

What is thermodynamics? and what can it do for us?

- The overall goal of thermodynamics is to describe what happens to a system (anything of interest) when we change the variables that characterized the system such as temperature, pressure and volume.
- The laws of thermodynamics allow us to calculate things about the system that we are interested in such as its energy, heat, work, entropy, Gibbs energy etc. and also to predict whether a system will spontaneously change when a variable is changed.



First Law of Thermodynamics

- The 1st Law of Thermodynamics is “the law of conservation of Energy”, which is a book keeping equation to account for the interchange and relationship among energy, work and heat.
- Leads to the definition of new thermodynamic state function called internal energy (u) and also the enthalpy (H) which can be defined in terms of p, V , and U .
- First Law also deals with thermochemistry (heat produced or absorbed during chemical reaction and solution process).



DEFINITION OF TERMS

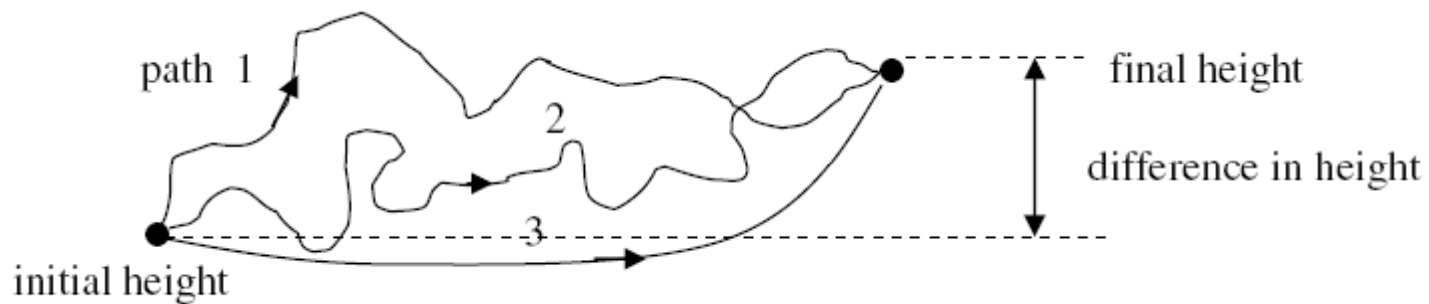
1. **Universe = System + Surroundings**
2. **Types of Systems** (open, closed, and isolated)
3. **Properties of the System** (Extensive and Intensive)
4. **State of the System** (condition or state of the thing of interest)
5. **Path:** This refers to how the initial state is changed to the final state and specifies how the variables like temperature, pressure and volume are changed to bring about the change in state. (how you will go from Jeddah to Madinah)

REVERSIBLE PATH: one in which the changes are done infinitely slowly so that the system is always in a state of “equilibrium”. (moving piston slowly)

IRREVERSIBLE PATH: this refers to a change which is done quickly and with large finite changes in the variables – this is what happens in real life. (drop weight on the piston suddenly).



7. **PATH FUNCTION:** (work, heat) this is a quantity whose value depends on **how** the system goes from the initial to final state – it only appears when a system is undergoing a change. For example, work is only done when an object is moved against a force.
- **STATE FUNCTION:** (energy, entropy, enthalpy, Gibbs energy) this is a quantity whose value depends on the state of the system and not how it got there.



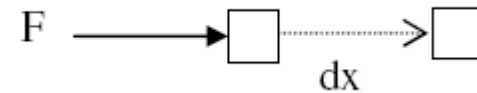
- 8. **INTERNAL ENERGY U** is the total energy of all the molecules in the system
- $U = \sum \text{kinetic energy (translation, vibration, rotation)} + \text{potential energy (due to the interaction of the molecules)}$



Work, w

- **Work** : transfer of energy that can cause motion against an opposing force.
- **In mechanics**: work is defined in terms of the distance x that a force F moves an object.
Work = Force (F)x Length(L)

$$w = \int dw = - \int F dx$$



- **In thermodynamics**: work is usually expressed in terms of a pressure changing a volume rather than a force moving through a distance. But these are equivalent.

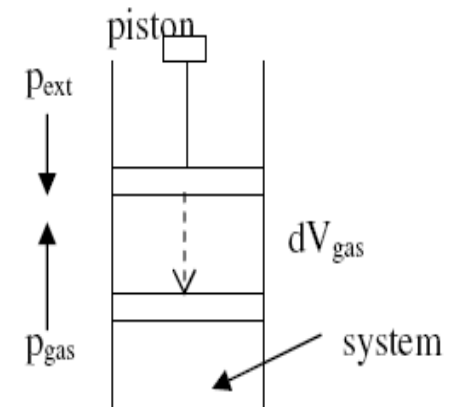
$$dw = - p_{\text{ext}} dV_{\text{gas}}$$

where p_{ext} is the external pressures due to the weight;
 dV_{gas} is the volume change of the gas.

Note that:

pressure = force/area so force = pressure x area
 $w = \text{force} \times \text{distance} = (\text{pressure} \times \text{area}) \times \text{distance}$
 $= \text{pressure} \times \text{volume}$

Work unit is Joule = $\text{kg m}^2 \text{s}^{-2}$



Conventions for Work

Work is DONE ON the system [weight drops, gas is compressed, gas energy increases] by the surroundings **OR** is DONE BY the system [weight rises and gas expands] on the surroundings. Doing work on the system [compressing a gas to a higher pressure] increases the system energy since the gas has now a greater potential to push back and do work back on the surroundings - like compressing a spring.

**Work is done ON system
by surroundings**

work is positive $w > 0$
weight (in surroundings) drops
gas (system) is compressed
gas pressure increases
gas has more energy

**Work is done BY system
on surroundings**

work is negative $w < 0$
weight rises
gas expands
gas pressure falls
gas has less energy



How many paths do we have?

PATH 1: *irreversible expansion*

by knocking off two of the weights to get to V_f .

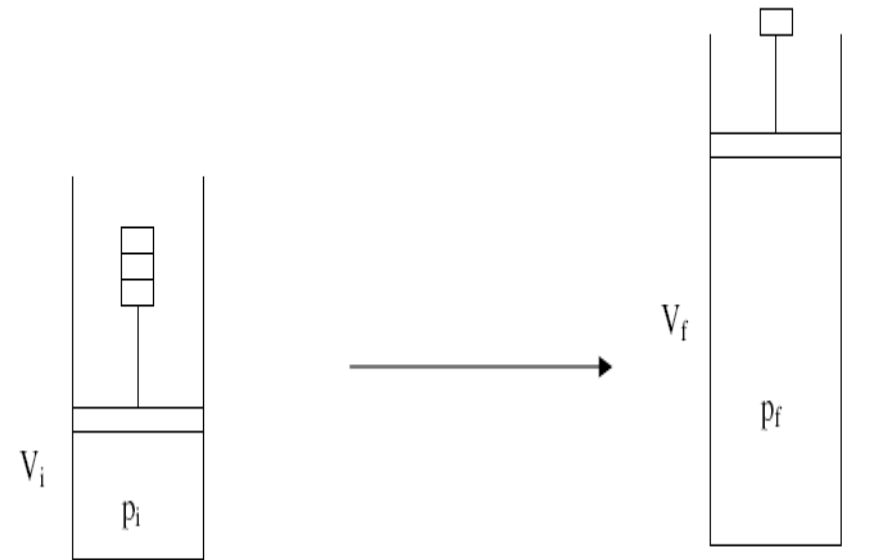
PATH 2: irreversible expansion

by knocking off one weight and then knocking off a second weight soon after i.e. get to V_f by two successive step changes in pressure.

PATH 3: reversible expansion

in which the weight is reduced in infinitesimal steps so that as p_{ext} changes it differs from p_{gas} by an infinitesimal amount, dp , and V_i changes to V_f in a smooth even fashion. Since the gas is ideal we know how p changes with V in this case.

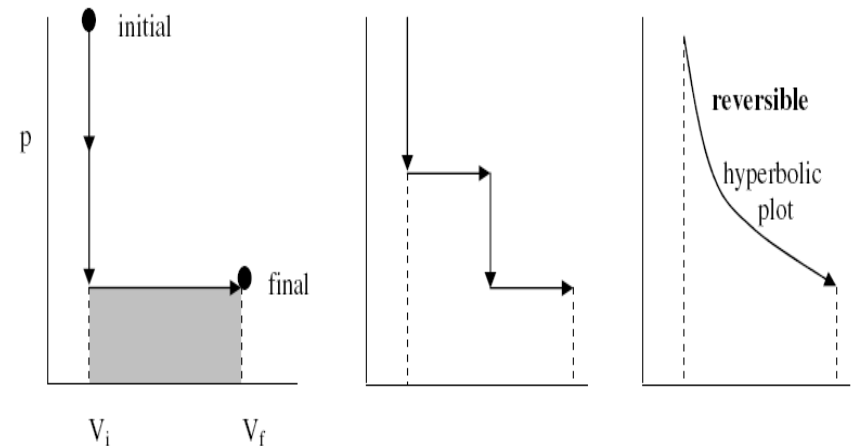
i.e. $p = nRT/V$ and a plot of p vs V is hyperbolic.



PATH 1

PATH 2

PATH 3



w for an irreversible isothermal process

$$\delta w = -p_{ext} dV$$

$$\delta w_{irrev} = -p_{ext} \int_i^f dV$$

irreversible & const. pressure

$$\int_i^f \delta w = -p_{ext} \int_i^f dV$$

$$w_{irrev} = -p_{ext} (V_f - V_i)$$



Reversible, isothermal expansion work, w_{rev}

$$\delta w = -p_{ext} dV$$

$$\delta w_{rev} = -p_{system} dV(\text{reversible}); pV = nRT(\text{ideal. gas})$$

$$\delta w_{rev} = -nRT \frac{dV}{V}$$

$$\int_i^f \delta w_{rev} = -nRT \int_i^f \frac{dV}{V}$$

$$w_{rev} = nRT \ln \frac{V_f}{V_i}$$

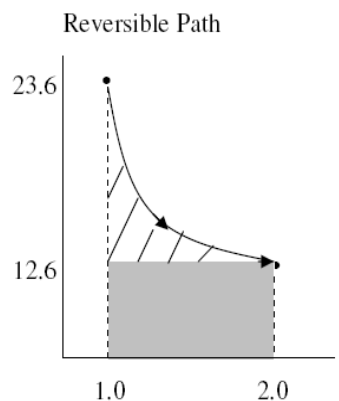
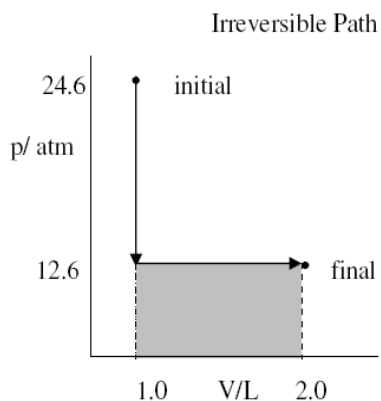


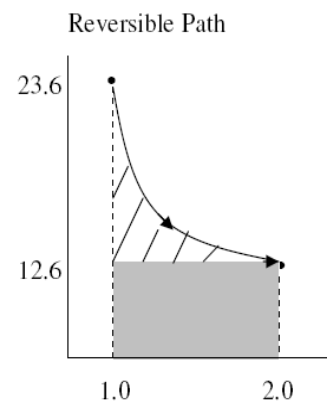
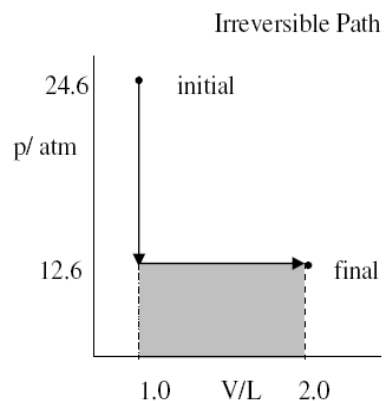
One mole of an ideal gas at 300 K in 1.0 L is expanded to 2.0 L isothermally via two different paths. Calculate the work.

Path A: an irreversible expansion against a constant external pressure of 12.3 atm –gas will expand until its pressure matches 12.3 atm.

Path B: a reversible, isothermal expansion until the final pressure is 12.3 atm.

- So, before doing any calculation you should do a simple analysis to predict something about your answers and what equations to use.
- (i) Both paths are expansions so the work should be negative in value.
- (ii) Both paths lead to the same final state ($p=12.3 \text{ atm}$, $V=2 \text{ L}$) but we know that the irreversible work done BY the system is less in magnitude so the magnitude of the work for path A should be less
- (iii) Irreversible work, constant external pressure $w = -p_{\text{ext}}\Delta V$
 Reversible work, constant pressure $w = -p\Delta V$





For the calculation you should first specify what you can about the initial and final states.

Initial State

$$\begin{aligned}
 T_1 &= 300 \text{ K} \\
 V_1 &= 1.0 \text{ L} \\
 p_1 &= nRT_1/V_1 \\
 &= \frac{1 \text{ mol} \times .08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{1.0 \text{ L}} \\
 &= 24.6 \text{ atm}
 \end{aligned}$$

Final State

$$\begin{aligned}
 T_2 &= 300 \text{ K} \\
 V_2 &= 2 \text{ L} \\
 p_2 &= nRT_2/V_2 \\
 &= 12.3 \text{ atm}
 \end{aligned}$$

Path A

$$\begin{aligned}
 w &= -p_{\text{ext}}(V_2 - V_1) \\
 w &= -12.3 \text{ atm} (2 - 1) \text{ L} \\
 &= -12.3 \text{ L atm} \times 101.3 \text{ J/L atm} \\
 &= -1.25 \text{ kJ}
 \end{aligned}$$

Path B

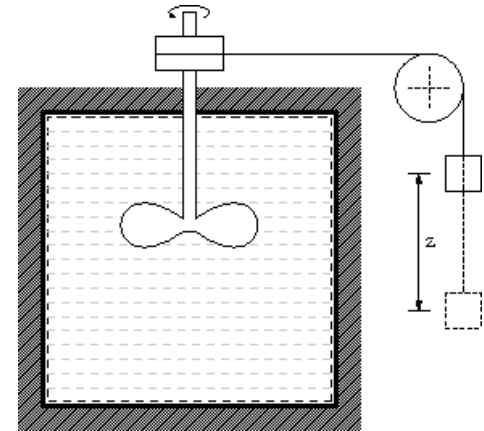
$$\begin{aligned}
 w &= -nRT \ln (V_2/V_1) \\
 w &= -1 \times .08206 \times 300 \ln (2/1) \\
 &= -17.6 \text{ L atm} \times 101.3 \text{ J/L atm} \\
 &= -1.73 \text{ kJ}
 \end{aligned}$$



Don't Ignore or Drop or Forget the Negative Sign

Joule's experiments

Adiabatic process: is one in which the system is thermally isolated so that there is no exchange of heat with the surroundings.



It was well known that heat and work both change the energy of a system. Joule conducted a series of experiments under adiabatic condition which showed the relationship between heat and work in a thermodynamic cycle for a system.

He used a paddle to stir an insulated vessel filled with fluid.

The amount of work done on the paddle was noted (the work was done by lowering a weight, so that work done = mgz).

The property of the system whose change calculated in this way is called the **internal energy (U)**.

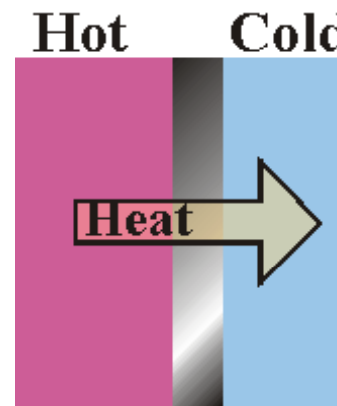
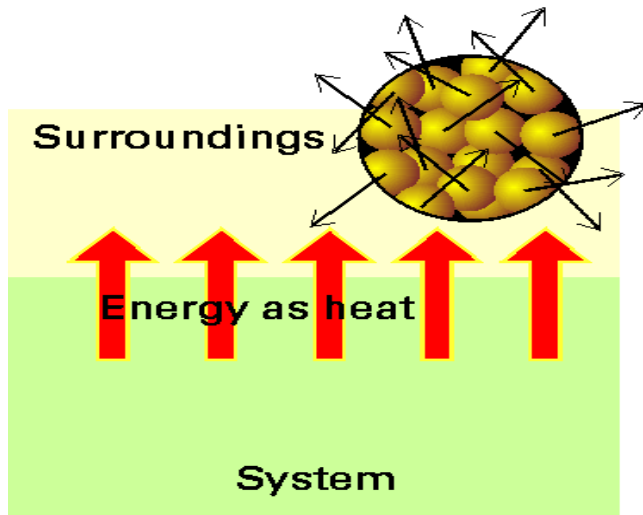
$$\Delta U = w \text{ (in an adiabatic process)}$$

Later, this vessel was placed in a bath and cooled. The energy involved in increasing the temperature of the bath was shown to be equal to that supplied by the lowered weight.

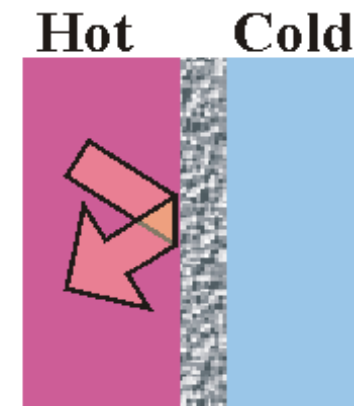


Heat, q

Heat: Transfer of energy as a result of Temp difference between System & Surrounding
Or a change in the state of system (change in U) by allowing heat to flow in and out.



(a) Diathermic



(b) Adiabatic

- Heat change (δq): that which is transferred from hot bodies to cold ones during equilibration.

- Convention:

heat transfer into the system from hot surroundings is positive

heat transfer by the system to cold surroundings is negative.



First Law of Thermodynamics

The increase in internal energy as a result of heat absorbed is diminished by the amount of work done on the surroundings

The internal energy of a given system can be changed from adding both heat and work

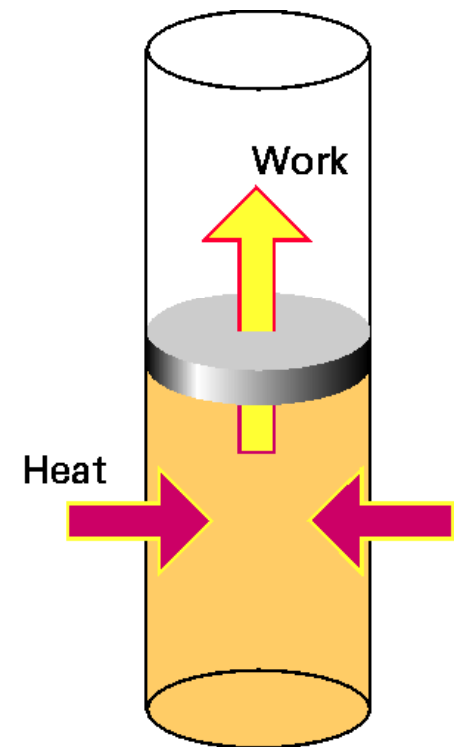
$$\Delta U = q + W$$
$$dU = \delta q + \delta w = \delta q - pdV$$

By convention, heat added to the system,

δQ is positive

and work done by the system on its surroundings,

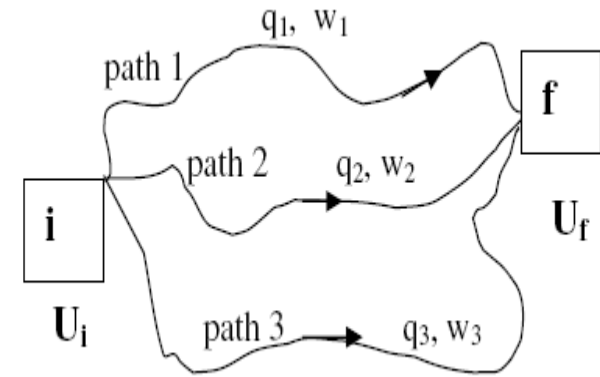
δw is negative.



This is also called the Law of Conservation of Energy



For a closed system from an initial state (P_1, V_1, T_1) to a new state (P_2, V_2, T_2) , and back to (P_1, V_1, T_1) that the sum of 'q' and 'w' transferred across the boundaries of the system is zero.



Neither 'q' nor 'w' is a variable of state; the quantities exchanged around closed paths of both heat and work can be non-zero; only the sum is conserved.

We can, however, define a variable of state U, the internal energy, whose change for a closed system is given by

$$dU = \delta q + \delta w = \delta q - pdV$$

This is the First Law of Thermodynamics. Note: absolute values of U are arbitrary; only its changes dU are significant



A gas was compressed by 300 J as work from the surrounding, and 70 J heat was transferred from the gas to the surrounding. Calculate the internal energy of the gas.

What is given:

The gas accept work from the surrounding

W is positive = +300 J

But, it lost heat to the surrounding

q is negative = -70 J

$$\Delta U = q + W = (-70 \text{ J}) + 300 \text{ J} = 230 \text{ J}$$

For the Surrounding

$$\Delta U = - 230 \text{ J}$$



If a gas is compressed from 400 ml to 200 ml under external pressure with 3 atm and the gas evolved 13 J as heat, calculate the change in the internal energy (ΔU) and work for the gas and change in the internal energy (ΔU) for the surrounding.

What is given:

$$V_1 = 400 \text{ ml} = 0.4 \text{ L}$$

$$V_2 = 200 \text{ ml} = 0.2 \text{ L}$$

$$\Delta V = V_2 - V_1 = 0.2 - 0.4 = -0.2 \text{ L}$$

$$q = -13 \text{ J}$$

and

$$p_{\text{ext}} = 3 \text{ atm}$$

$$W = - p_{\text{ext}} \times \Delta V = -3 \text{ atm} \times (-0.2 \text{ L}) = 0.6 \text{ atm L}$$

$$1 \text{ atm L} = 101.3 \text{ J}$$

$$W = 0.6 \times 101.3 = 60.78 \text{ J}$$

$$q = -13 \text{ J}$$

$$\Delta U = q + W = (-13 \text{ J}) + 60.78 \text{ J} = 47.78 \text{ J}$$

For the Surrounding

$$\Delta U = - 47.78 \text{ J}$$



Two moles of gas at 1 bar and 298 K are compressed at constant T by use of 5 bar pressure. How much work is done on gas? If the compression is driven by 100 kg mass, how far will it fall in the earth's gravitational field?



According to VDW equation

$$\left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$\left(p + \frac{an^2}{V^2} \right) = \frac{nRT}{(V - nb)}$$

$$p = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

The equation for the max work of isotherm expansion of a VDW gas:

$$dW_{rev} = -pdV$$

$$W_{rev} = \int dW_{rev} = - \int_{V_1}^{V_2} \left(\frac{nRT}{(V - nb)} - \frac{an^2}{V^2} \right) dV$$

$$W_{rev} = \int dW_{rev} = - \int_{V_1}^{V_2} \left(\frac{nRT}{(V - nb)} - \frac{an^2}{V^2} \right) dV$$

$$W_{rev} = -nRT \ln \frac{V_2 - nb}{V_1 - nb} + an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$



Heat Capacity, C

The change in the internal energy U produced by the transfer of heat q to a system when no work is done is given by:

$$\Delta U = q \quad (V \text{ is constant, no work is done})$$

In words, “the heat absorbed by a closed system in a process in which no work is done is equal to the increase in the internal energy of the system.”

The amount of heat transferred is (usually) proportional to the temperature gradient and the proportionality constant is the heat capacity.

$$dq = C dT$$

$$q = \int dq = \int C dT$$

$$q = C \int_{T_1}^{T_2} dT \quad \therefore q = C(T_2 - T_1) = C \Delta T \quad \text{and} \quad C = \frac{q}{\Delta T}$$

Heat capacity is an easily measured property. A measured amount of energy in the form of heat is put into a system [usually by electrical heating] and the temperature change is measured with a thermometer or thermocouple.



Constant Volume Heat Capacity (C_v)

This is an easy condition to fulfill for gases in a firm container but a difficult condition to achieve for solids and liquids if the temperature is changed –requires hundreds of atmos pressure to keep its volume constant when heated.

when heat $(dq)_v$ is added to the system held at constant volume and the temperature change is dT .

The constant volume heat capacity is

$$C_v = (dq)_v / dT \quad \text{and} \quad (dq)_v = C_v dT$$

If C_v does not change with temperature then integrating gives

$$(q)_v = C_v DT \quad \text{True for constant volume process.}$$



When $V = \text{constant}$ $dV = 0$ and so the work $dw = -p_{\text{ext}} dV = 0$.
Thus $dU = (dq)_V + 0 = C_V dT$ and

$$\Delta U = \int dU = (q)_V = C_V \Delta T$$

(constant volume process)

$$(dU)_V = C_V dT \quad \therefore \quad C_V = \frac{(dq)_V}{dT} = \frac{(dU)_V}{dT}$$

This means differentiate U with respect to T but treat V as a constant. This is called a partial derivative and is written as:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

The symbol ∂ is pronounced 'di' and the partial is di U over di T at constant V

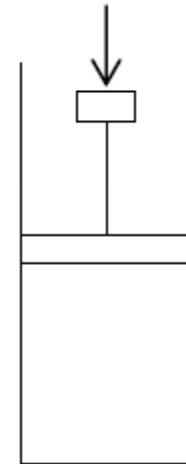


Constant Pressure Heat Capacity (C_p)

changing T or V but ensuring that p stays constant. This is an easy condition to satisfy for solids and liquids if we do the process in the open at constant atmospheric pressure = 1 atm.

We don't have to do anything special to satisfy the path. **That's why a constant pressure path is even more special than a constant volume path.**

For a gas, a constant weight on the piston keeps the pressure constant. Heating the gas will increase the volume of the gas but the pressure will remain the same.



$$C_p = \frac{(dq)_p}{dT} \therefore (dq)_p = C_p dT$$

$$\therefore (q)_p = \int C_p dT = C_p \Delta T \quad \text{For } C_p \text{ constant}$$



Since $\Delta U = q + W$

For a reversible and constant pressure process the first law gives $\Delta U = q_p - p \Delta V$

For the initial and final states:

$$\int_i^f dU = \int_i^f (dq)_p - p \int_i^f dV$$

Integrating gives $U_f - U_i = (q)_p - p (V_f - V_i)$.

Rearranging gives $(U_f - U_i) + p (V_f - V_i) = (q)_p$

$$(U + pV)_f - (U + pV)_i = (q)_p$$

Since U , p and V are all state functions, this leads naturally to a new state function

ENTHALPY $\mathbf{H = U + pV}$

$$\Delta H = (q)_p = C_p \Delta T \quad \text{True for constant pressure}$$

$$\Delta H = H_2 - H_1 = q_p$$



Enthalpy

“The heat absorbed in a process at constant pressure is equal to the change in enthalpy if the only work done is reversible pressure-volume work”

$$\Delta H = H_2 - H_1 = q_p$$

This means that any ΔH for a system can be obtained by going from the initial to final state under constant pressure conditions and measuring the heat that develops.



For example, the heat of a reaction ΔH can be obtained by doing a reaction in the open (a constant pressure path) and measuring the resulting heat. This is very convenient because we can get what we want, the heat of a reaction, without having to do anything very special with regard to conditions i.e. establishing the path.

It's for this reason that the constant pressure path is the most special of all and why we have tables of ΔH values and not ΔU values.

$$(dq)_p = dH \quad \text{and} \quad C_p = \frac{(dq)_p}{dT} \quad \therefore C_p = \frac{dH}{dT} \quad \text{at constant pressure}$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad \text{This is analogous to the definition for } C_v$$



The relation between the two heat capacities can be derived easily for IDEAL gases.

$$\begin{aligned} H &= U + pV & \text{and} & \quad pV = nRT \\ dH &= dU + d(pV) & \text{and} & \quad d(pV) = nRdT \\ \therefore dH &= dU + nRdT \end{aligned}$$

For an ideal gas

$$dH = C_p dT \quad \text{and} \quad dU = C_v dT$$

$$C_p dT = C_v dT + nR dT$$

Thus dividing by dT gives

$$C_p - C_v = nR \quad \text{or}$$

$$C_{p,m} - C_{v,m} = R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Since $C_{p,m}$ values for gases are about $30 \text{ J K}^{-1} \text{ mol}^{-1}$ the difference is large.



10 g of CO₂ (molecular weight 44 g mol⁻¹, C_{p,m} = 46.5 J/K mol) behaving as an ideal gas are heated from 200 K to 430 K reversibly and isobarically at p = 0.75 atm. Analyze the signs and the equations to be used for w, q, ΔU and ΔH. Calculate the values and then comment on the reasonableness of the answers. First write as much information about the initial and final state as possible.

$$\text{moles of gas } n = 10 \text{ g} / 44 \text{ g mol}^{-1} = 0.227$$

initial state

$$T_1 = 200 \text{ K}$$

$$p_1 = 0.75 \text{ atm}$$

$$V_1 = nRT_1/p_1$$

$$= \frac{.227 \times .08206 \times 200}{0.75}$$

$$= 4.967 \text{ L}$$

final state

$$T_2 = 430 \text{ K}$$

$$p_2 = 0.75 \text{ atm}$$

$$V_2 = nRT_2/p$$

$$= \frac{.227 \times .08206 \times 430}{0.75}$$

$$= 10.67 \text{ L} \quad \text{expansion so } V_2 > V_1$$

Analysis

(i) isobaric, reversible ∴ $w = -p\Delta V$; gas expansion ∴ $w < 0$

(ii) isobaric ∴ $q_p = C_p \Delta T = nC_{p,m} \Delta T = \Delta H$; T increases ∴ **heat absorbed $q > 0$**

$\Delta U = w + q$; since heat absorbed and T increases **$\Delta U > 0$**



moles of gas $n = 10 \text{ g} / 44 \text{ g mol}^{-1} = 0.227$	
initial state	final state
$T_1 = 200 \text{ K}$	$T_2 = 430 \text{ K}$
$p_1 = 0.75 \text{ atm}$	$p_2 = 0.75 \text{ atm}$
$V_1 = nRT_1/p_1$	$V_2 = nRT_2/p$
$= \frac{.227 \times .08206 \times 200}{0.75}$	$= \frac{.227 \times .08206 \times 430}{0.75}$
$= 4.967 \text{ L}$	$= 10.67 \text{ L}$ <i>expansion so $V_2 > V_1$</i>

Most work, heat and energy change calculations are less than 5 kJ unless the number of moles is very large or the changes in pressure, temperature or volume are very large

Calculations and Comments

(i) work

$$w = - p\Delta V = -0.75 \text{ atm} \times (10.67 - 4.967) \text{ L} = - 3.77 \text{ L atm} \times 101.3 \text{ J/L atm} = -382 \text{ J}$$

sign is as predicted (magnitude < 5 kJ is reasonable)

(ii) heat

$$q_p = nC_{p,m}\Delta T = 0.227 \text{ mol} \times 46.5 \text{ J K}^{-1} \text{ mol}^{-1} \times (430 - 200) \text{ K} = 2428 \text{ J} \text{ or } 2.43 \text{ kJ} = \Delta H$$

sign as predicted magnitude OK

(iii) energy

$$\Delta U = w + q = -382 + 2428 = 2046 \text{ J} \text{ or } 2.05 \text{ kJ}$$

sign as predicted magnitude OK



Adiabatic process with gases

If a gas system expands adiabatically (no heat is gained or lost by the gas) against external pressure p_{ext}

$$dU = dw = -p_{ext} dV$$

This apply for any adiabatic process, reversible or irreversible , if PV work kind.

If $p_{ext} = \text{zero}$ (adiabatic expand into vacuum) no work is done and there is no change in U . If the expand is opposed by p_{ext} , work is done on the surrounding, and the temperature drops as internal energy converted into work,

so

$$\int_{U_1}^{U_2} \delta U = - \int_{V_1}^{V_2} p_{ext} dV$$

$$\Delta U = U_2 - U_1 = W$$

For an ideal gas, U is a function of T only so,

$$dU = C_V dt$$



If C_V is independent of temperature,

$$\int_{U_1}^{U_2} dU = C_V \int_{T_1}^{T_2} dT$$

$$\Delta U = U_2 - U_1 = C_V (T_2 - T_1)$$

$$W = \Delta U = C_V \int_{T_1}^{T_2} dT = C_V (T_2 - T_1)$$



A mole of monoatomic ideal gas at 1 bar and 273.15 K is allowed to expand adiabatically against pressure 0.395 bar until equilibrium is reached (a) what is the final temperature, (b) what is the final volume, (c) how much work is done, (d) what is the change in the internal energy of the gas?

