

# Lecture 3

ERD Sections 2.7 through 2.9 and 3.1

## Key points of the last lecture

- Reversible vs. irreversible change

reversible  $\longrightarrow$  maximizing profit, ideal case

- Heat

## Key points of today's lecture

- Heat capacity and Specific heat capacity
- First law of thermodynamics
- State functions vs. path functions

# Heat (q)

Heat is a form of energy associated with temperature

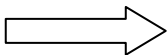
Random motion of molecules

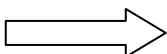
Energy that flows between system and surroundings and vice versa to change the temperature of either the system or surroundings

At thermal equilibrium, heat stops flowing between system and surroundings

Historically, defined in units of calories.

1 calorie was the energy required to raise the temperature of 1 g of H<sub>2</sub>O by 1 C from 14.5 C to 15.5 C There are 4.18 J per calorie.

+ q       heat added to the system. Energy of the system increases.

- q       heat transferred from the system to the surroundings. Energy of the system decreases.

# Heat capacity

Units of C = J/K

Heat required to change the temperature by one degree for a particular system

$$C = \frac{q}{\Delta T} = \frac{dq}{dT} = \frac{q}{dT} \qquad C = \frac{dq}{dT}$$

$$q = \int_{T_i}^{T_f} C dT$$

$\overline{C}_P$  (J mole<sup>-1</sup> K<sup>-1</sup>)

At constant volume  $C_V$

H<sub>2</sub>O(liquid, 25°C): 75.3

At constant pressure  $C_P$

H<sub>2</sub>O(gas, 100°C): 37.5

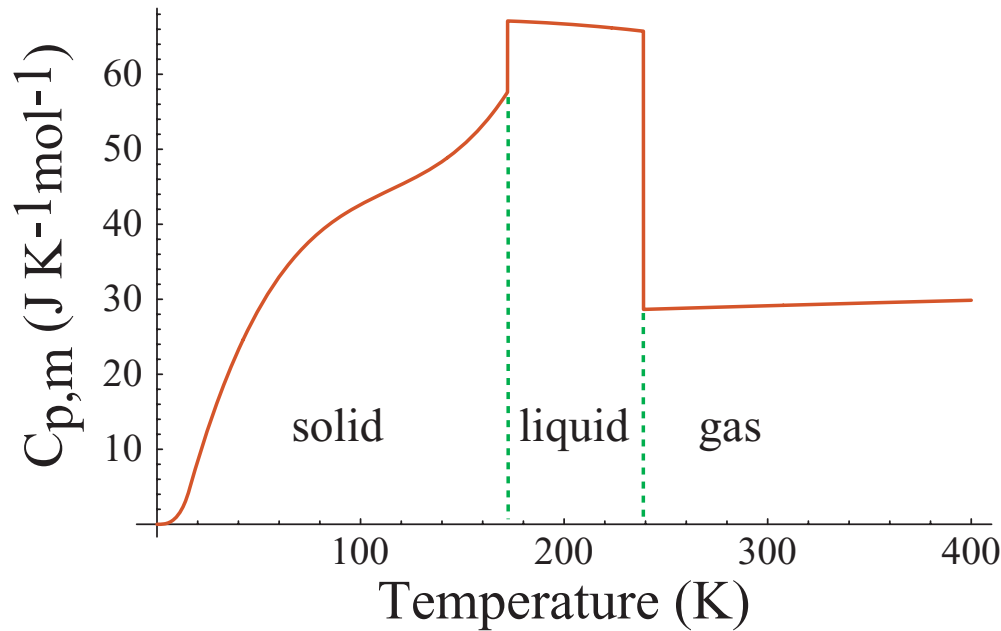
H<sub>2</sub>O(solid, -10°C): 38.1

$\overline{C}$  Specific heat capacity or Molar heat capacity is the heat capacity of one mole of the substance; or the heat capacity per mole of system.

# Heat capacity

$$C = \lim_{\Delta T \rightarrow 0} \frac{q}{T_f - T_i} = \frac{dq}{dT}$$

- $C$  has the units  $J K^{-1} kg^{-1}$  in SI units. It is an extensive quantity.
- $C_p$  and  $C_v$  distinguish method of measurement; the first at constant pressure and the second at constant volume.
- $C_m$  is an intensive quantity with the units  $J K^{-1} mol^{-1}$ .
- Convenient to measure  $q$  through electrical work  $w = \phi \cdot I \cdot t$
- Numerical value depends on path between initial and final states. Most common are constant  $V$  or  $P$ .



- $C_{P,m}$  for the solid rises rapidly at low  $T$  vibrations of the solid activated.
- $C_{P,m}$  increases discontinuously as the solid melts to form a liquid because the liquid retains the local vibrational modes of the solid shifted to lower more accessible frequencies.
- $C_{P,m}$  decreases discontinuously at the vaporization temperature because local vibrational modes in the liquid are converted to translations, which can't take up <sup>2-13</sup> as much energy as vibrations.

Once  $C_{P,m}$  is known,  $q$  can be determined from  $\Delta T$  of reservoir

$$q_P = \int_{T_{sys,i}}^{T_{sys,f}} C_P^{system}(T) dT = - \int_{T_{surr,i}}^{T_{surr,f}} C_P^{surroundings}(T) dT$$

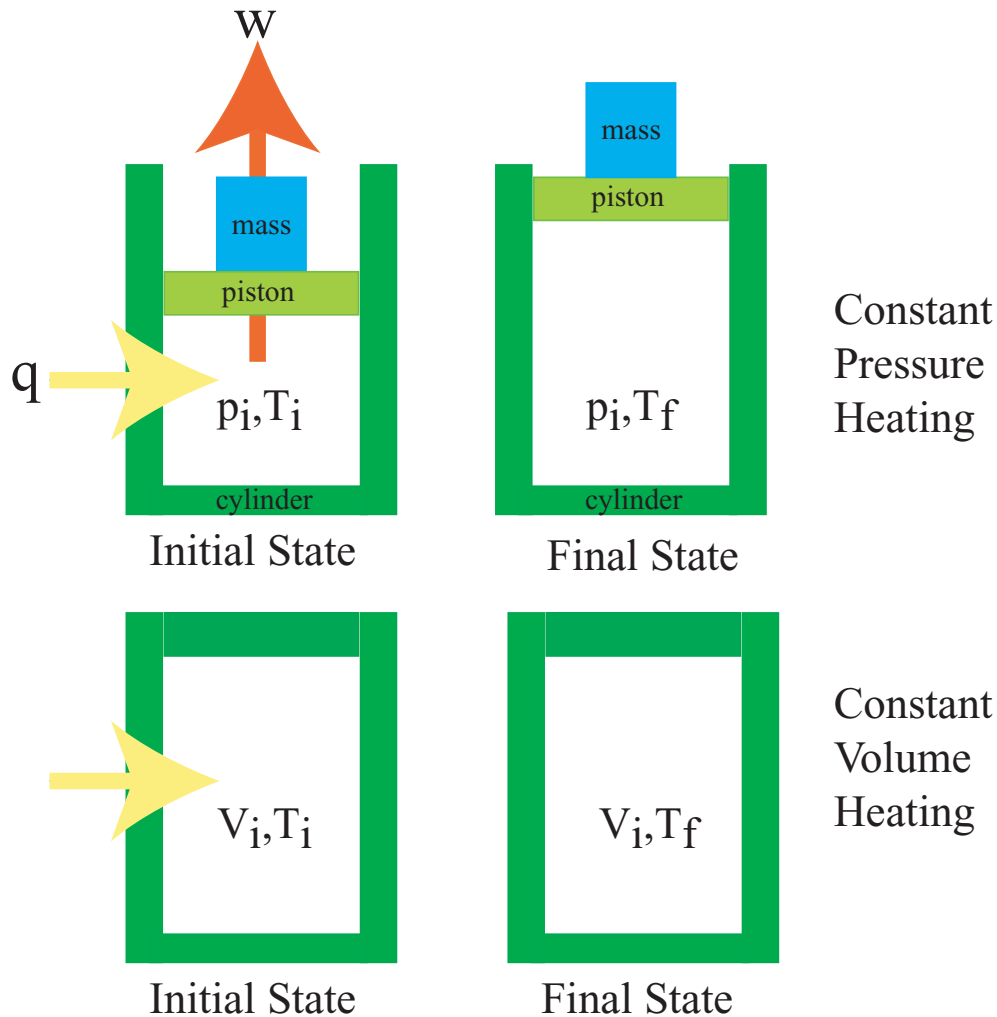
Water is a convenient choice of material for a heat bath in experiments because  $C_P$  is nearly constant at the value

$4.19 J g^{-1} K^{-1}$  or  $75.4 J mol^{-1} K^{-1}$  over the range  $0^\circ C$ - $100^\circ C$ .

From the idea of the equipartition of energy: each mode that can access the energy gets  $\frac{1}{2} R$  added to the heat capacity. For water

We have 3 rotational and 3 translational degrees of freedom and 3 vibrational degrees of freedom. This gives at most  $3+3+2*3=12$  modes, or  $96 J mol^{-1} K^{-1}$

$C_{P,m} > C_{V,m}$  for gases



For ideal gas

$$C_P - C_V = nR \text{ or}$$
$$C_{P,m} - C_{V,m} = R$$

# First law of thermodynamics

$$\Delta U = q + w$$

Internal energy      heat      work

The diagram shows the equation  $\Delta U = q + w$ . Below the equation, three labels are placed: 'Internal energy' under  $\Delta U$ , 'heat' under  $q$ , and 'work' under  $w$ . Arrows point from each label to its corresponding term in the equation.

For infinitesimally small changes

$$dU = \cancel{d}q + \cancel{d}w = q + w$$

There is a thermodynamic property  $U$ , defined above.

It is a function of the state variables of the system ( $P, V, T, \dots$ )

$\Delta U$  for a closed system is given by the above equation.

# First law of thermodynamics (Cont) $\Delta U = q + w$

(1) Internal energy is conserved

(a) total energy of an isolated system is a constant

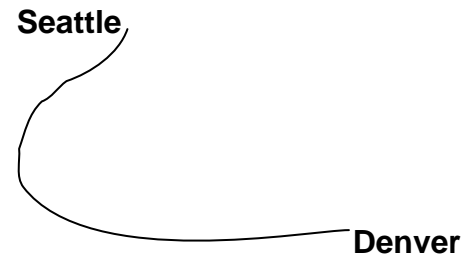
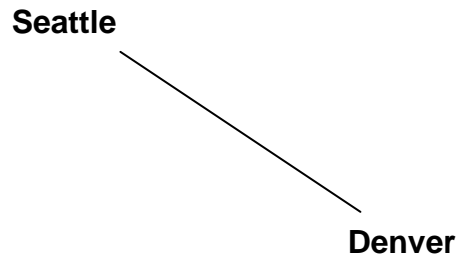
(b) change in U for a closed system is given by the first law.

(2) Internal energy is a state function and not a path function, i.e. it depends only on the initial and final state of the system and not on the path taken to get there.

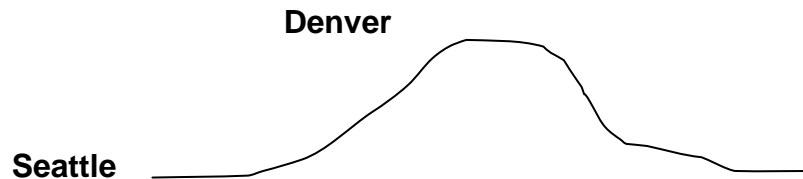
# State function analogy

Say you drive from Seattle, WA to Denver, CO

Is the distance you travel a state function?

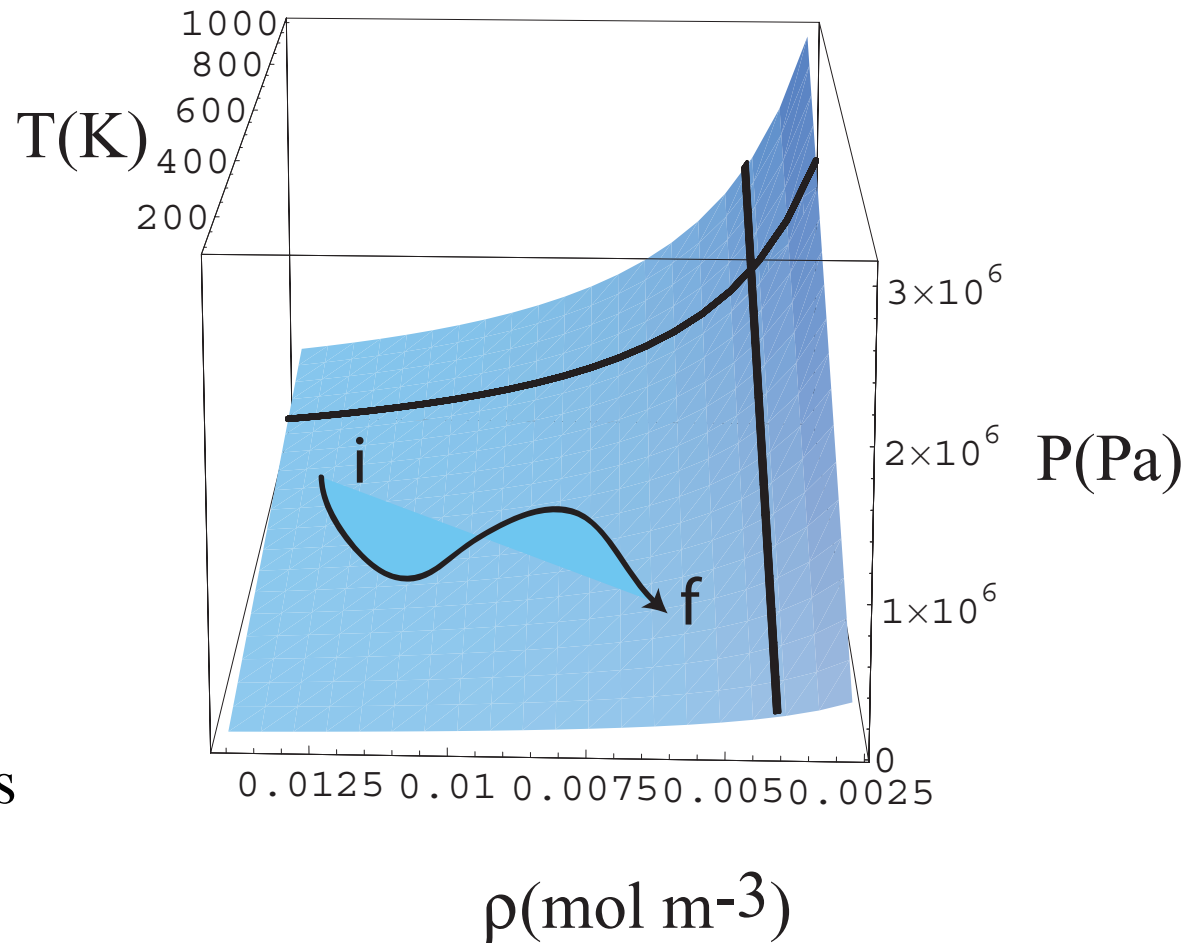


Is the elevation you gain a state function?

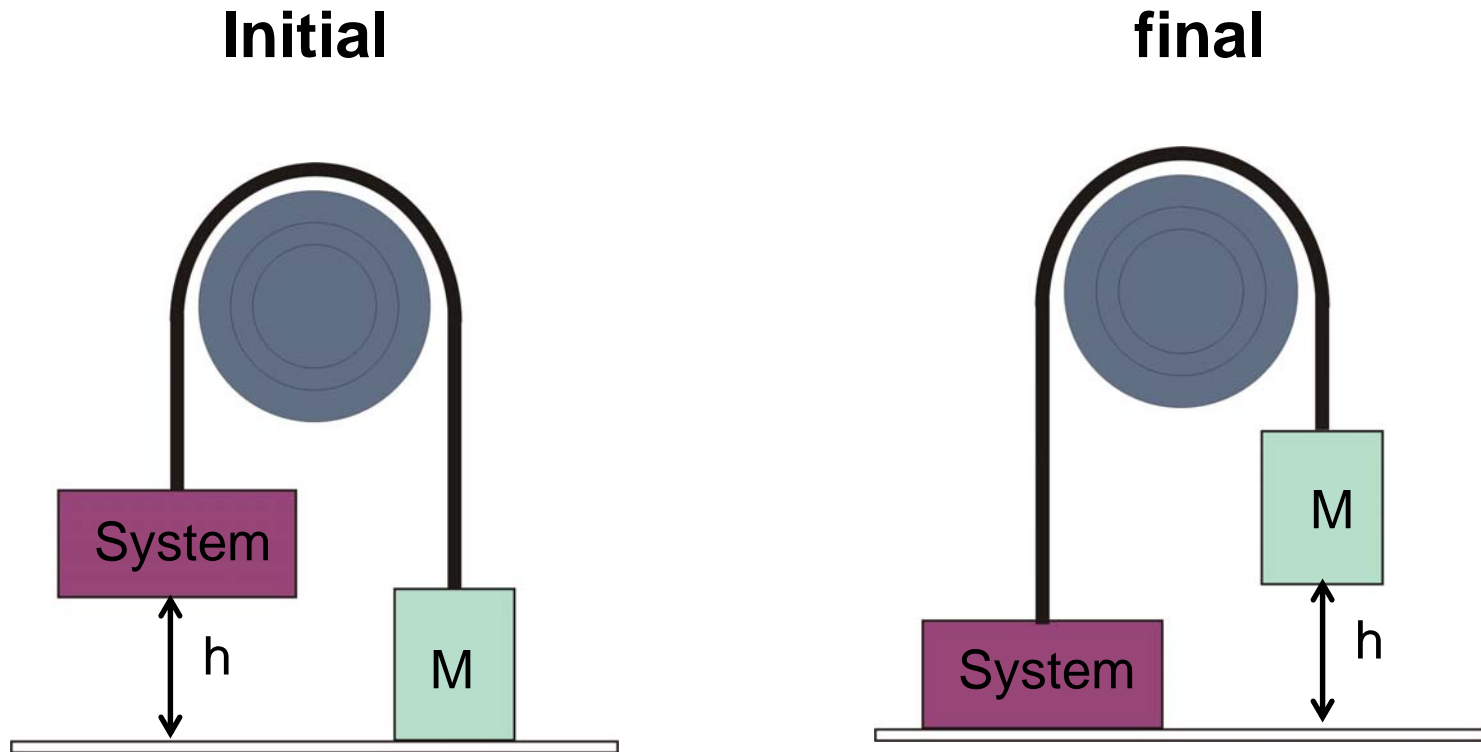


Thermodynamics can only be applied to systems in internal equilibrium, and a requirement for equilibrium is that the overall rate of change of all processes such as diffusion or chemical reaction is zero. How do we reconcile these statements with our calculations of  $q$ ,  $w$ , and  $\Delta U$  associated with processes in which there is a macroscopic change in the system?

## Quasi-static process



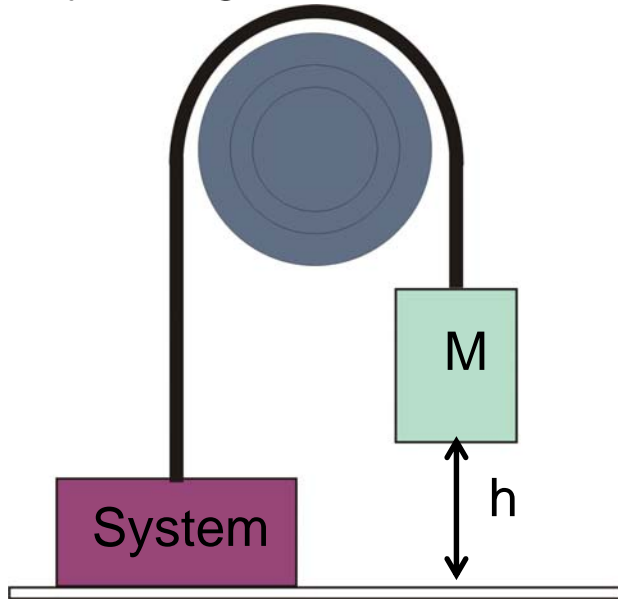
# Internal Energy as a state function



System and mass  $M$  have the same mass; system changes reversibly.

# Two Distinct final positions from the initial one (previous slide)

System descends infinitesimally slowly and generates no heat



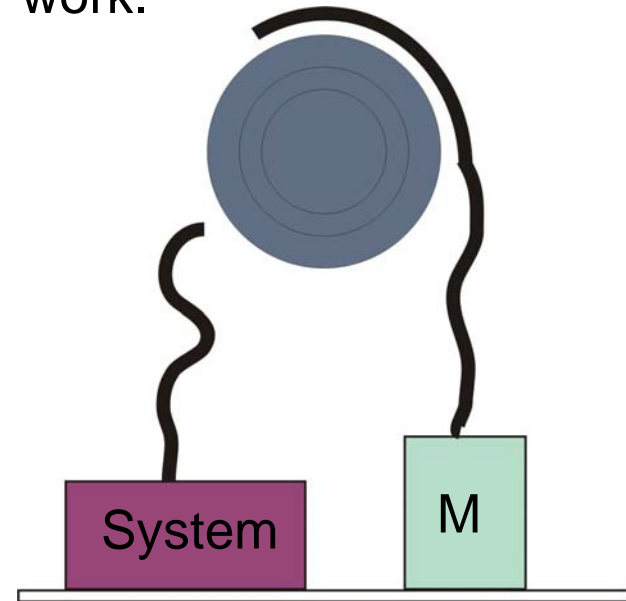
$$q = 0$$

$$w = -Mgh$$

$$\Delta U = q + w$$

$$\Delta U = -Mgh$$

The rope is cut and the system crashes. It does no work.



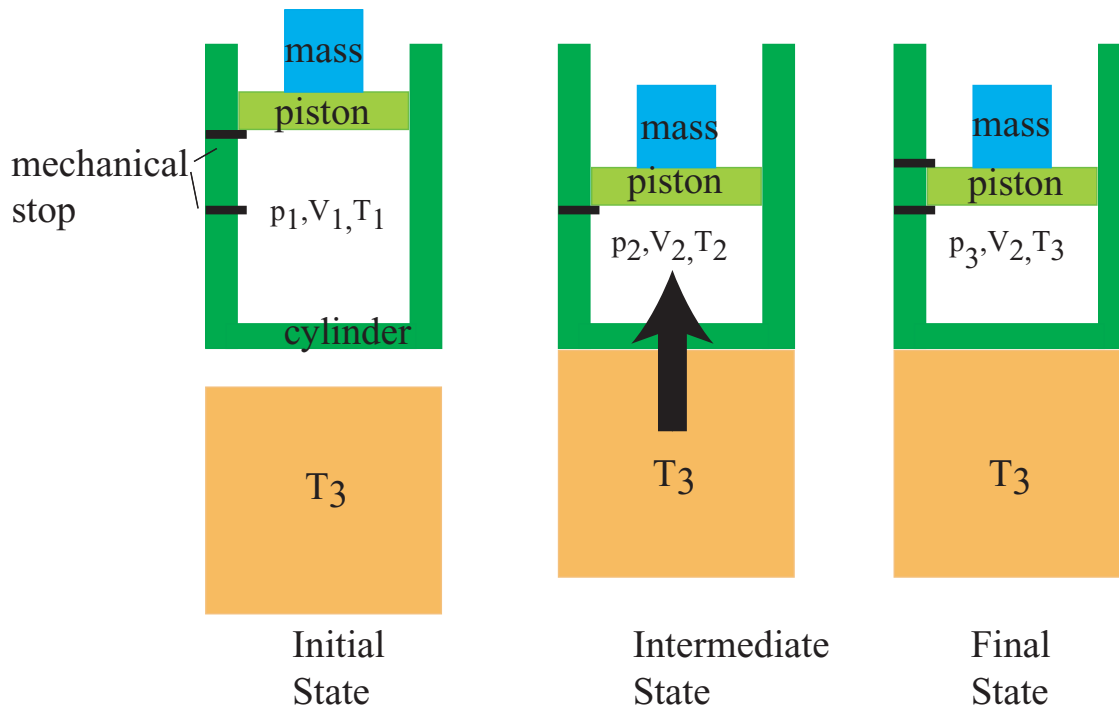
$$q = -Mgh$$

$$w = 0$$

$$\Delta U = q + w$$

$$\Delta U = -Mgh$$

# Is $w$ a state function?



$$T_1 < T_2 < T_3$$

Repeat process with different masses. For each path

$$P_1, T_1 \rightarrow P_3, T_3$$

therefore  $\Delta U$  same

$$w = -P_{\text{external}} \Delta V$$

Work different for each path.

Therefore, work is a **path function**, not a **state function**.

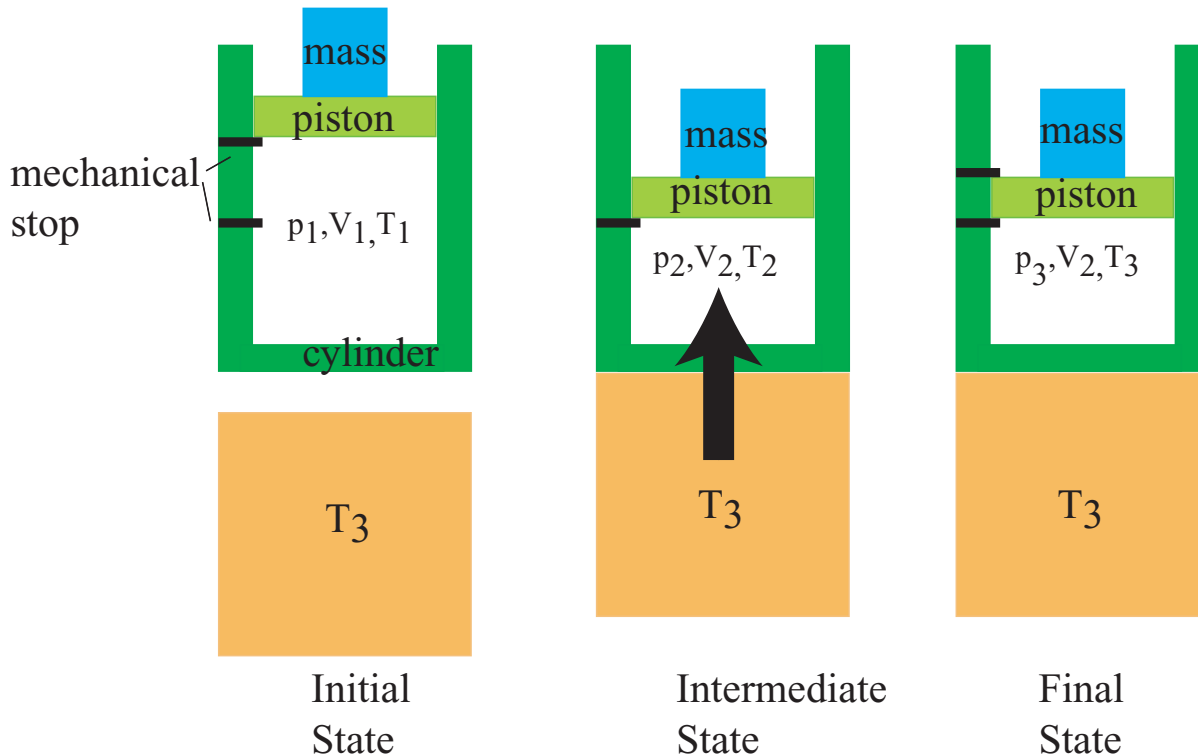
$$P_{\text{ext}} = \frac{mg}{A} > P_3$$

Redo this for the case of expansion.

# Is $q$ a state function?

If  $w$  is a path function and  $U$  is a state function,

$q = \Delta U - w$  must be a path function.



$$\Delta q \neq \int_i^f dq \neq q_f - q_i$$

$$\Delta w \neq \int_i^f dw \neq w_f - w_i$$

# Following Changes in State Functions

Using Mathematics to help us keep track of changes in state functions.

In one dimension, a relation in calculus:

$$f = f(x) \quad df = \left( \frac{df}{dx} \right) dx \quad \text{Chain Rule}$$

$$f = \int \left( \frac{df}{dx} \right) dx \quad \text{Indefinite Integral}$$

$$\Delta f = f(x_2) - f(x_1) = \int_{x_1}^{x_2} \left( \frac{df}{dx} \right) dx \quad \text{Definite Integral}$$

# Apply Differentials to Newton's Mechanics

- Distance is a function of time
- Velocity is the derivative of position in time

$$f = x(t) \quad \frac{df}{dt} = v = v(t) \quad \Delta x = \int_{t_1}^{t_2} v(t) dt$$

Suppose the velocity is a constant (object in free space)

$$v = v_o \quad \Delta x = v_o \Delta t$$

Suppose the velocity increases linearly with time

(object falling under gravity)

$$v(t) = gt \quad \Delta x = \int_{t_1}^{t_2} gt dt \quad \Delta x = \frac{1}{2} g (t_2^2 - t_1^2) = \frac{1}{2} g (t_2 + t_1) \Delta t$$

## Notation to include multiple variables

- Change the derivative symbol from  $d \rightarrow \partial$
- Use subscripts to tell which variables are held constant (when taking derivatives)
- Can write changes so that only one variable changes at a time.

# The Mathematical Properties of State Functions

$$P = f(V, T) = n \frac{RT}{V}$$

$$dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV$$

The above notation already implies that  $n$  is fixed.

If  $n$  can vary also, we can generalize the equations further.

$$dP = \left( \frac{\partial P}{\partial T} \right)_{V,n} dT + \left( \frac{\partial P}{\partial V} \right)_{T,n} dV + \left( \frac{\partial P}{\partial n} \right)_{T,V} dn$$

These statements are always correct.

# Evaluating Partial Derivatives

Demonstrate derivatives, called partial derivatives, with the

I.G. E.o.S. 
$$dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV$$

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\partial \left( \frac{nRT}{V} \right)}{\partial T} \bigg|_V = \frac{1}{V} \frac{d(nRT)}{dT} = \frac{nR}{V} = \frac{P}{T}$$

$$\left( \frac{\partial P}{\partial V} \right)_T = \frac{\partial \left( \frac{nRT}{V} \right)}{\partial V} \bigg|_T = nRT \frac{dV^{-1}}{dV} = -\frac{nRT}{V^2} = -\frac{P}{V}$$

Use Reciprocal rule 
$$\left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{\left( \frac{\partial P}{\partial V} \right)_T} = -\frac{V}{P}$$

## Derivates in different order

$$\left( \frac{\partial}{\partial T} \left( \frac{\partial f(V, T)}{\partial V} \right) \right)_V = \left( \frac{\partial}{\partial V} \left( \frac{\partial f(V, T)}{\partial T} \right) \right)_T \quad \text{or} \quad \frac{\partial^2 P}{\partial T \partial V} = \frac{\partial^2 P}{\partial V \partial T}$$

Demonstrates that the order does not matter for state functions

$$\left( \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial V} \right) \right)_V = \frac{\partial^2 P}{\partial T \partial V} = \frac{\partial \left( \frac{\partial \left( \frac{nRT}{V} \right)}{\partial V} \right)_T}{\partial T} = \left( \frac{\partial \left( -\frac{nRT}{V^2} \right)}{\partial T} \right)_V = -\frac{nR}{V^2}$$

$$\left( \frac{\partial}{\partial V} \left( \frac{\partial P}{\partial T} \right) \right)_T = \frac{\partial^2 P}{\partial V \partial T} = \frac{\partial \left( \frac{\partial \left( \frac{nRT}{V} \right)}{\partial T} \right)}{\partial V} = \frac{\partial \left( \frac{nR}{V} \right)}{\partial V} = -\frac{nR}{V^2}$$

# Integrate State Function

State functions can be integrated over the various variables.

For example the pressure is a function of the temperature and volume. However:

When we have a process where only the temperature varies:

$$\Delta P = P_{final} - P_{initial} = \int_{T_i}^{T_f} \left( \frac{\partial P}{\partial T} \right)_V dT$$

For Ideal Gas (for changes at constant V)

$$\Delta P = \frac{nR}{V} \Delta T$$

This equation says that  $P$  can be expressed as an infinitesimal quantity,  $dP$ , that when integrated depends only on the initial and final states.  $df$  is called an *exact differential*.  $U$  is also an example of a state function.

# Review of notation

$\partial \equiv$  partial derivative

$d \equiv$  infinitesimal change (for a total derivative)

$\Delta \equiv$  large change (often after integration)

$$G(x, y) = xy^3$$

$$w = -P_{\text{constant}} \int_{V_i}^{V_f} dV$$

$$\left( \frac{\partial G}{\partial x} \right)_y = y^3 \quad \left( \frac{\partial G}{\partial y} \right)_x = 3xy^2$$

$$w = -P_{\text{constant}} (V_f - V_i) = -P_{\text{constant}} \Delta V$$

Change X only

Change Y only

$$\Delta G = \int_{x_1}^{x_2} \left( \frac{\partial G}{\partial x} \right)_y dx = G(x_2, y) - G(x_1, y)$$

$$\Delta G = \int_{y_1}^{y_2} \left( \frac{\partial G}{\partial y} \right)_x dy = G(x, y_2) - G(x, y_1)$$

$$G(x_2, y) - G(x_1, y) = x_2 y^3 - x_1 y^3 = y^3 (x_2 - x_1)$$

$$G(x, y_2) - G(x, y_1) = x y_2^3 - x y_1^3 = x (y_2^3 - y_1^3)$$

$$\int_{x_1}^{x_2} \left( \frac{\partial G}{\partial x} \right)_y dx = \int_{x_1}^{x_2} y^3 dx = y^3 x \Big|_{x_1}^{x_2}$$

$$\int_{y_1}^{y_2} \left( \frac{\partial G}{\partial y} \right)_x dy = \int_{y_1}^{y_2} 3xy^2 dy = xy^3 \Big|_{y_1}^{y_2}$$

Both X and Y change????

# Important results from differential calculus.

For a function  $z = f(x,y)$ , which can be rearranged to  $x = g(y,z)$  or  $y = h(x,z)$ . For example, if

$$P = \frac{nRT}{V}, \text{ then } V = \frac{nRT}{P} \text{ and } T = \frac{PV}{nR}$$

$$P = P(V, T)$$

Reciprocal Rule

$$\left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_z}$$

Cyclic rule

$$\left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1$$

$$\left( \frac{\partial x}{\partial y} \right)_z = - \frac{\left( \frac{\partial z}{\partial y} \right)_x}{\left( \frac{\partial z}{\partial x} \right)_y}$$

# Test for a state function (exact and inexact differentials)

For a function  $z$ , that is a state function and depends on 2 state variables,  $x$  and  $y$ , the following holds true.

$$z = z(x, y) \quad (1) \quad dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy$$

$$(2) \quad \left[ \frac{\partial z}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y \right]_x = \left[ \frac{\partial z}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right]_y$$

Try it with this test function,  $G$ :

$$G(x, y) = xy^3$$

$$\left( \frac{\partial G}{\partial x} \right)_y = y^3 \quad \left( \frac{\partial G}{\partial y} \right)_x = 3xy^2$$

## Key points of today's lecture

- Heat
- Specific heat capacity
- First law of thermodynamics
- State functions vs. path functions
- Internal energy is a state function, work and heat are not state functions.
- Mathematical tests for state functions