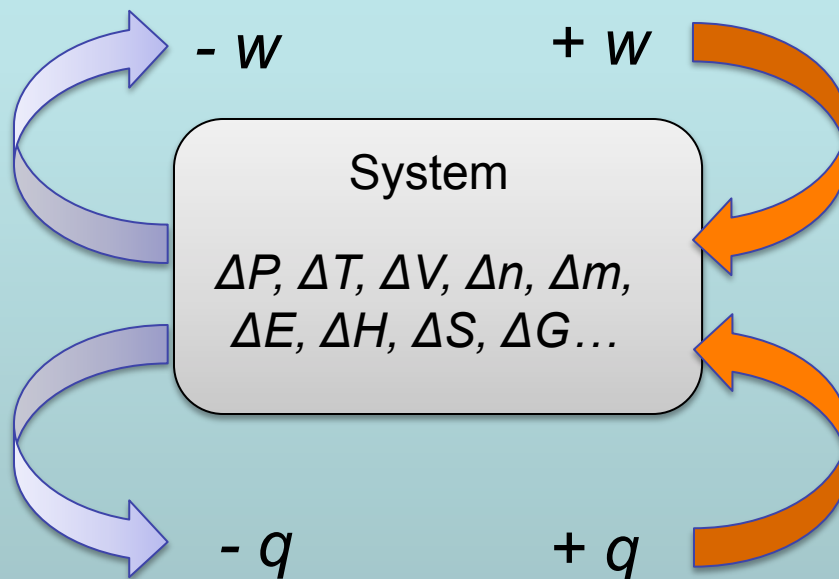
$\Delta P, \Delta T, \Delta V, n, \Delta m, \Delta m,$   
 $\Delta E, \Delta H, \Delta S, \Delta G \dots$

State variables are functions of the state of the system alone.

Changes in state variables depend only on the initial and final states of the system.

When the system changes state, its state variables change.

Surroundings



From the outside, we see only fluxes of heat and work.  
Heat and work associated with any change in state depend sensitively on the path (not state variables).

When the system changes state, and fluxes appear as measurable quantities at the boundaries of the system.

Sometimes positive and sometimes negative

When the system and surroundings reach equilibrium, there are no net macroscopic flows of matter or of energy

# Learning objectives

By the end of this section (Chapter 1, p5-18), successful learners will be able to:

- Define the terms: system, surroundings, state variables and equation of state
- Recognize what properties are state variable
- Recognize what properties are extensive and intensive
- Refer to fluxes of heat and work to describe the interactions between a system and its surroundings

# Clicker question #1

This freshly brewed cup of coffee represents:

- A. An open system
- B. A closed system
- C. An isolated system
- D. Something I really really need right now!
- E. A and D



## Clicker question #2

To fully describe the state of my cup of coffee, I need to specify:

- A. The temperature of the coffee
- B. The pressure of the system
- C. The concentration of caffeine
- D. The volume of of the coffee
- E. All of the above



## Clicker question #3

In my cup of coffee system, the sign of the heat flow is:

- A. negative
- B. positive
- C. neither



## Clicker question #4

In my cup of coffee, the volume of coffee represents:

- A. An extensive variable
- B. An intensive variable
- C. Both
- D. Neither



## Clicker question #5

In my cup of coffee, the concentration of caffeine represents:

- A. An extensive variable
- B. An intensive variable
- C. Both
- D. Neither



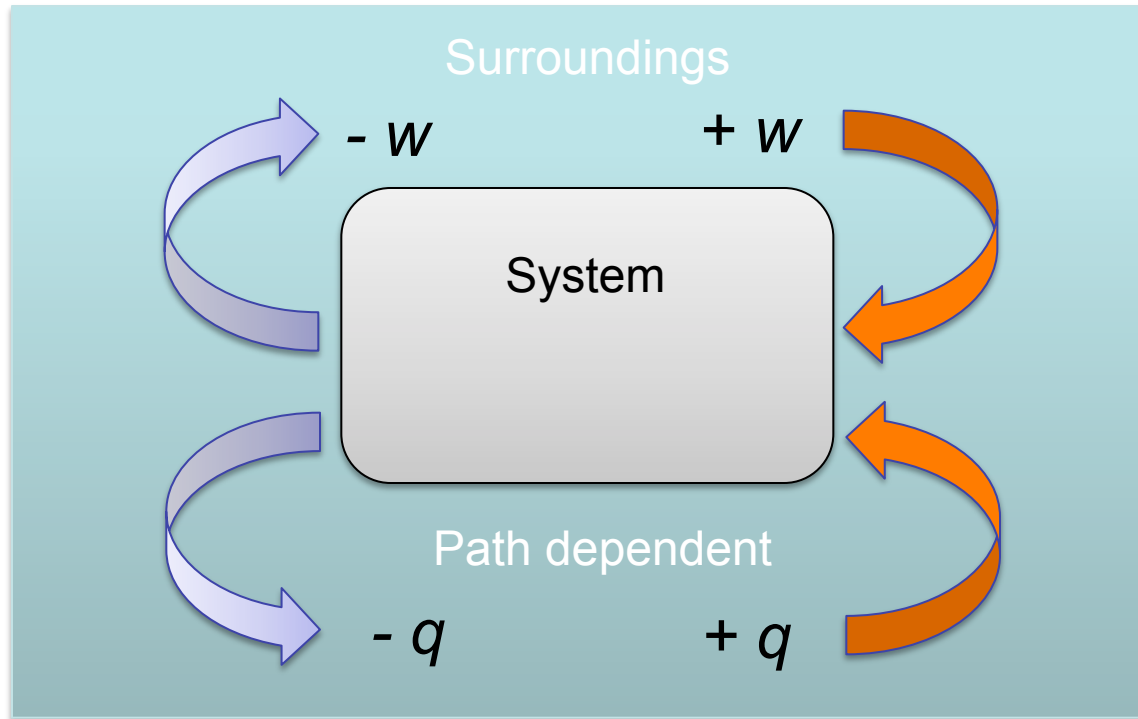
# Chapter 3. The first Law of Thermodynamics

(p39-50)

## Learning Objectives

By the end of this section, successful learners will be able to:

- Recognize internal energy is a state variable
- Describe the first law of thermodynamics and apply it to determine the internal energy, work and heat of a system



# The First Law of Thermodynamics:

**Conservation of Energy:** Energy can neither be created nor destroyed, although it can be converted from one form to another.

There exists a state variable called **internal energy**  $E$ .  $E$  is the sum of all forms of energy in the system. For a closed system:

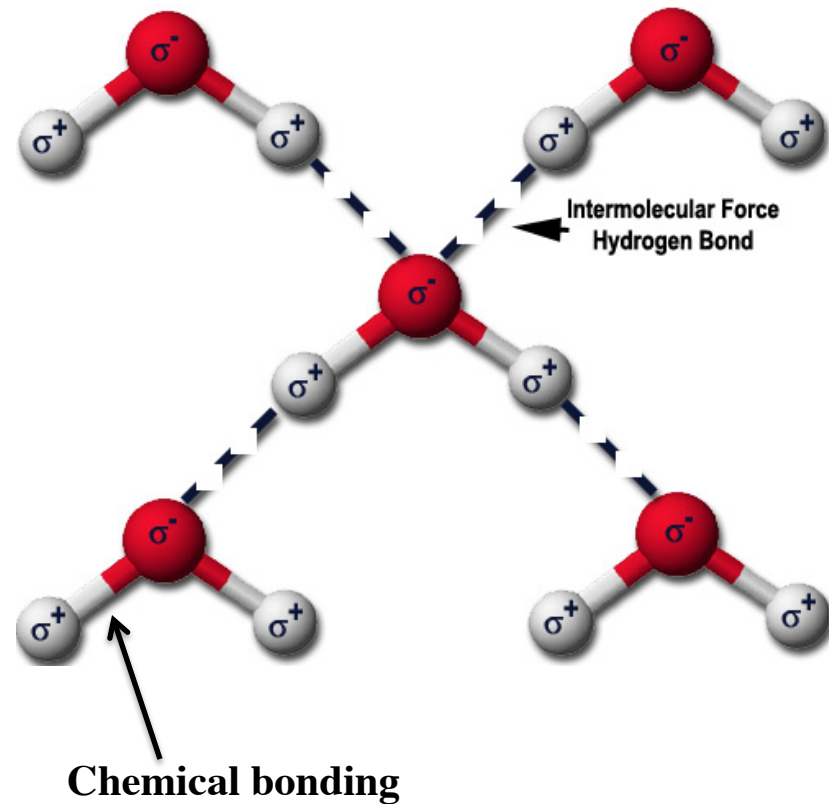
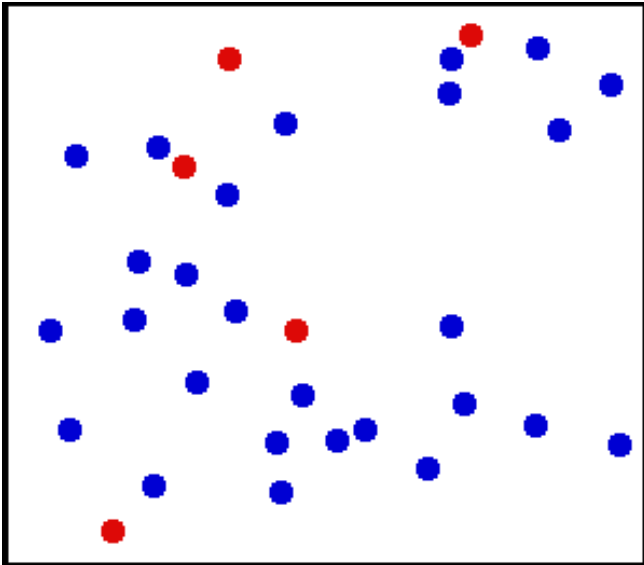
$$\Delta E = q + w$$

*(for all paths)*

Internal Energy:  $E$  [J]

Internal energy is comprised of:

- Kinetic energy of molecules (thermal motion)
- Potential energy (intramolecular and intermolecular)



Energy can be exchanged between a closed system and its surroundings in the following ways:

1. Transfer of **Heat** ( $q$ )

2. Exchange of **Work** ( $w$ )

**Heat**  $q$ :

$q$  is the amount of heat transferred between the system and the surroundings.  $[q] = [\text{J}]$  (Joules)

$q > 0$ : If heat is added to the system from the surroundings

$q < 0$ : If the system releases heat to the surroundings

## Work $w$ :

$w$  is the amount work transferred between the system and the surroundings.  $[w] = [J]$  (Joules)  
( $dw$  stands for an infinitesimal amount of work transferred)

$w > 0$ : If the surroundings do work on the system

$w < 0$ : If the system does work on the surroundings

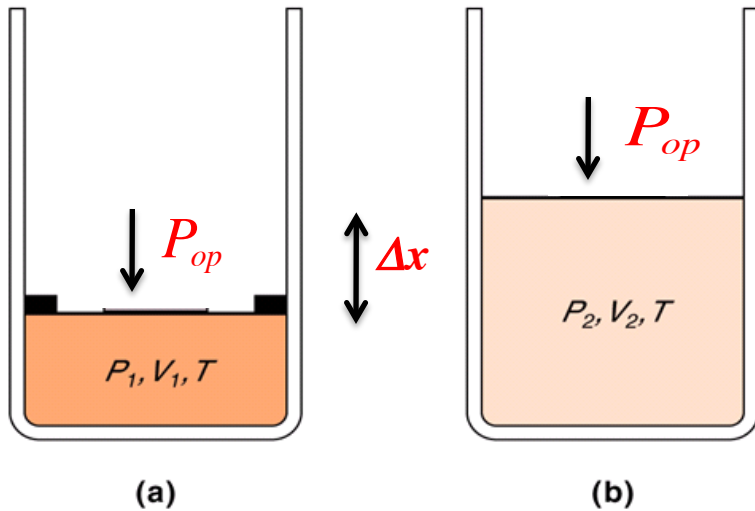
# Type of work

**TABLE 6.1** Varieties of Work

Type of work	$w$	Comment
expansion	$-P_{\text{ex}}\Delta V$	$P_{\text{ex}}$ is the external pressure $\Delta V$ is the change in volume
extension	$f\Delta l$	$f$ is the tension $\Delta l$ is the change in length
weight lifting	$mg\Delta h$	$m$ is the mass $g$ is the acceleration of free fall $\Delta h$ is the change in height
electrical	$\phi\Delta q$	$\phi$ is the electrical potential $\Delta q$ is the change in charge
surface expansion	$\gamma\Delta A$	$\gamma$ is the surface tension $\Delta A$ is the change in area

\* For work in joules (J). Note that  $1 \text{ N}\cdot\text{m} = 1 \text{ J}$  and  $1 \text{ V}\cdot\text{C} = 1 \text{ J}$ .

## Expansion Work:

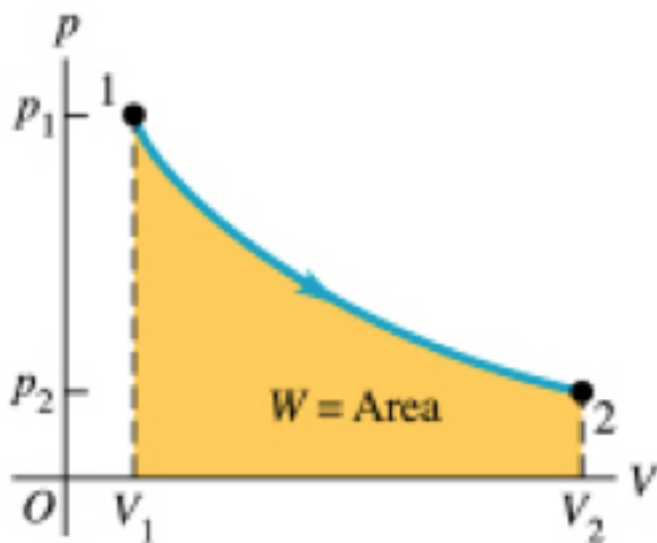
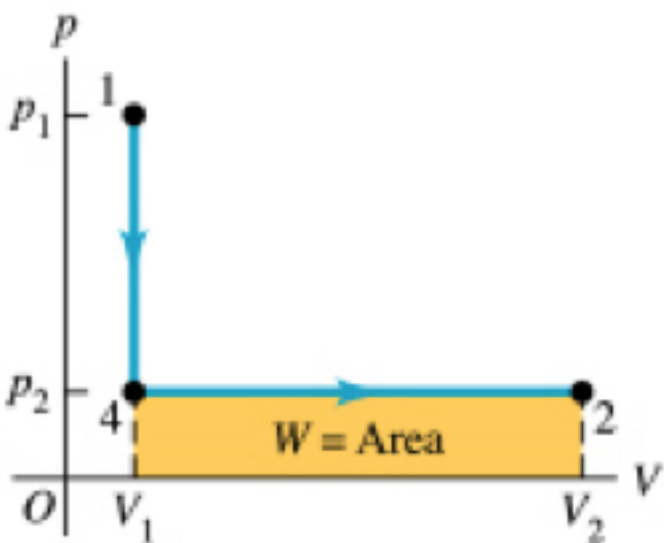
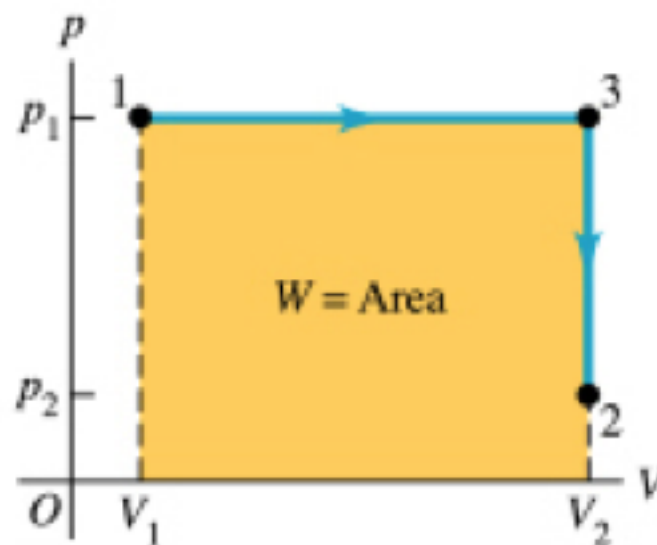
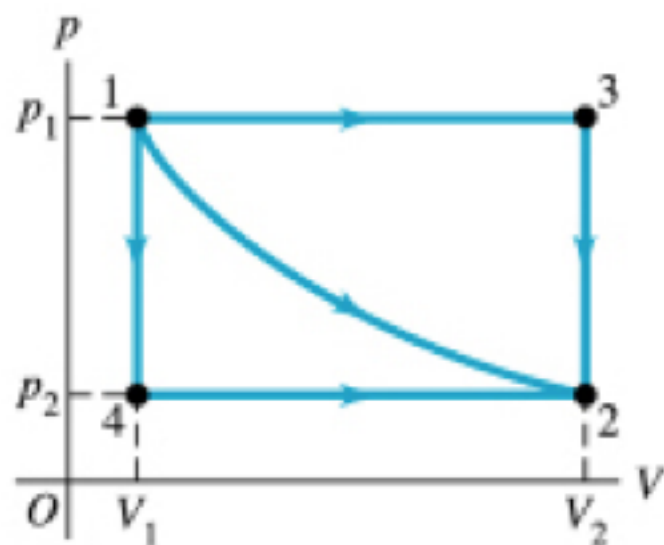


Expansion Work:

$$w = -P_{op} \Delta V$$

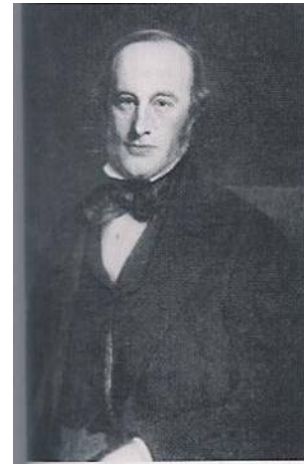
$$(w = -f \Delta x = -P_{op} A \Delta x = -P_{op} \Delta V)$$

# Work (and heat): path dependent





Nicolas Leonard Sadi Carnot  
(1796-1832)



James Prescott Joule  
(1818-1889)

For a **closed system**, the first law can be expressed as:

$$\Delta E = E_B - E_A = q + w$$

$\Delta E$  is the change in internal energy of the system.

Important!

**$U$  is a state function.**

**$q$  and  $w$  are not state functions (they are path dependent)**

**Conservation of Energy:** Energy can neither be created nor destroyed, although it can be converted from one form to another.