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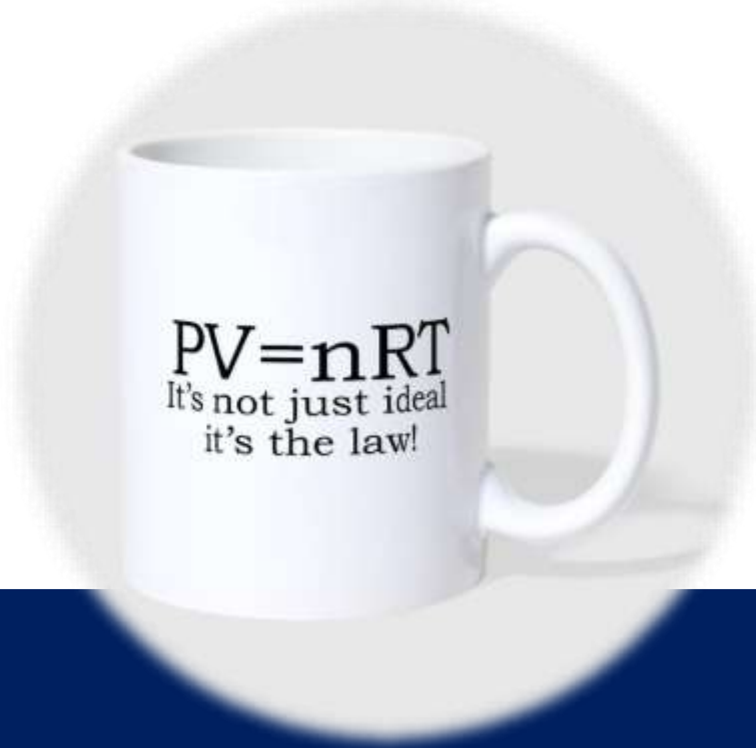

Lecture 7

Thermodynamics (for life & Health science)

29 September 2018

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Forms of Energy

Light Energy

(Radiant)

Energy of Motion

(Kinetic Energy)

Heat (thermal) Energy

Electrical Energy

Nuclear Energy

(Not at 5th grade)

Chemical Energy

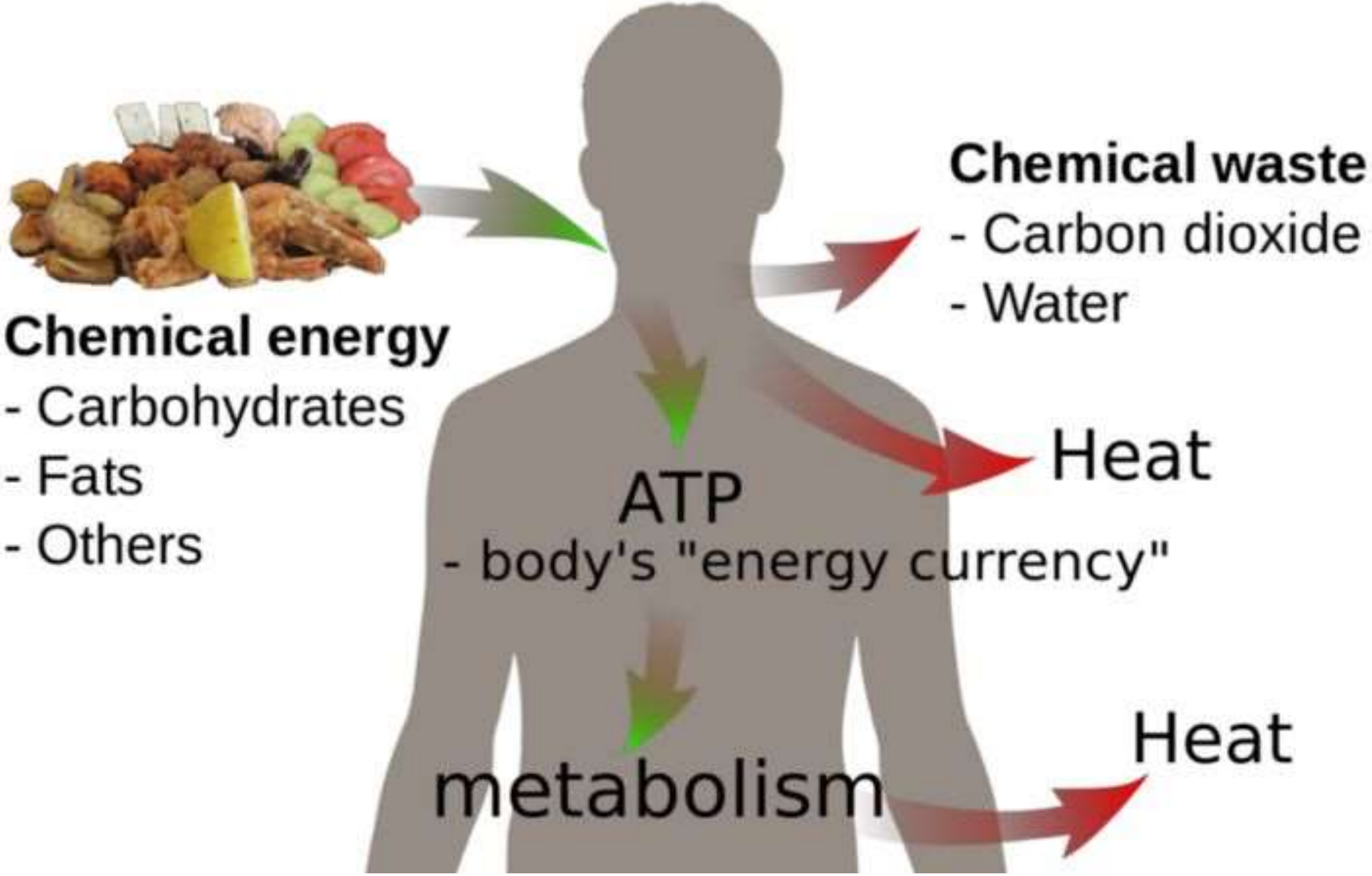
Food Energy

Potential Energy

Stored energy

Sound Energy

Energy and human life



WHAT IS THERMODYNAMICS?

Thermodynamics: A collection of laws and principles describing the flow and interchange of heat, energy and matter in a system of interest.

Thermodynamics allows us to determine whether a chemical process or reaction will occur spontaneously (in the direction written).

Thermodynamics does not tell us about rates (that's kinetics!).

Thermodynamics matters!

Thermodynamics tells us which reactions will go forward and which ones won’t.

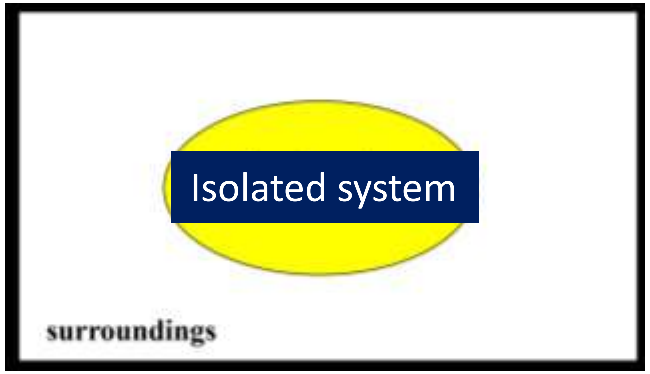
Thermodynamic Concepts:

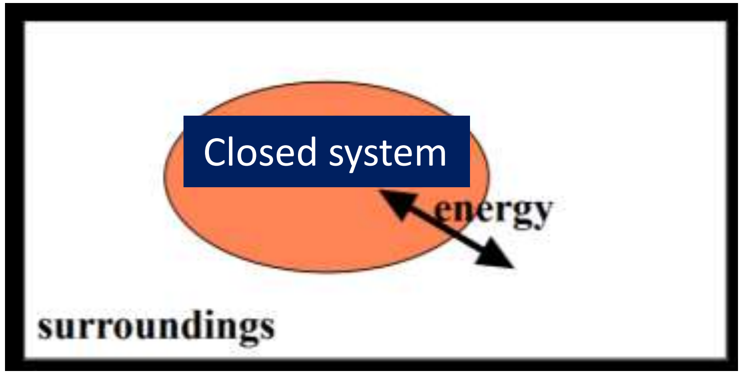
The system is the portion of the universe we are concerned with; everything else is the surroundings. **The system + surroundings = universe**

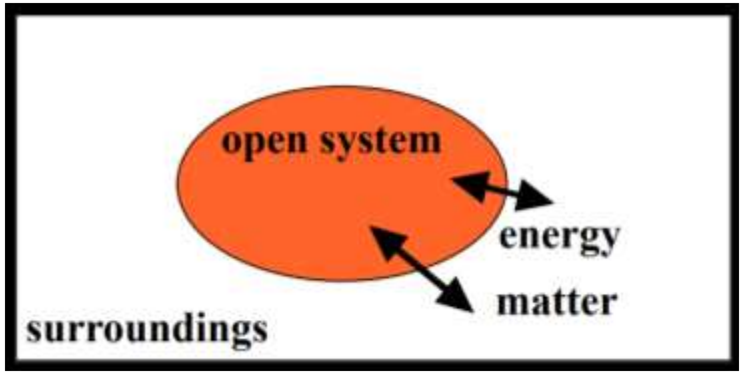
Isolated system:
No exchange of energy or matter

Closed system:
Energy exchange occurs

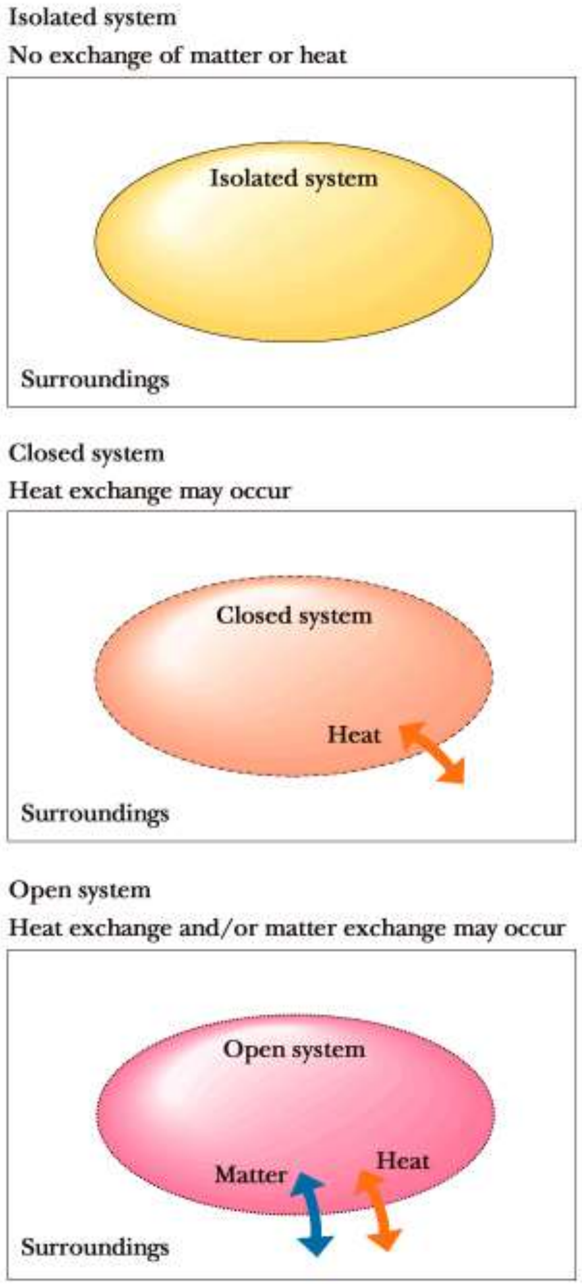
Open system:
Energy or matter exchange occurs





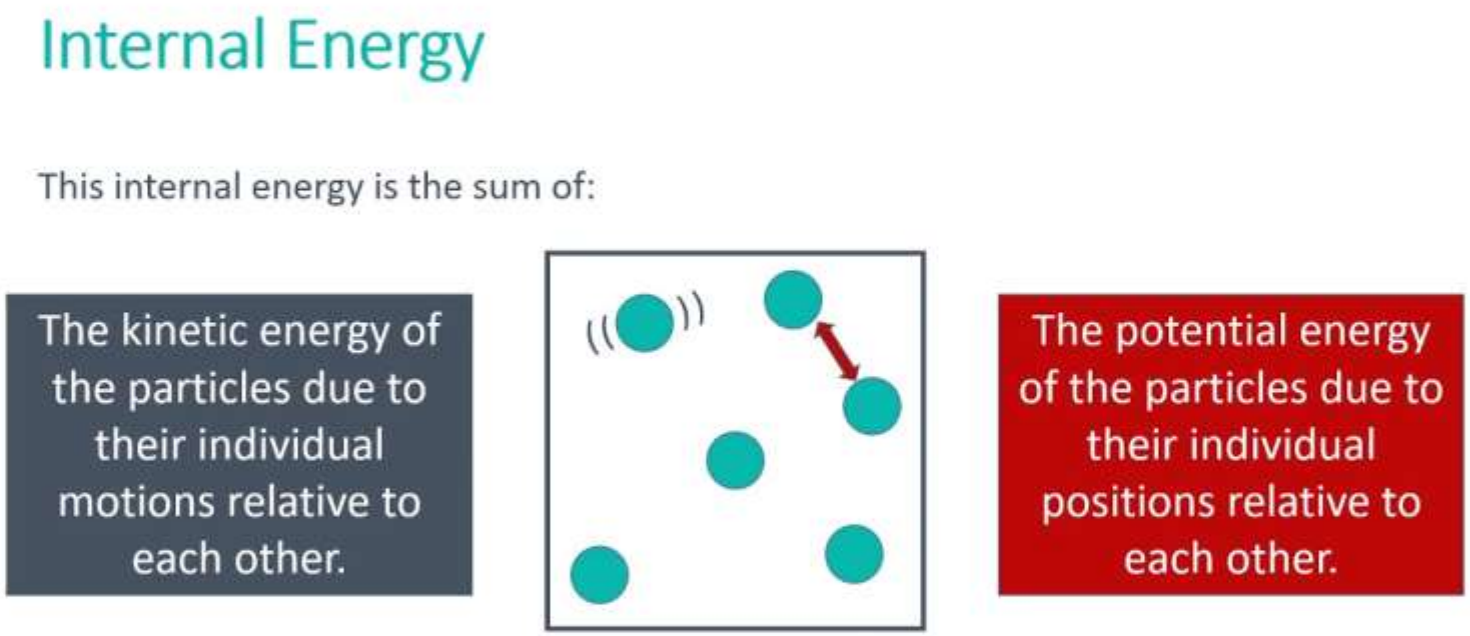


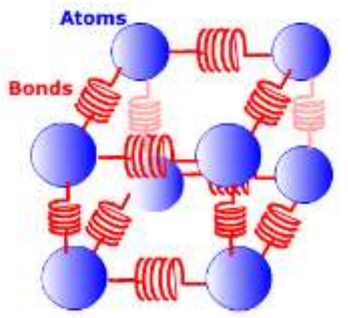
- The system: the portion of the universe with which we are concerned
- The surroundings: everything else
- Isolated system cannot exchange matter or energy
- Closed system can exchange energy
- Open system can exchange either or both

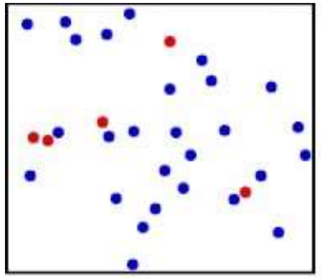


Internal energy - Wikipedia

In thermodynamics, the internal energy of a system is the energy contained within the system, excluding the kinetic energy of motion of the system as a whole and the potential energy of the system as a whole due to external force fields.

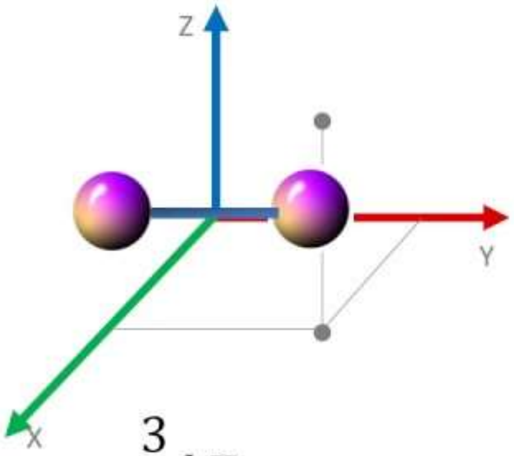






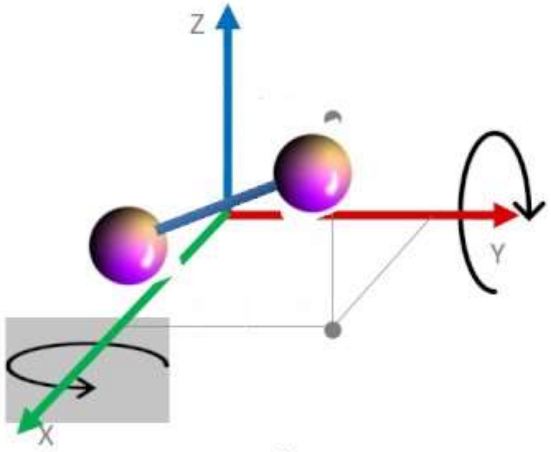
Internal Energy of Gas ΔU

Translation Energy
Di-atomic Molecule



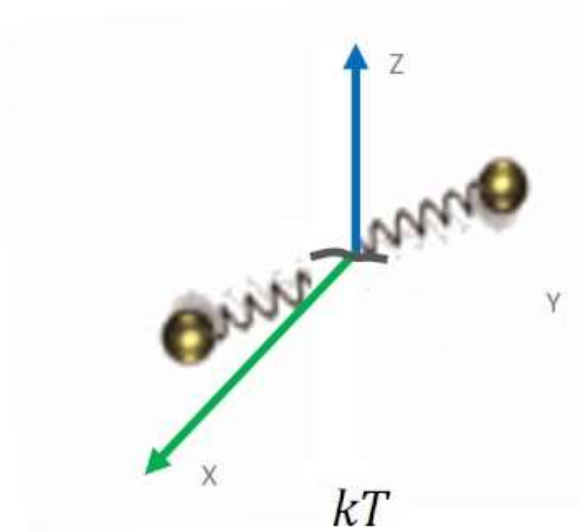
$$\frac{3}{2}kT$$

Rotation Energy
Di-atomic Molecule



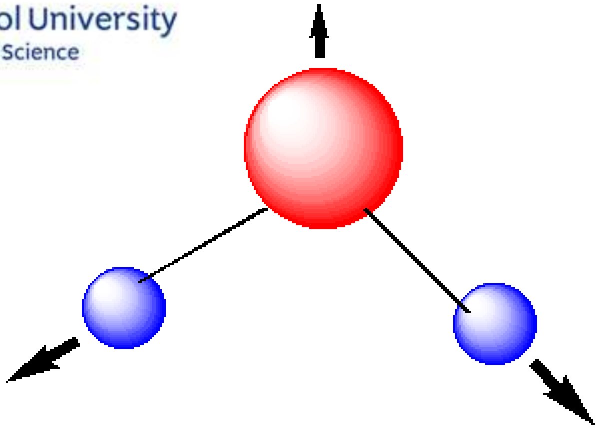
$$kT$$

Vibrational Energy
Di-atomic Molecule



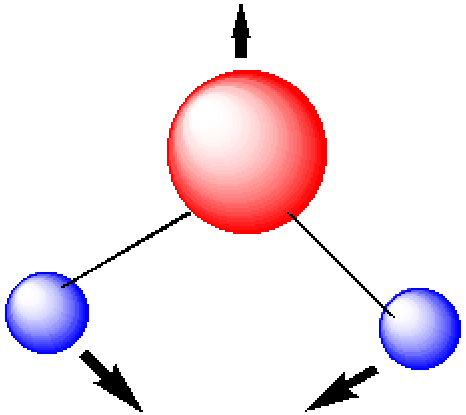
$$kT$$

at high temperature

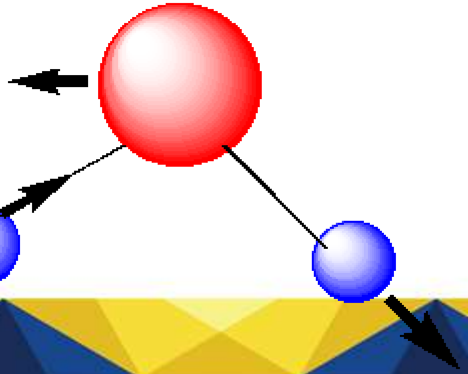


Symmetric Stretch

3657 cm^{-1}



Bend 1595 cm^{-1}



Asymmetric Stretch

3756 cm^{-1}

Internal Energy, *U,* of Monoatomic Gas

Monoatomic gases have one atom per molecule: *e.g.* He, Ne, Xe, and Kr.

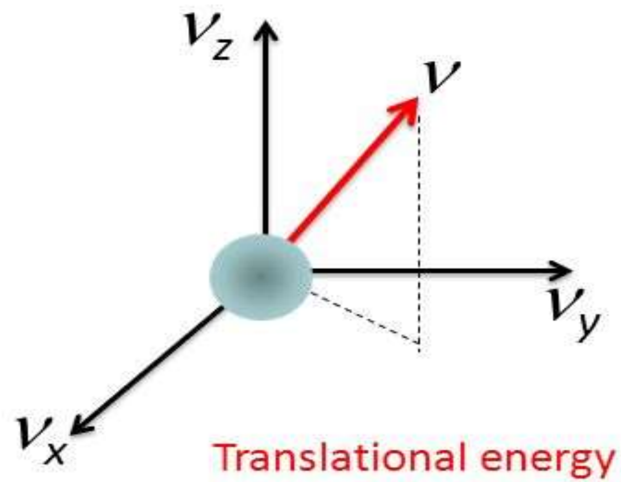
All of the kinetic energy of a monoatomic gas is contained in *translational* motion with a velocity ν.

There are three degrees of freedom.

Each d.o.f. has ½ *kT* in thermal energy.

$k = 1.38 \times 10^{-23}$ J/K

The total energy of **each molecule** (ignoring potential energy) is $\frac{3}{2}kT$.

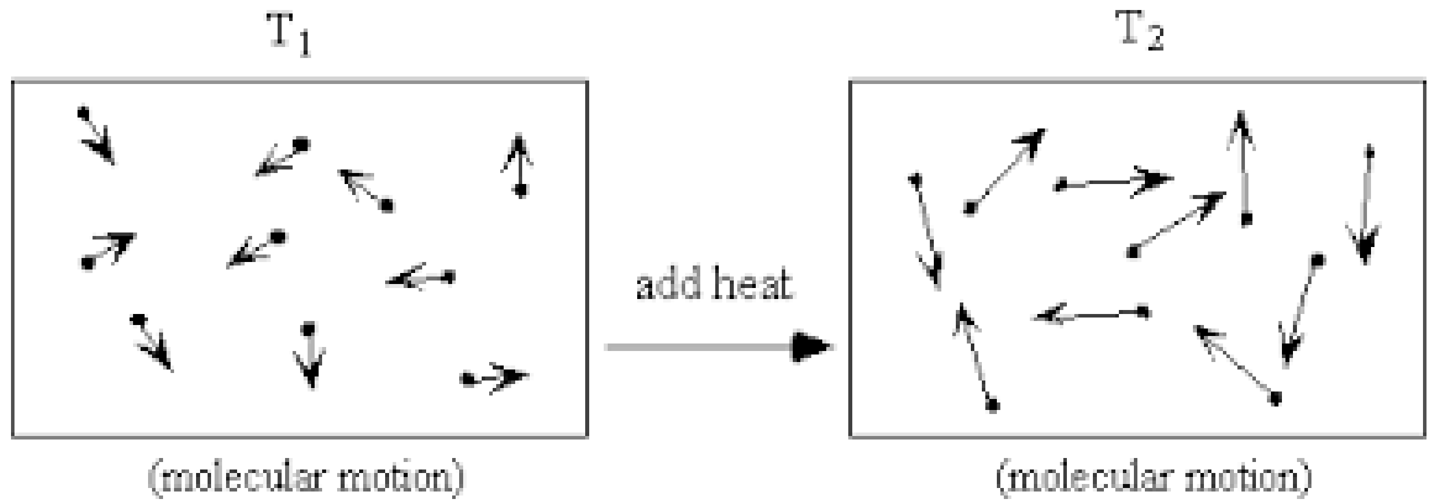


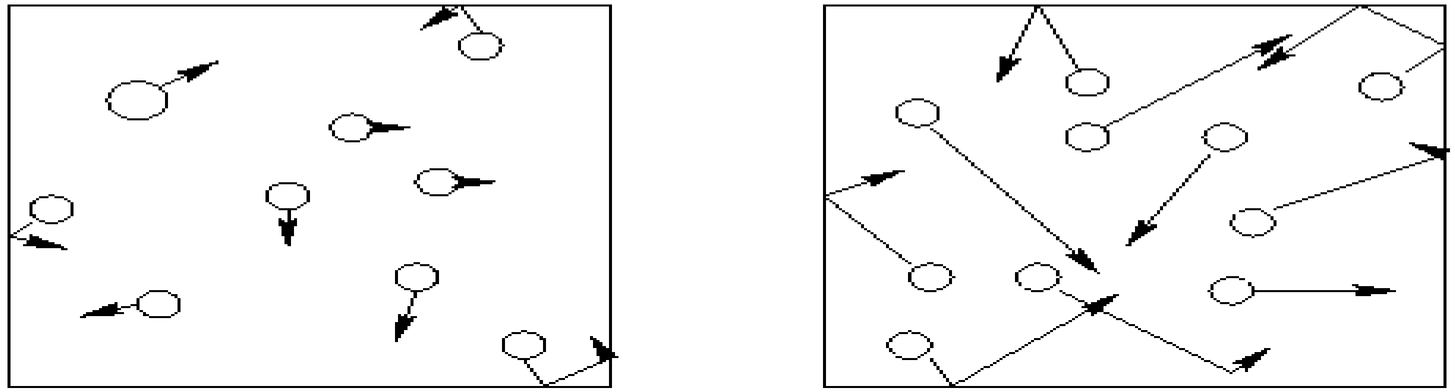
Translational energy

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x{}^2 + v_y{}^2 + v_z{}^2\right)$$

Ideal Gas

That is due to transfer of heat kinetic energy and potential energy changes from bottle to the balloon. This results in the change of internal energy.





Cool gas, fewer and less energetic collisions

Hot gas, more and more energetic collision

The Ideal Gas Law

An ideal gas is an idealized model for real gases that have sufficiently low densities.

The condition of low density means that the molecules of the gas are so far apart that they do not interact (except during collisions that are effectively elastic).

The ideal gas law expresses the relationship between the absolute pressure (P), the Kelvin temperature (T), the volume (V), and the number of moles (n) of the gas.

$$PV = nRT$$

Where R is the universal gas constant. R = 8.31 J/(mol · K).

Consider a sample of an ideal gas that is taken from an initial to a final state, with the amount of the gas also changing.

$$PV = nRT \qquad \frac{PV}{nT} = R = \text{constant} \qquad \frac{P_f V_f}{n_f T_f} = \frac{P_i V_i}{n_i T_i}$$

Constant T, constant n:	$P_f V_f = P_i V_i$	*Boyle's law*
Constant P, constant n:	$\frac{V_f}{T_f} = \frac{V_i}{T_i}$	*Charles' law*
Constant V, constant n:	$\frac{P_f}{T_f} = \frac{P_i}{T_i}$	*Gay-Lussac's law*
Constant P, constant T:	$\frac{V_f}{n_f} = \frac{V_i}{n_i}$	*Avogadro's law*

Measured

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

Correction for molecular attraction

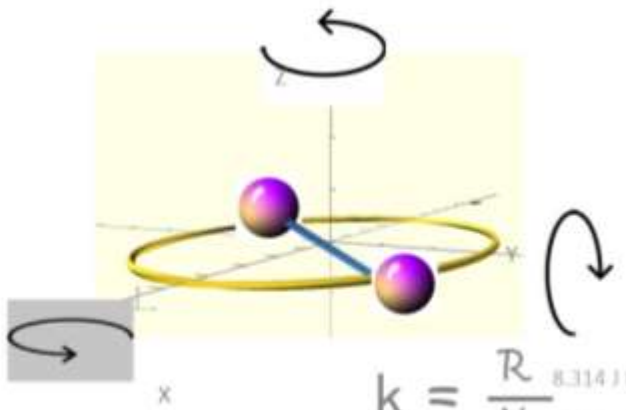
Correction for volume of molecules

Non-Ideal Gas

Equipartition of Energy

Equipartition of Energy Energy is distributed equally along all degrees of freedom

Di-atomic Molecule



Energy of molecule for 1 Dimension = $\frac{1}{2}kT$

$DOF_{Translatory\ Motion} = 3$

Energy of 3 $DOF_{Translatory\ Motion} = \frac{3}{2}kT$

$DOF_{Rotatory\ Motion} = 2$

Energy of 5 $DOF_{Translatory+Rotatory} = \frac{5}{2}kT$

$k = \frac{R}{N_A}$ — R: 8.314 J K^{-1}Mol^{-1}; N_A: 6.023 x 10^{23}

Boltzman Constant

$\frac{1}{2}kT$ per molecule

$\frac{1}{2}RT$ per mole

k = Boltzmann's constant

R = gas constant

$\frac{3}{2}kT$

$\frac{3}{2}RT$

For three translational degrees of freedom, such as in an ideal monoatomic gas.

Equipartition Theorem

- In a monatomic ideal gas, each molecule has

$$K = \tfrac{1}{2} m v^2 = \tfrac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

- There are three degrees of freedom.
- Mean kinetic energy is 3(1/2 *kT*) = 3/2 *kT*.

- In a gas of *N* helium molecules, the total internal energy is

$$U = N\overline{E} = \tfrac{3}{2} NkT$$

- The heat capacity at constant volume is C_V = 3/2 *Nk*.
- For the heat capacity for 1 mole,

$$c_V = \tfrac{3}{2} N_A k = \tfrac{3}{2} R = 12.5 \text{ J/K}$$

- The ideal gas constant *R* = 8.31 J/K.

Total energy of an ideal gas

U = Net sum of kinetic energy of a gas

$U = N(\overline{E}_k)$ = (# particles)(Average KE)

$$\bar{E}_K = \frac{3}{2} k_B T = \frac{3}{2} \frac{R}{N_A} T$$

E_k = average kinetic energy of a particle

k_B = Boltzmann's Constant (1.38×10^{-23} JK^{-1})

T = Temp in K

R = Gas Constant (8.31 $JK^{-1}mol^{-1}$)

N_A = Avocado's Number (6.02×10^{23} mol^{-1})

What is the change in internal energy?

Given:

An ideal gas is heated at constant specific heat. What is its change in internal energy?

T_1 = 300 K T_2 = 375 K

c_p = 0.48 kJ/(kg·K) m = 5.0 kg

M = 70.0 kg/kmol

$\overline{R}$ = 8.314 kJ/(kmol·K)

ΔU = ???

$$\Delta U = m\,\Delta u$$

$$\Delta u = \int_{T_1}^{T_2} c_v(T)\,dT$$

$$\Delta U = m \int_{T_1}^{T_2} c_v(T)\,dT$$

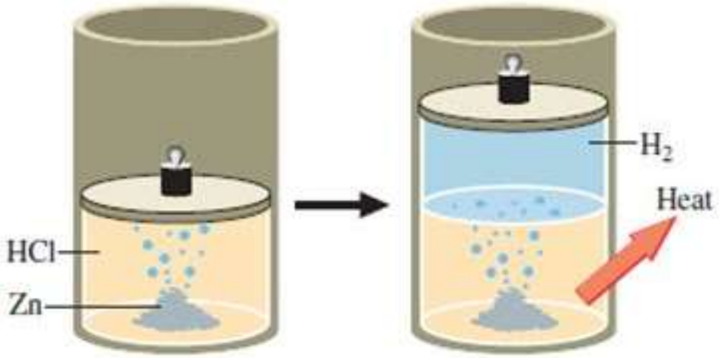
$$c_p(T) = c_v(T) + R$$

$$c_v(T) = c_p(T) - R$$

Explain why the work done by the system as a result of expansion or contraction during a chemical reaction is *P*Δ*V*. Or

$$Zn(s) + 2H_3O^+(aq) \longrightarrow Zn^{2+}(aq) + 2H_2O(l) + H_2(g)$$

As hydrogen is evolved, work must be done by the system to push back the atmosphere. How can you calculate this work?



The work done by the system in expanding of gas equals the force of gravity times the distance the piston moves.

$$w = F \cdot h$$

$$-F \times \frac{\Delta V}{A} = -\frac{F}{A} \times \Delta V$$

$$w = -P\Delta V$$

First law of thermodynamics:

Energy is neither created nor destroyed; the energy of the universe is a constant.

The total internal energy of an isolated system in conserved.

$$\Delta E = E_2 - E_1 = q + w$$

q – heat absorbed by the system from surroundings
w – work done on the system by the surroundings

Mechanical work is defined as movement through some distance caused by the application of force

Internal energy is independent of path and represents the present state of the system and is referred to as a State function

The First Law of Thermodynamics

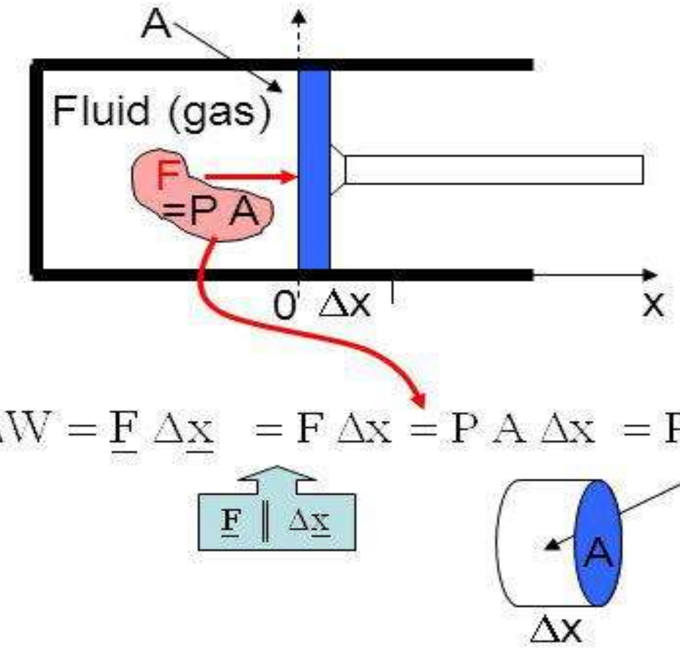
The total *internal energy* of an isolated system is conserved.

- E (or U) is the internal energy - a function that keeps track of heat transfer and work expenditure in the system
- E is heat exchanged at constant volume
- E is independent of path
- $E_2 - E_1 = \Delta E = q + w$
- q is heat absorbed BY the system
- w is work done ON the system

First Law of Thermodynamics

Work: Total energy transferred to a system by macroscopic forces exerted on it by other systems

- Work $W = \int_L \underline{F}\, d\underline{x}$ done by a gas on a piston



$$\Delta W = \underline{F}\, \Delta \underline{x} \quad = F\, \Delta x = P\, A\, \Delta x \quad = P\, \Delta V$$

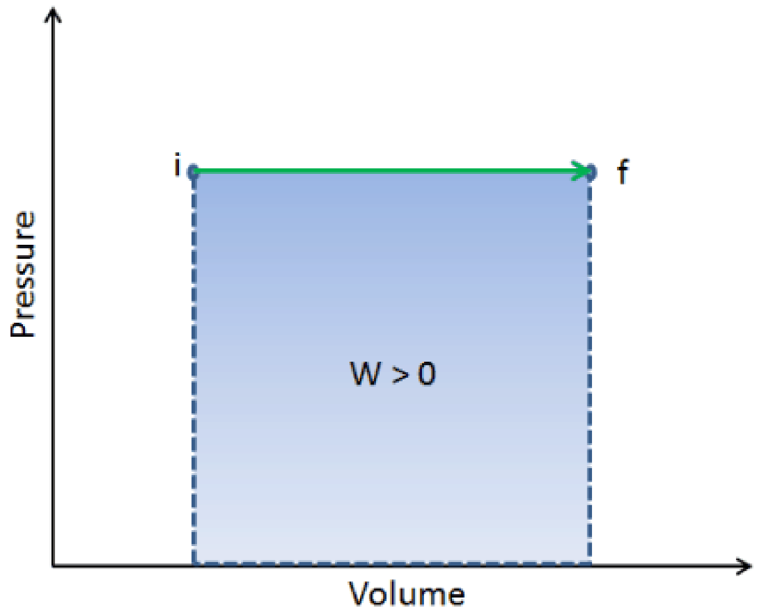
$\underline{F} \parallel \Delta \underline{x}$

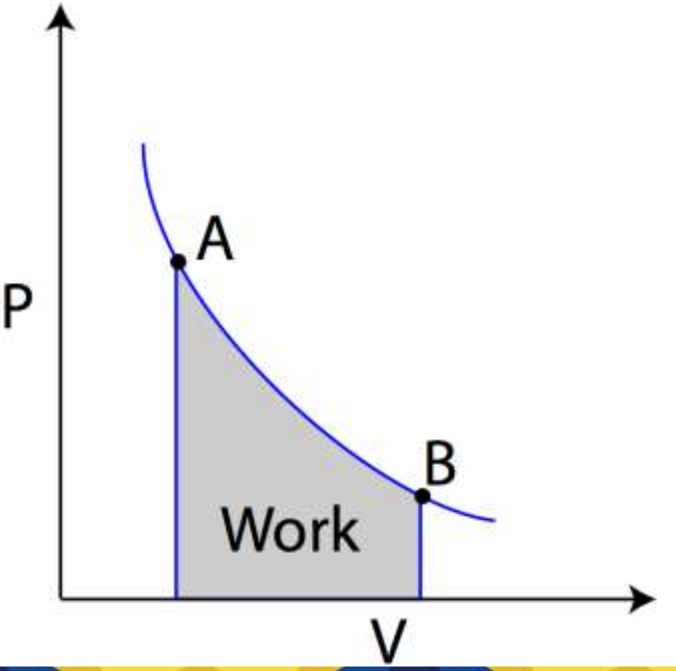
- Work done by a fluid as it expands from V_0 to V_f

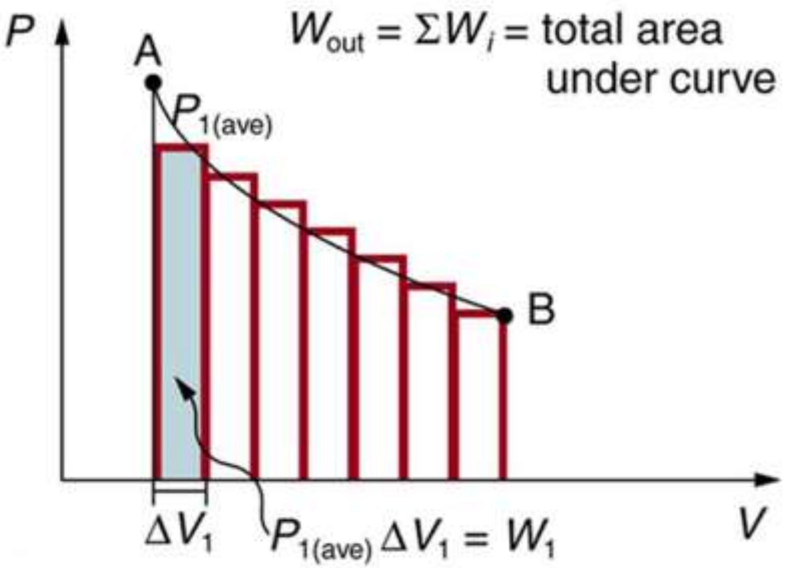
$$W = \int_{V_0}^{V_f} P(V)\, dV$$

$W > 0$ → Energy leaves the system

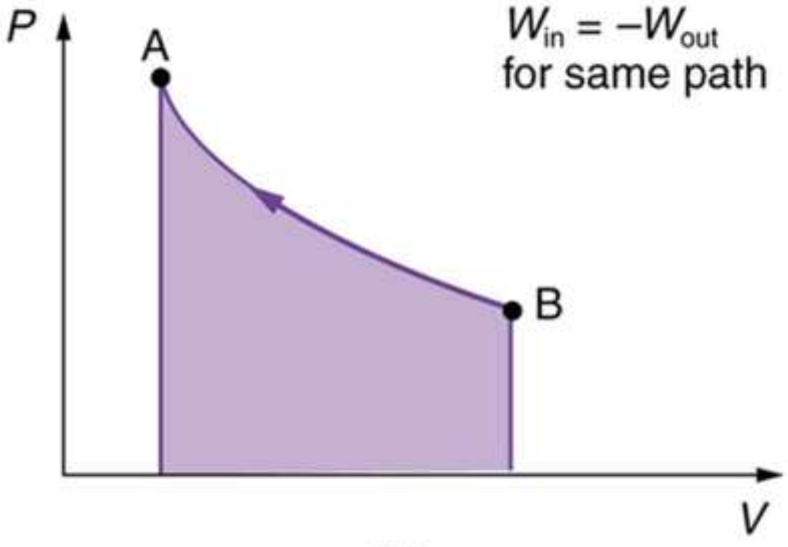
$W < 0$ → Energy feed in the system


Pressure
i
f
W > 0
Volume

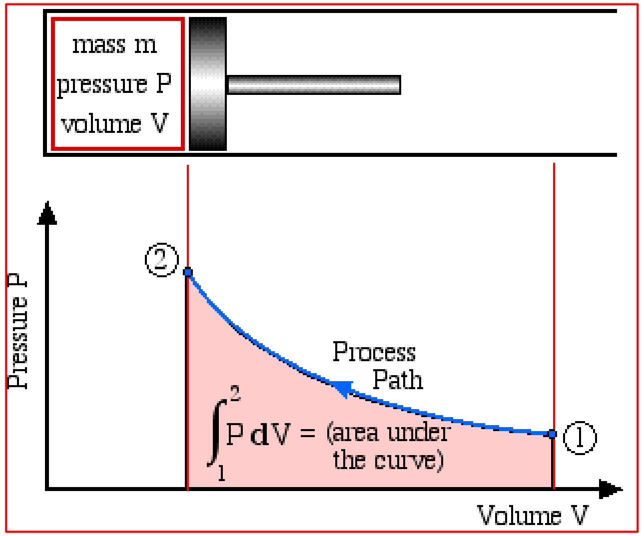

P
A
B
Work
V

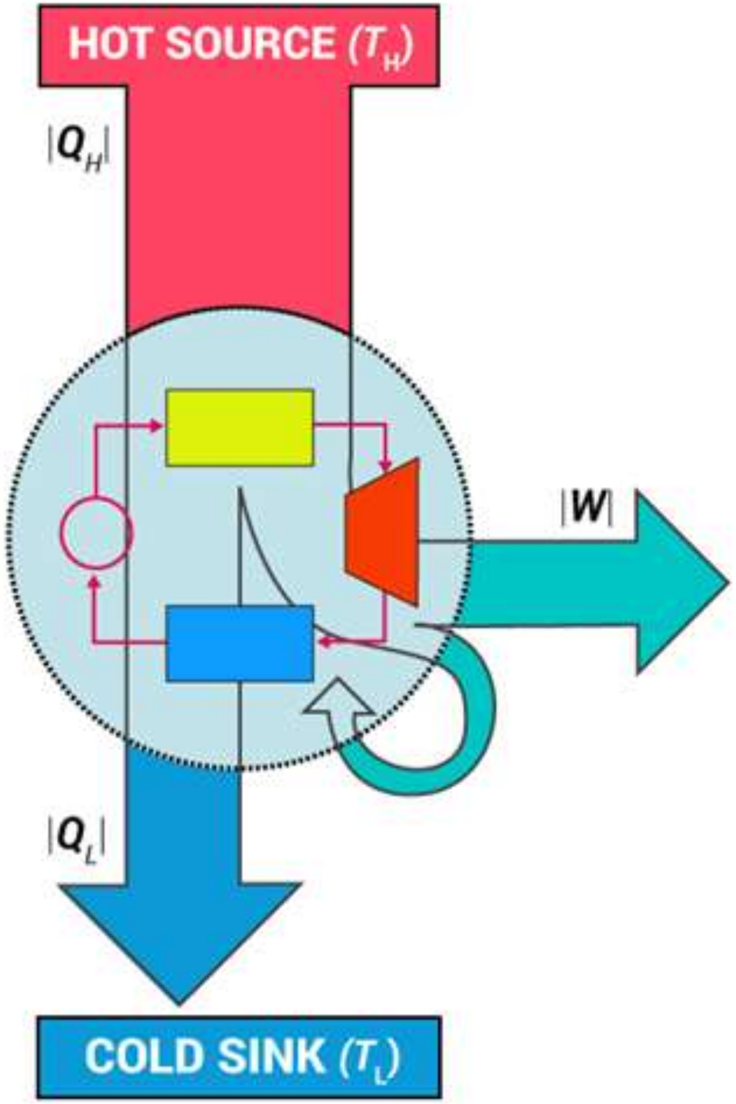

P
A
$W_{out} = \Sigma W_i$ = total area under curve
$P_{1(ave)}$
B
ΔV_1
$P_{1(ave)} \Delta V_1 = W_1$
V

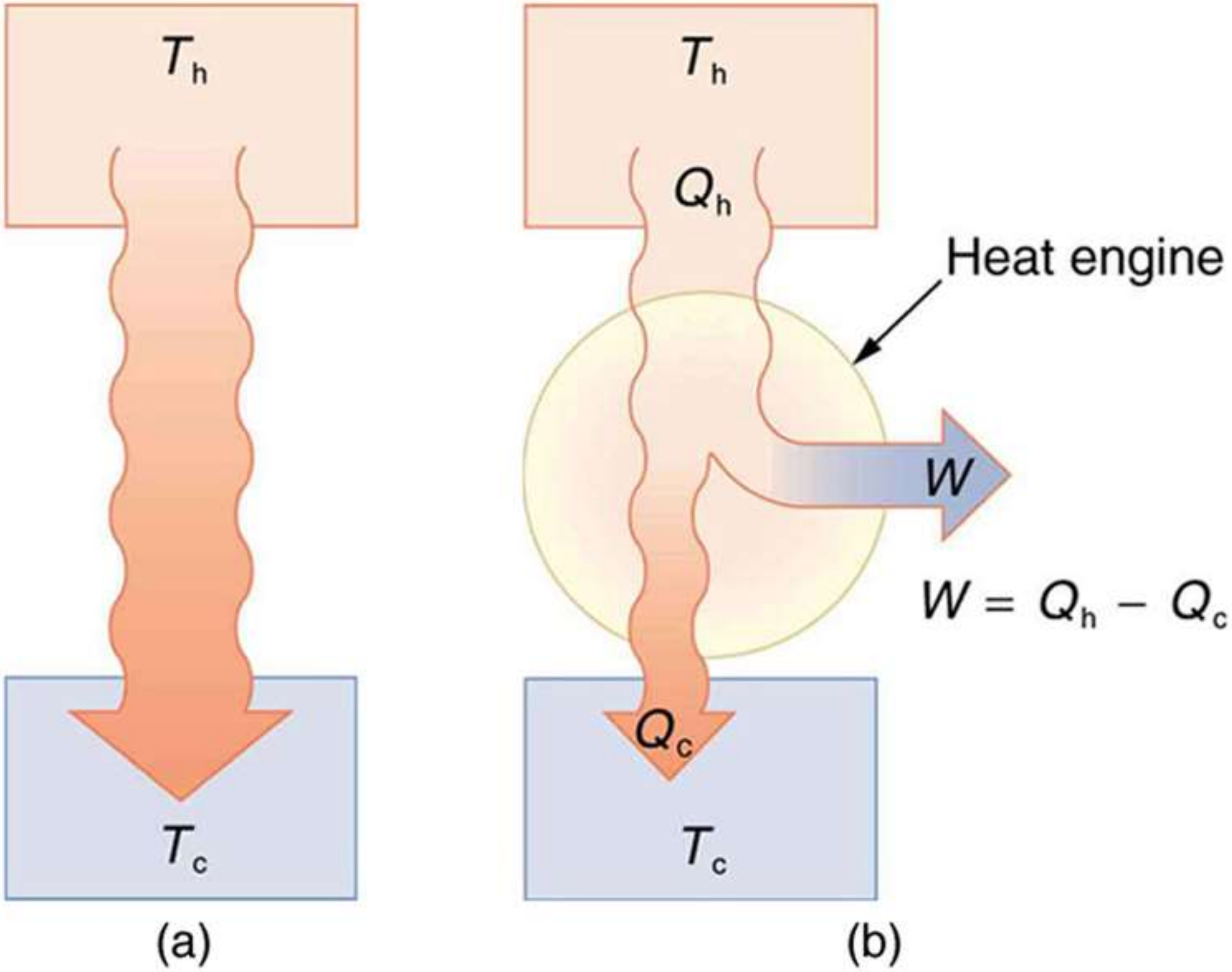
(a)

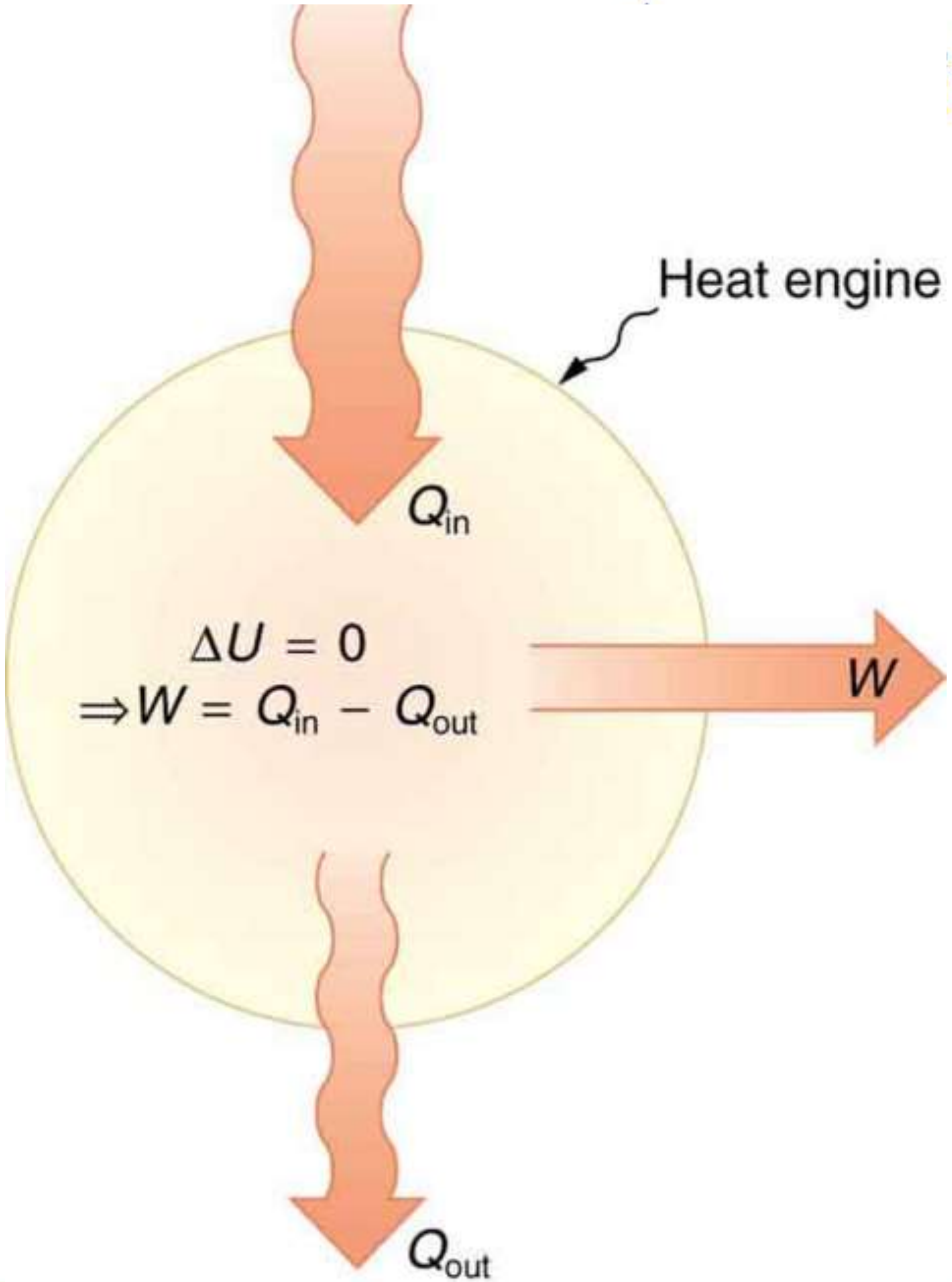

P
A
$W_{in} = -W_{out}$
for same path
B
V

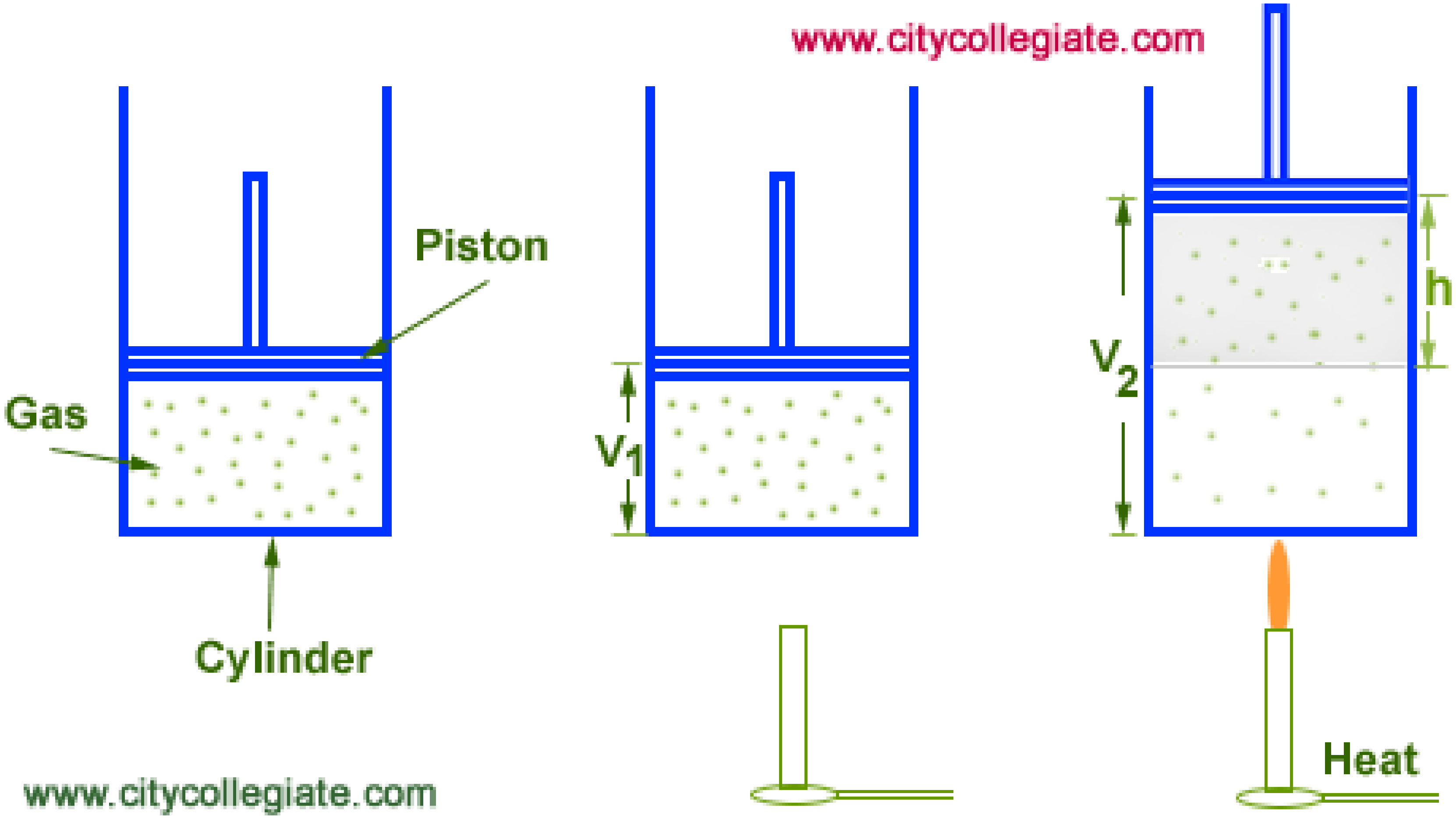
(b)


mass m
pressure P
volume V
Pressure P
②
Process
Path
$\int_1^2 P\,dV$ = (area under the curve)
①
Volume V


HOT SOURCE (T_H)
$|Q_H|$
$|W|$
$|Q_L|$
COLD SINK (T_L)

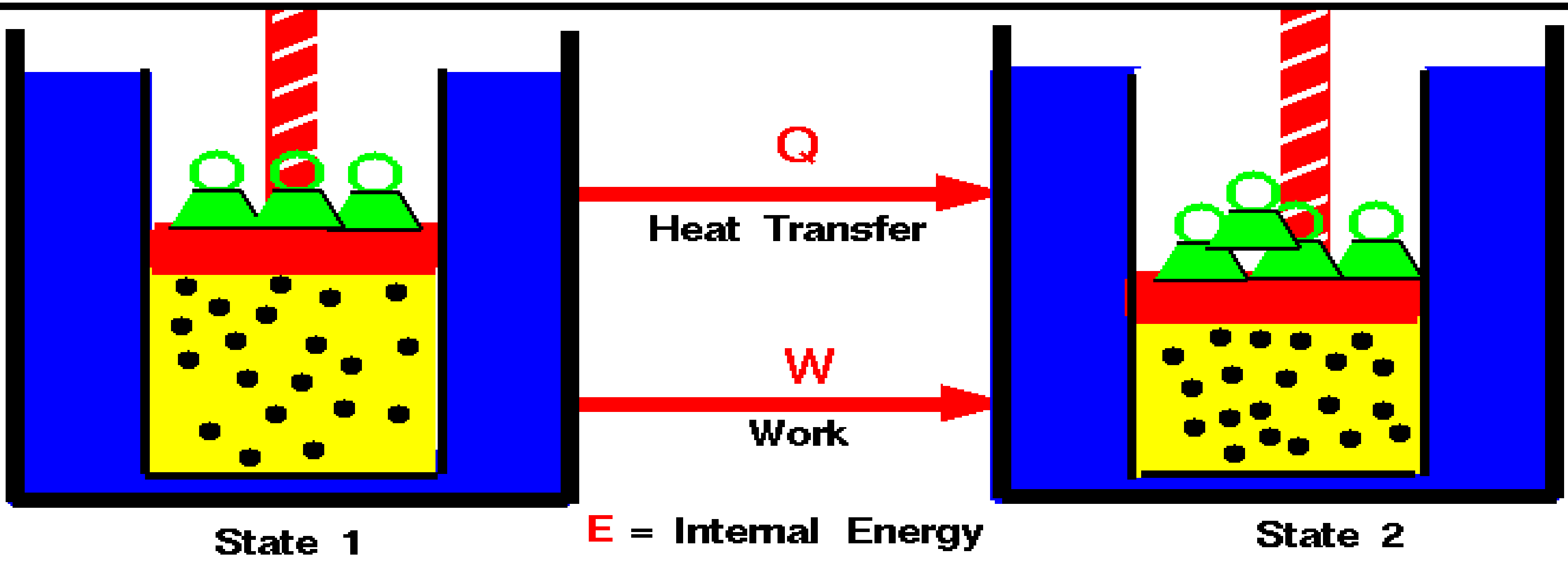

T_h
T_c
(a)
T_h
Q_h
Heat engine
W
$W = Q_h - Q_c$
Q_c
T_c
(b)


Heat engine
Q_{in}
$\Delta U = 0$
$\Rightarrow W = Q_{in} - Q_{out}$
W
Q_{out}


www.citycollegiate.com
Piston
Gas
Cylinder
V1
V2
h
Heat
www.citycollegiate.com

First Law of Thermodynamics

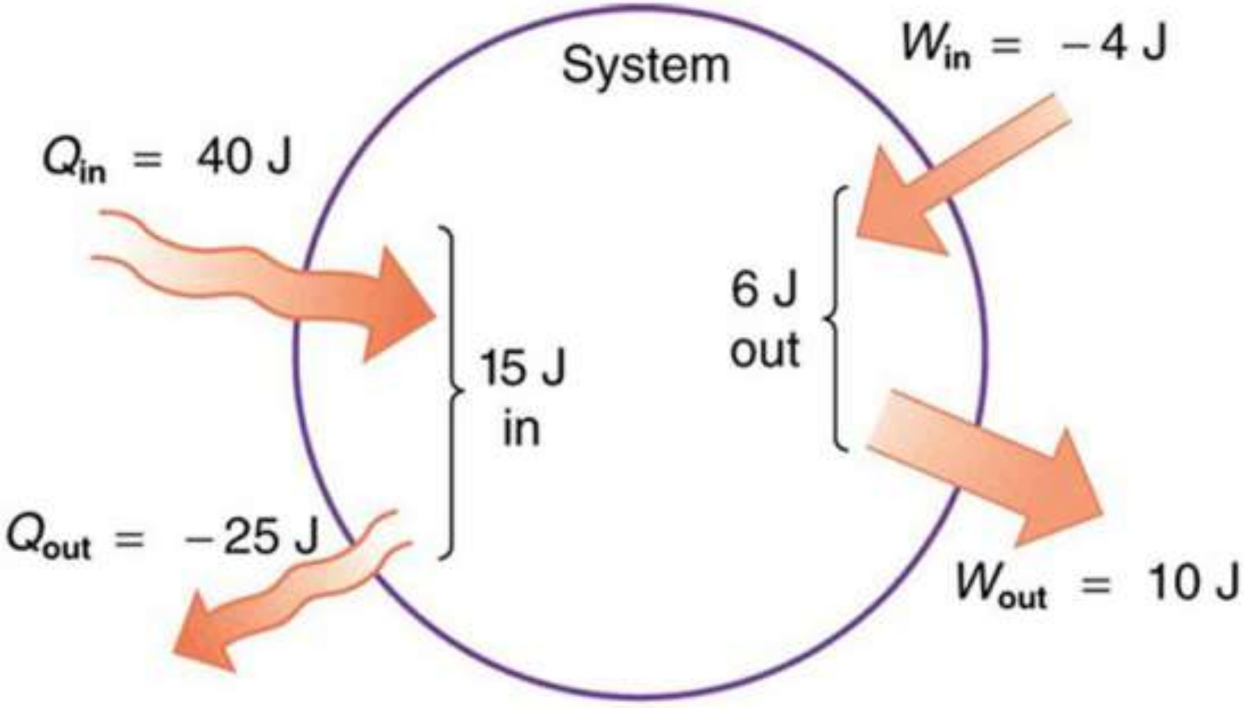
Glenn Research Center



E = Internal Energy

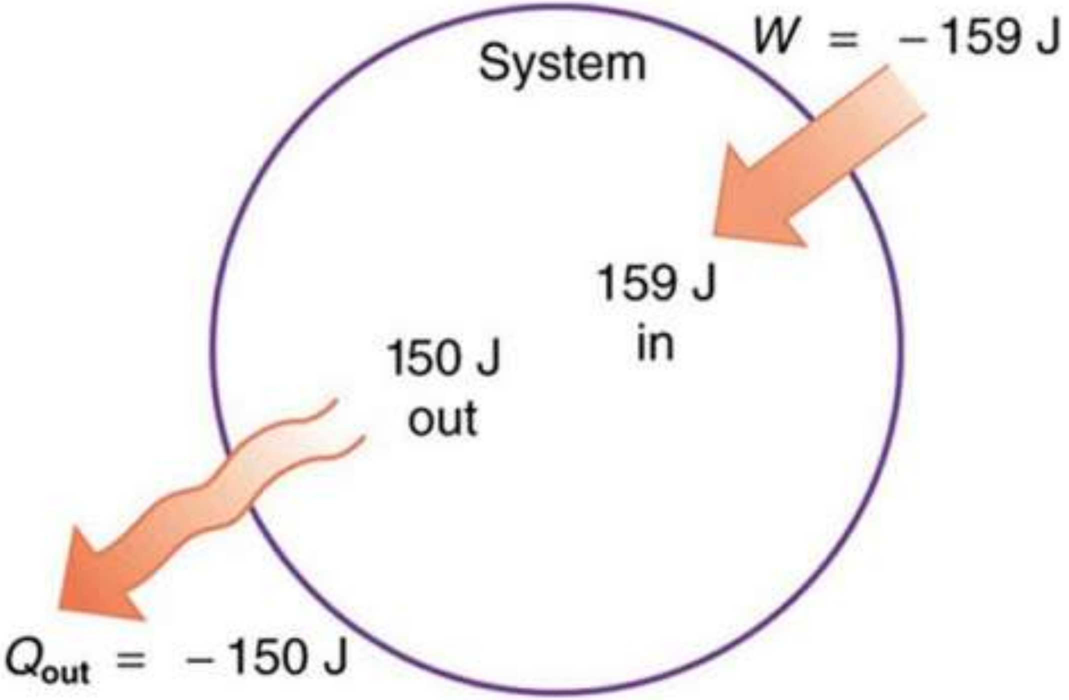
$E_2 - E_1 = Q - W$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.



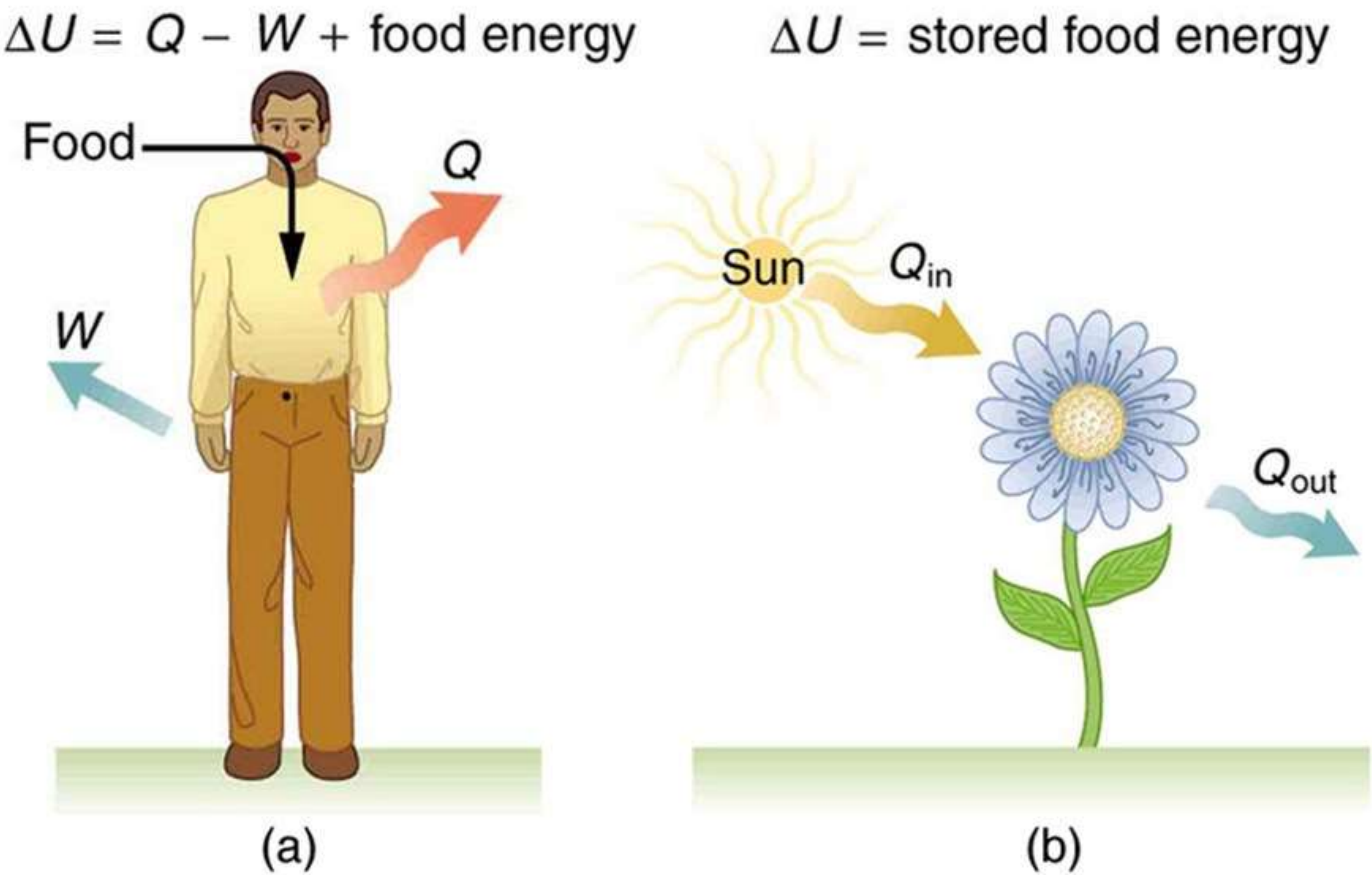
$$\Delta U = Q - W = 15\text{ J} - 6\text{ J} = +9\text{ J}$$

(a)



$$\Delta U = Q - W = -150\text{ J} - (-159\text{ J}) = +9\text{ J}$$

(b)


ΔU = Q − W + food energy
ΔU = stored food energy
Food
Q
W
Sun
Q_in
Q_out
(a)
(b)

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$$\Delta U = Q - W$$

1) constant **volume**

$W = 0$

isovolumetric

2) constant **temperature**

$\Delta U = 0$

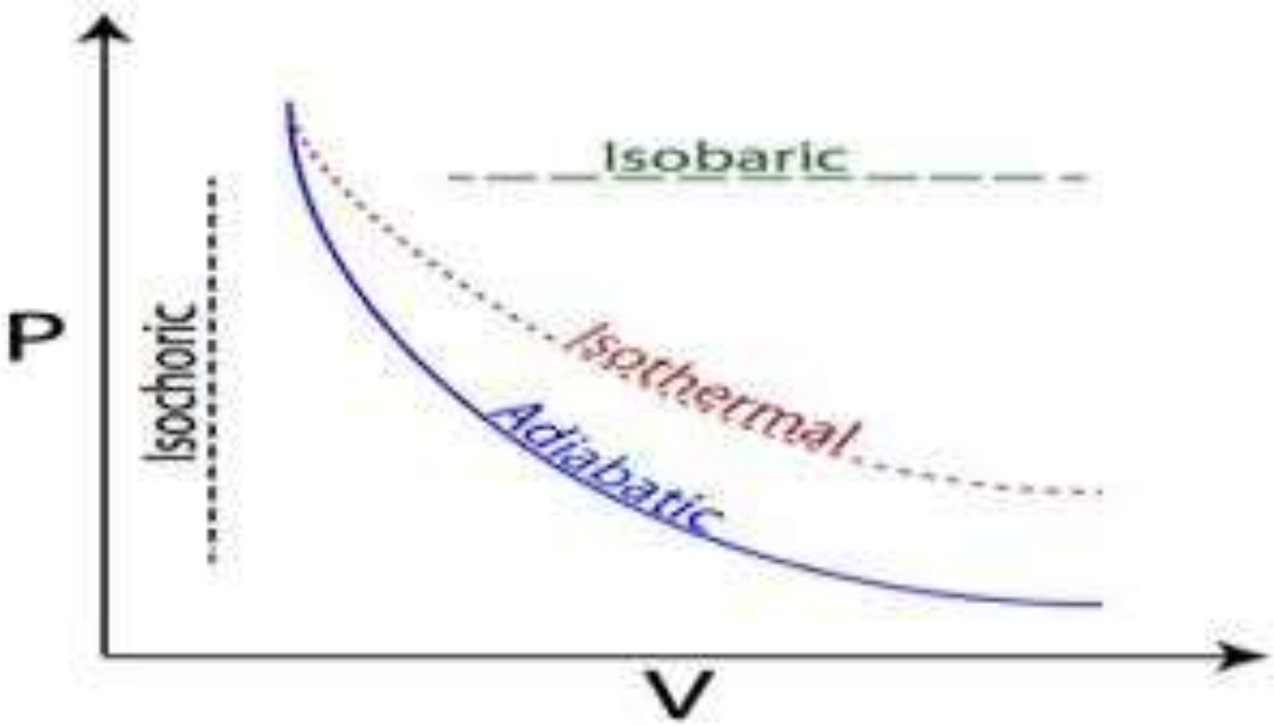
isothermal

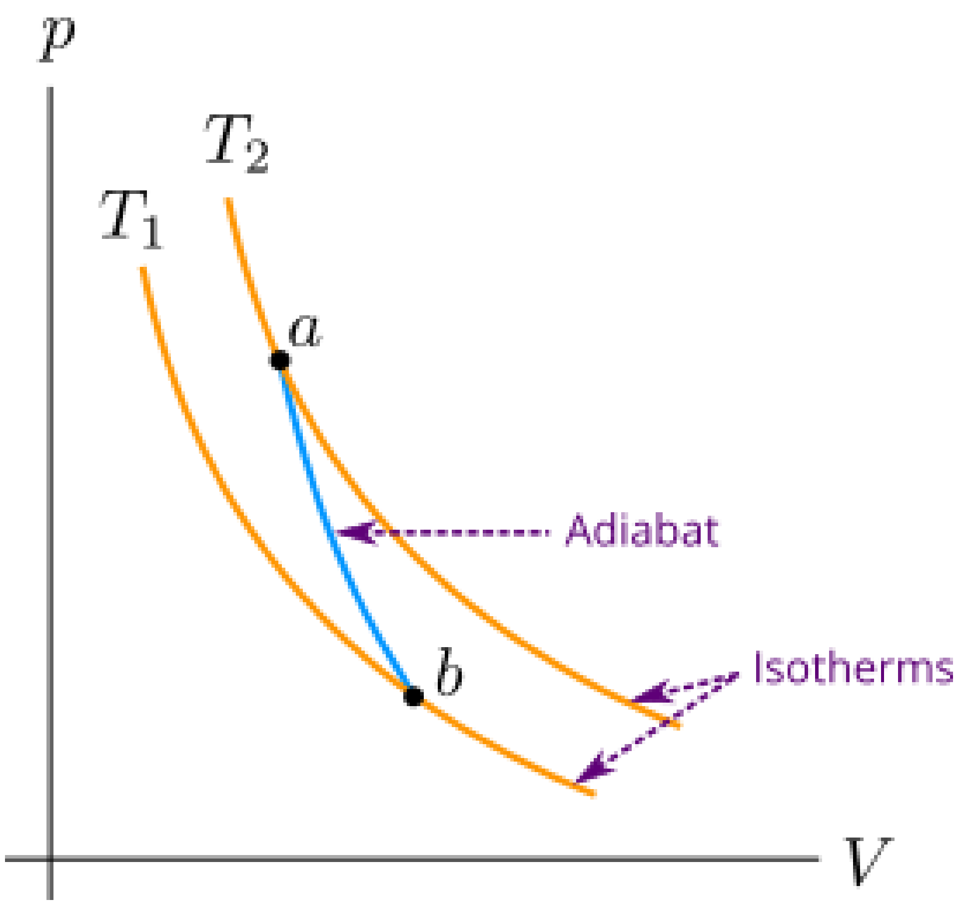
3) no **heat transfer**

$Q = 0$

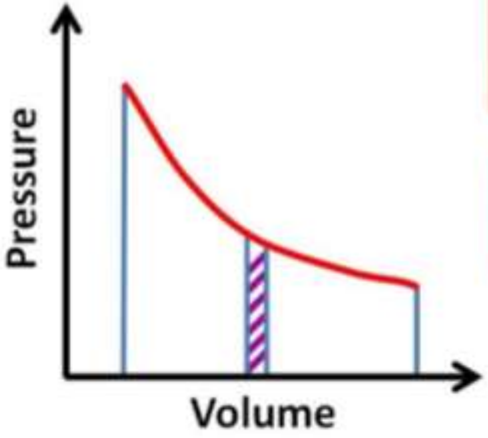
adiabatic

4) $Q = 0$ and $W = 0$


P
V
Isochoric
Isobaric
Isothermal
Adiabatic


p
V
T_1
T_2
a
b
Adiabat
Isotherms

Isothermal process
- Work done



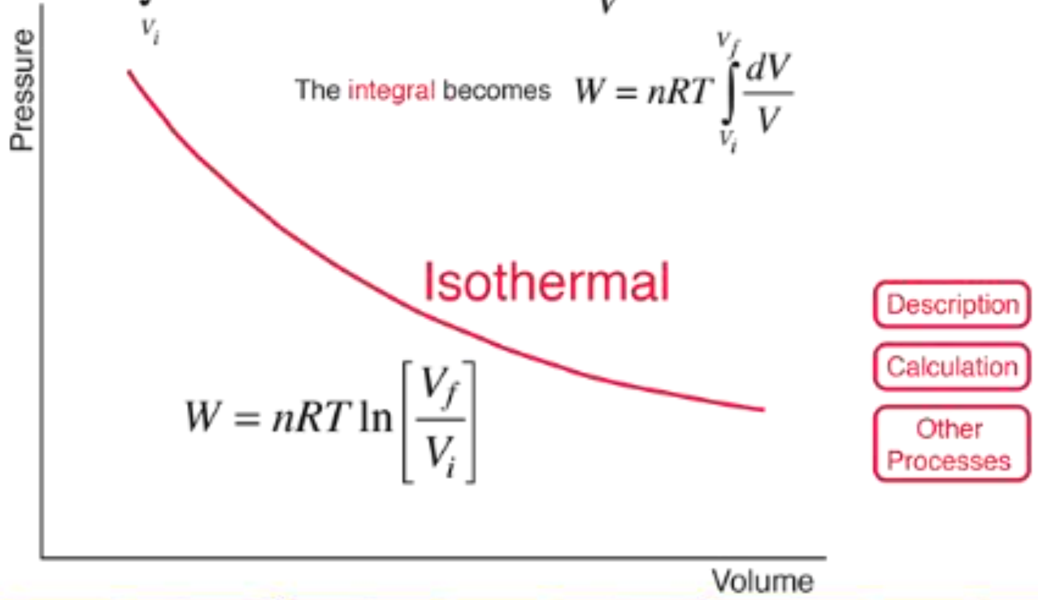
$$W = nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$W = nRT \ln\left(\frac{P_1}{P_2}\right)$$

Since the temperature is constant, the pressure P in the work integral

$W = \int_{V_i}^{V_f} P\,dV$ can be replaced by $P = \frac{nRT}{V}$ using the ideal gas law.

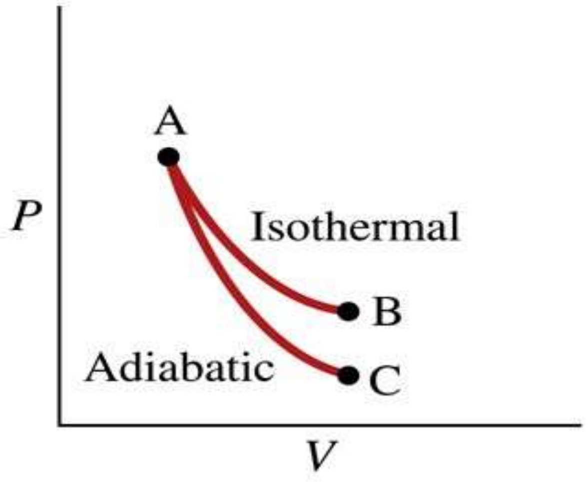
The integral becomes $W = nRT \int_{V_i}^{V_f} \frac{dV}{V}$

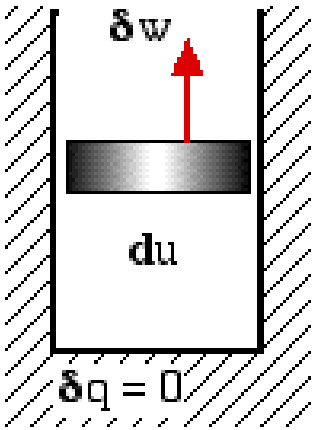


$$W = nRT \ln\left[\frac{V_f}{V_i}\right]$$

First law of thermodynamics. Adiabatic processes.

- An adiabatic process is a process in which there is no flow of heat (the system is an isolated system).
- Adiabatic processes can also occur in non-isolated systems, if the change in state is carried out rapidly. A rapid change in the state of the system does not allow sufficient time for heat flow.
- The expansion of gases differs greatly depending on the process that is followed (see Figure).





Energy $\Rightarrow$ $\delta q - \delta w = du$

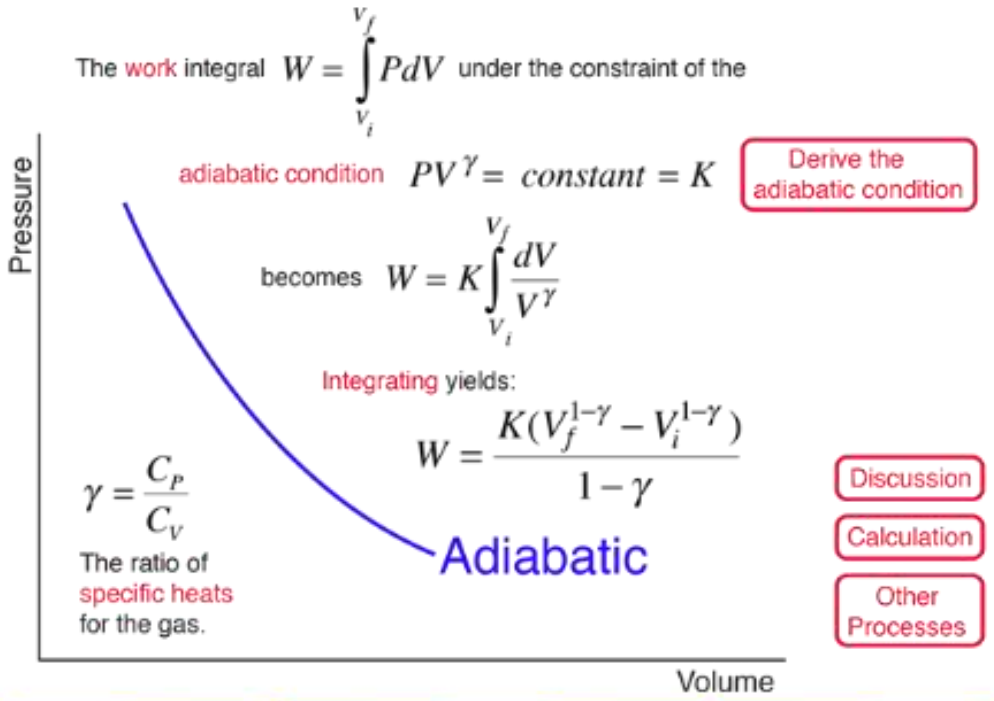
Adiabatic $\Rightarrow$ $\delta q = 0 = du + \delta w$

$$0 = du + P\,dv$$

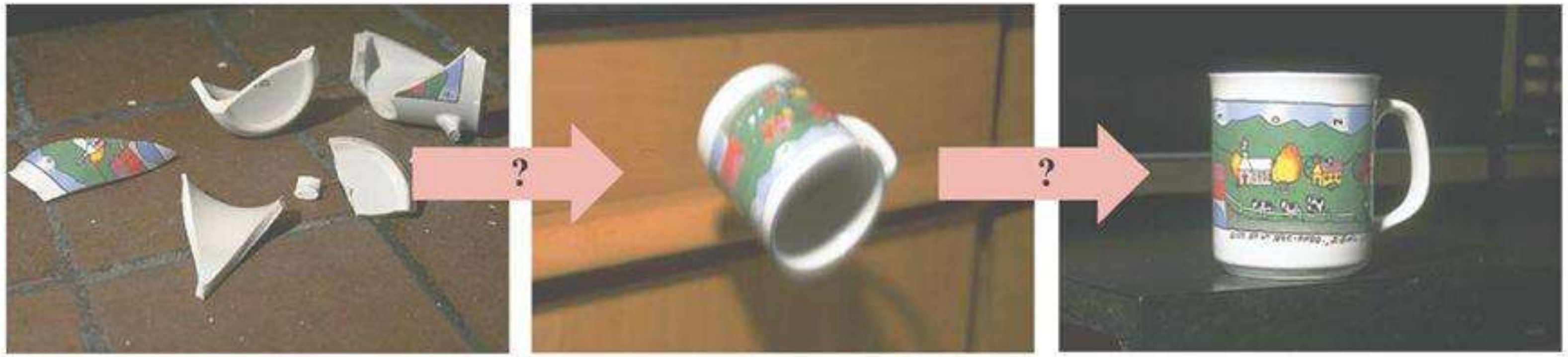
Ideal gas $\Rightarrow$ $P \cdot v = R \cdot T$, $du = C_V \cdot dT$

$$C_V dT + \left(\frac{R \cdot T}{v}\right) dv = 0 \;\Rightarrow\; \frac{dT}{T} = -\left(\frac{R}{C_V}\right)\frac{dv}{v}$$

Integrating $\Rightarrow$ $\ln\left(\frac{T_2}{T_1}\right) = \left(\frac{R}{C_V}\right)\ln\left(\frac{v_1}{v_2}\right) \;\Rightarrow\; \left(\frac{T_2}{T_1}\right) = \left(\frac{v_1}{v_2}\right)^{R/C_V}$



The Second Law of Thermodynamics—Introduction

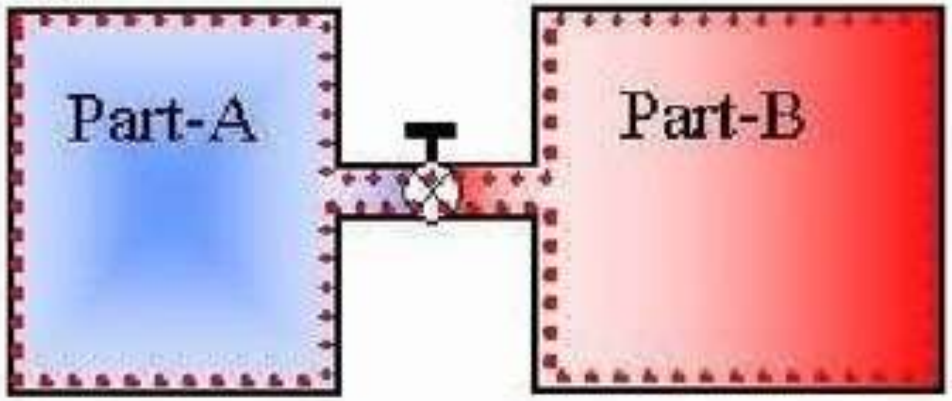


Initial state. Later: cup reassembles and rises up. Later still: cup lands on table.

The first law of thermodynamics tells us that energy is conserved. However, the absence of the process illustrated above indicates that conservation of energy is not the whole story. If it were, movies run backwards would look perfectly normal to us!

What is the 2nd Law of Thermodynamics

Entropy in an isolated system that is not in equilibrium will tend to increase over time until it reaches a maximum equilibrium level



If you keep the door open between two adjoining rooms of different temperatures the cooler room will become warmer and the warmer room will cool down until they both reach the same final temperature

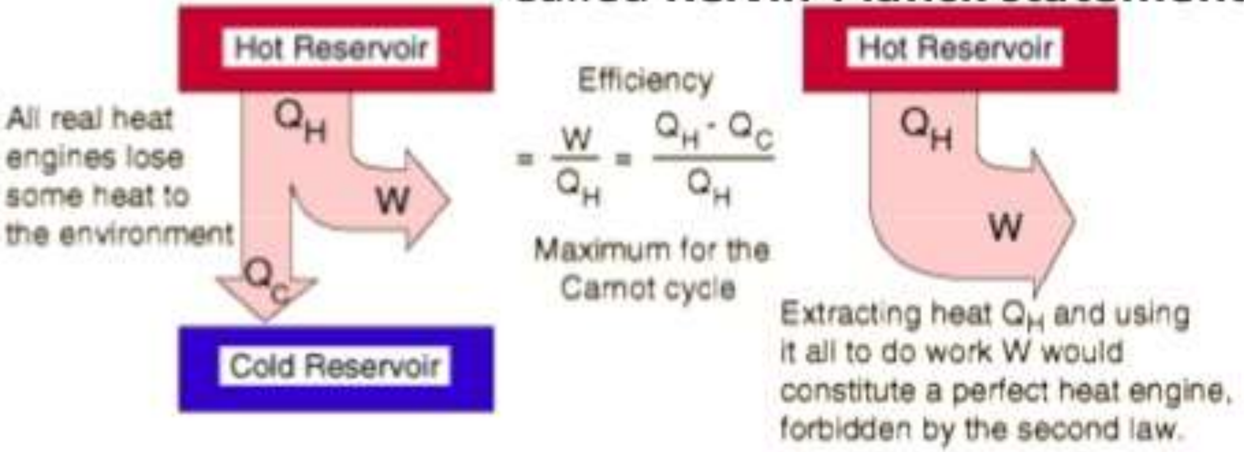
Hardy, M. (2009, November 18). Second law of thermodynamics. Retrieved from http://en.wikipedia.org/wiki/Second_law_of_thermodynamics

Second law of thermodynamics

- **Second Law for Heat Engines**

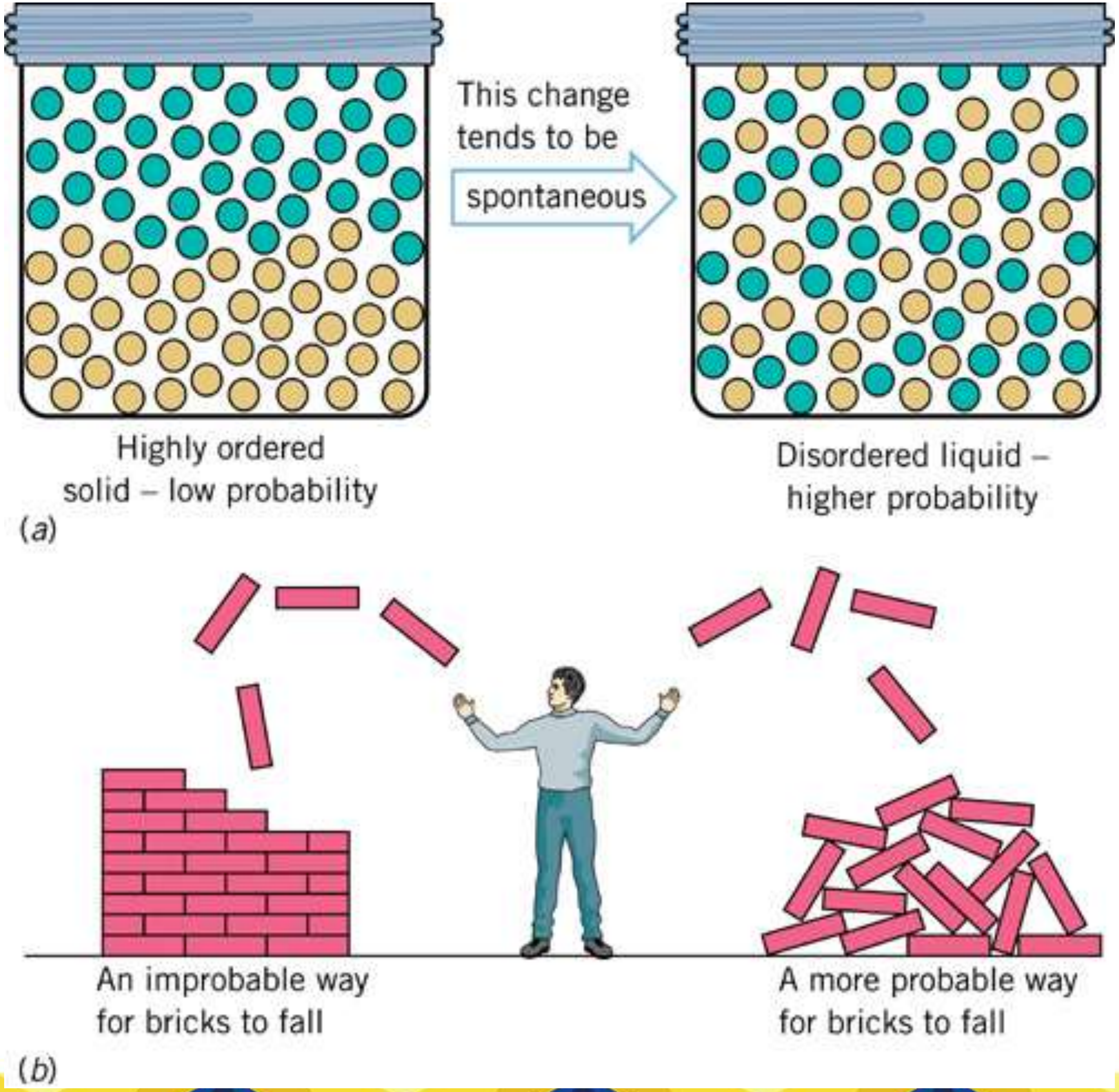
It is impossible to extract heat Q_{Hot} from a hot reservoir and use it all to do work W . Some amount of heat Q_{Cold} must be exhausted to a cold reservoir.

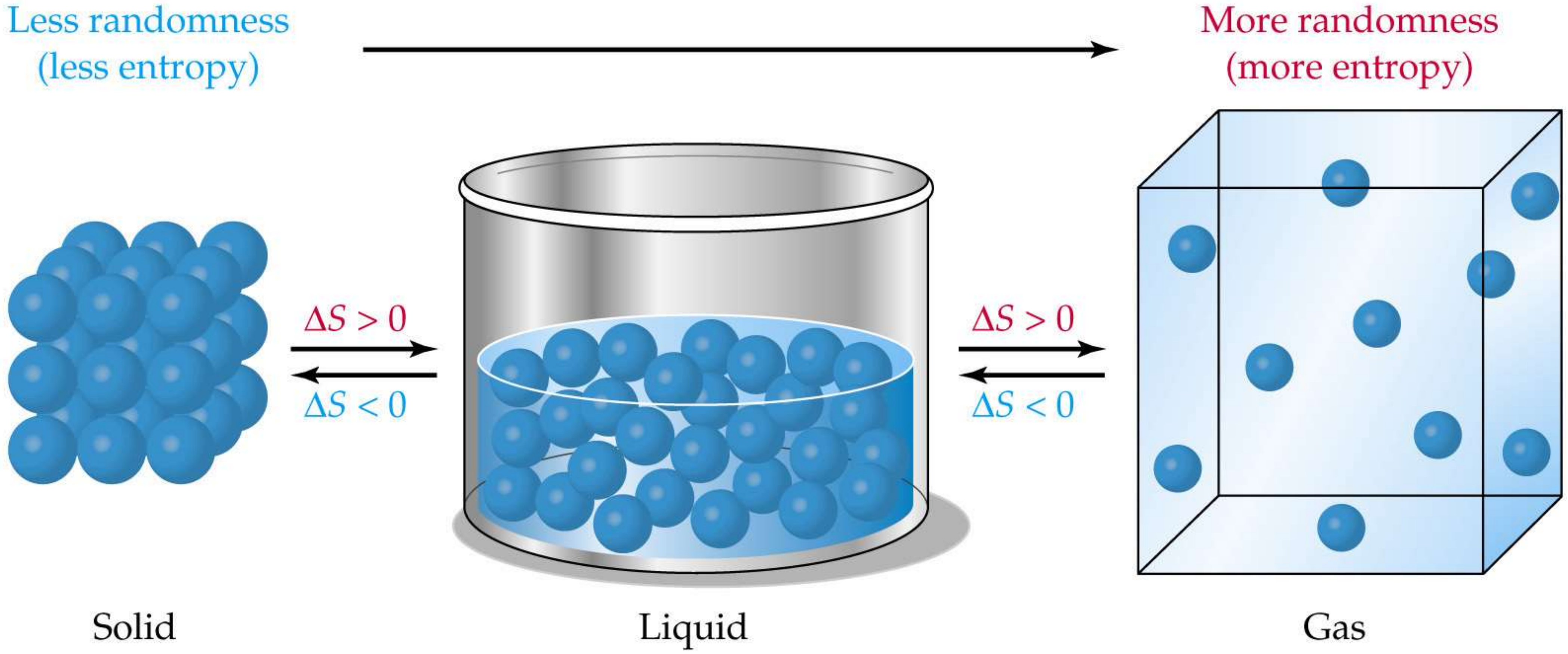
Called **Kelvin-Planck statement**



Mahidol University
Faculty of Science

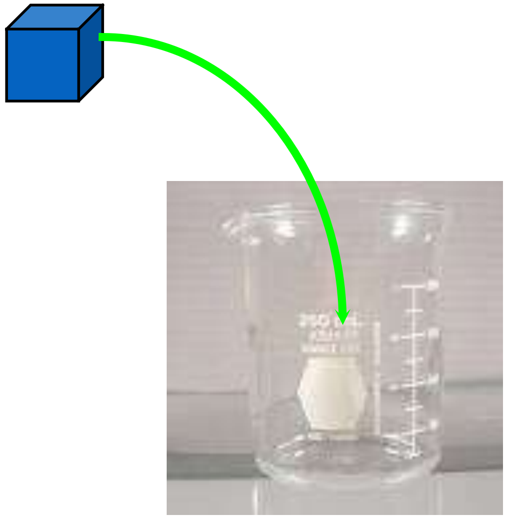
60 YEARS MAHIDOL UNIVERSITY SCIENCE




Less randomness
(less entropy)
More randomness
(more entropy)
ΔS > 0
ΔS < 0
ΔS > 0
ΔS < 0
Solid
Liquid
Gas

Entropy in solvation: solute

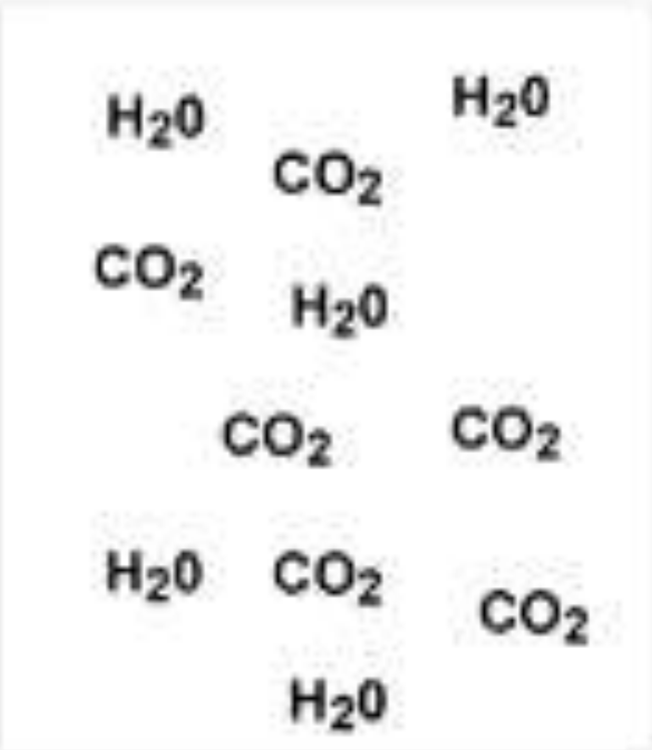
- When molecules go into solution, their entropy *increases* because they're freer to move around



Entropy in solvation: Solvent

- Solvent entropy usually *decreases* because solvent molecules must become more ordered around solute
- Overall effect: often slightly negative

vs.



- ordered
- unstable
- High Free Energy
- Low Entropy

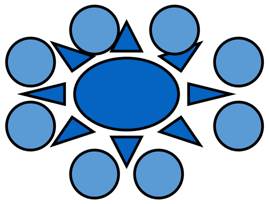
- Disordered
- stable
- Low Free Energy
- High Entropy

Entropy matters a lot!

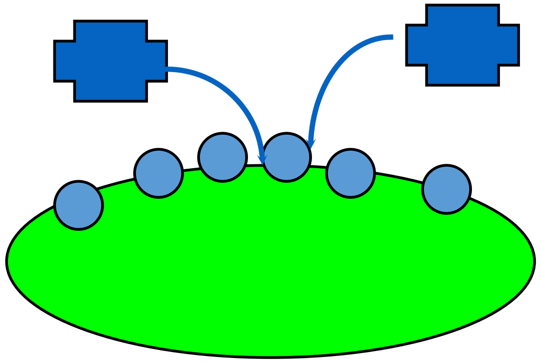
- Most biochemical reactions involve very small (< 10 kJ/mol) changes in enthalpy
- Driving force is often entropic
- Increases in sol*ute* entropy often is at war with decreases in sol*vent* entropy.
- The winner tends to take the prize.

Apolar molecules in water

- Water molecules tend to form ordered structure surrounding apolar molecule
- Entropy decreases because they're so ordered

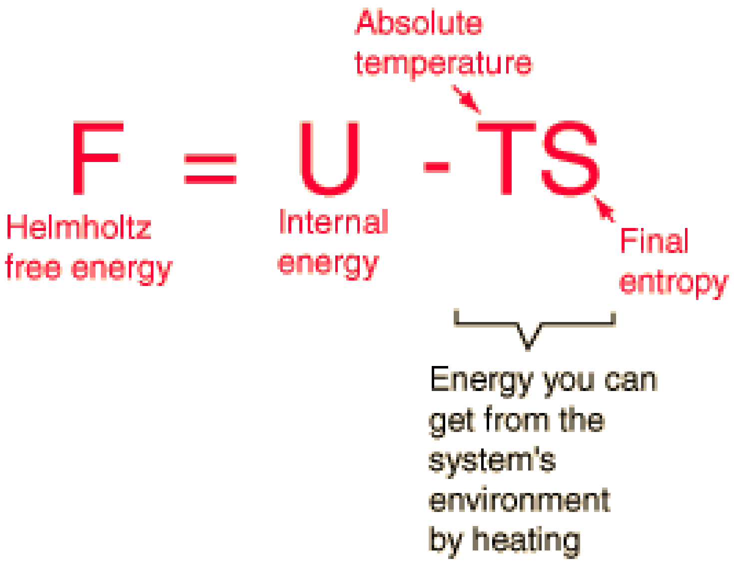


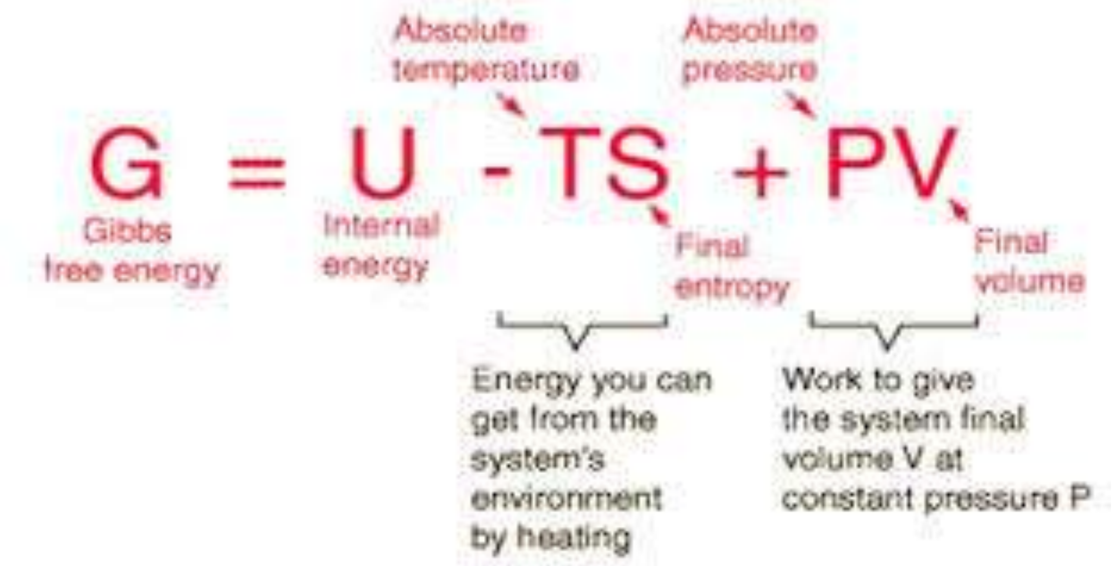
Binding to surfaces



- Happens a lot in biology, e.g.
  binding of small molecules to relatively immobile protein surfaces
- Bound molecules suffer a decrease in entropy because they're trapped
- Solvent molecules are displaced and liberated from the protein surface

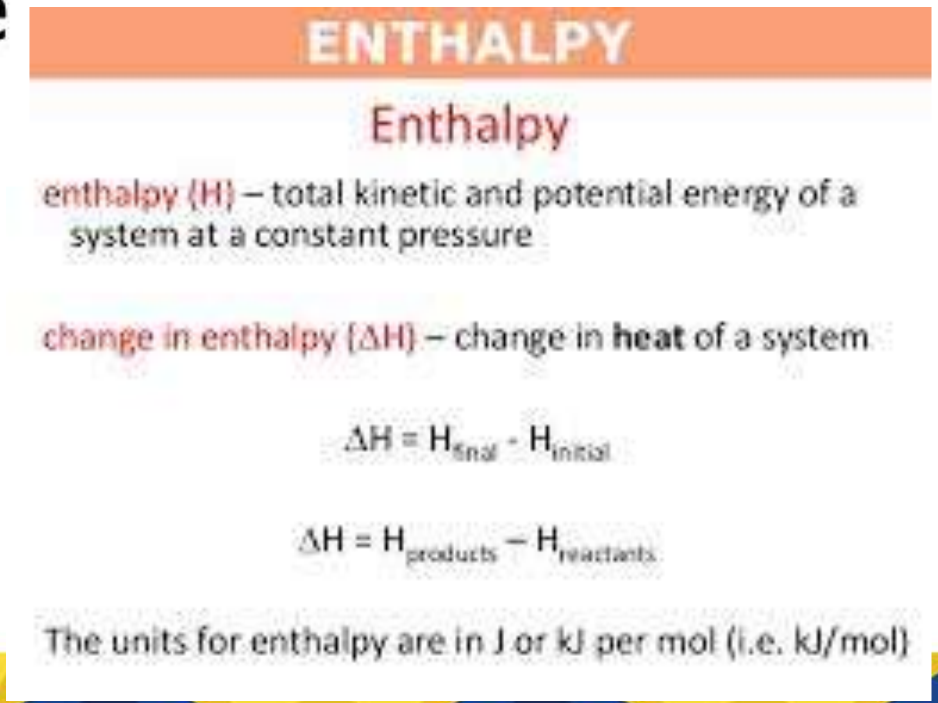
FREE ENERGY


Absolute temperature
F = U - TS
Helmholtz free energy
Internal energy
Final entropy
Energy you can get from the system's environment by heating


Absolute temperature
Absolute pressure
G = U - TS + PV
Gibbs free energy
Internal energy
Final entropy
Final volume
Energy you can get from the system's environment by heating
Work to give the system final volume V at constant pressure P

What is enthalpy?

- Enthalpy (H,or heat content) is the amount of heat energy possessed by substances.
- It is the sum of internal energy (U) and the product of the pressure and volume of a system.(H=U+PV)



GIBBS FREE ENERGY

How are entropy and enthalpy related?

entropy

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

Gibbs free energy (J or kJ)

enthalpy

Temperature (K)

Gibbs free energy is the energy that is available to do useful work.

A reaction will spontaneously occur if $\Delta G<0$ (exergonic reaction)

A reaction will NOT spontaneously occur if $\Delta G>0$ (endergonic reaction)

$$\Delta G = \Delta H - T\Delta S$$

Gibbs free energy change = total energy change for system

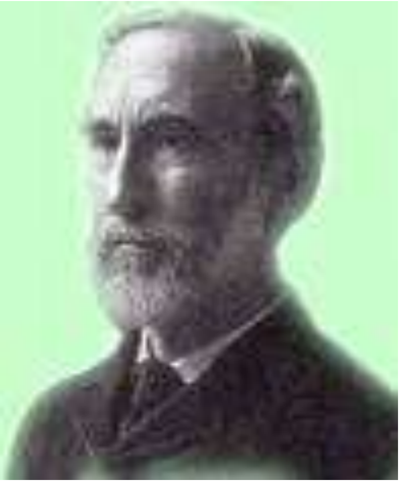
- energy lost in disordering the system

If the reaction is

- exothermic (negative ΔH)
- and entropy increases (positive ΔS^o)

- then ΔG must be NEGATIVE
- the reaction is spontaneous (and product-favored) at ALL temperatures.

Free Energy



- Gibbs:

  Free Energy Equation

  $G = H - TS$

- So if isothermal, $\Delta G = \Delta H - T\Delta S$
- Gibbs showed that a reaction will be spontaneous (proceed to right) if and only if $\Delta G < 0$

Free energy and equilibrium

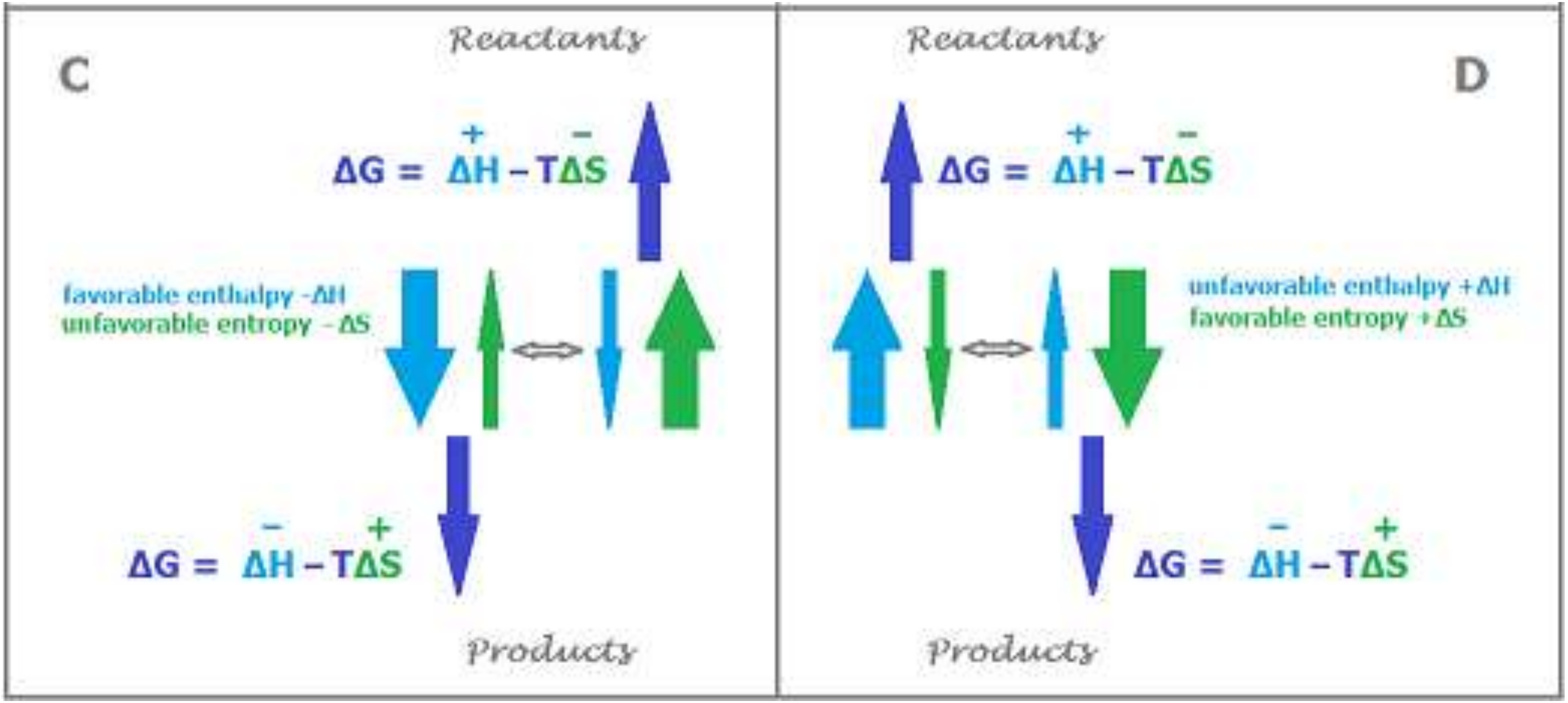
- Gibbs: $\Delta G^\circ = -RT \ln K_{eq}$
- Rewrite: $K_{eq} = \exp(-\Delta G^\circ/RT)$
- K_{eq} is equilibrium constant; formula depends on reaction type
- For $aA + bB \longrightarrow cC + dD$, $K_{eq} = ([C]^c[D]^d)/([A]^a[B]^b)$

Spontaneity and free energy

- Thus if reaction is just spontaneous, i.e. $\Delta G^{\circ} = 0$, then $K_{eq} = 1$
- If $\Delta G^{\circ} < 0$, then $K_{eq} > 1$: *Exergonic*
- If $\Delta G^{\circ} > 0$, then $K_{eq} < 1$: *Endergonic*
- You may catch me saying "exoergic" and "endoergic" from time to time:
  these mean the same things.

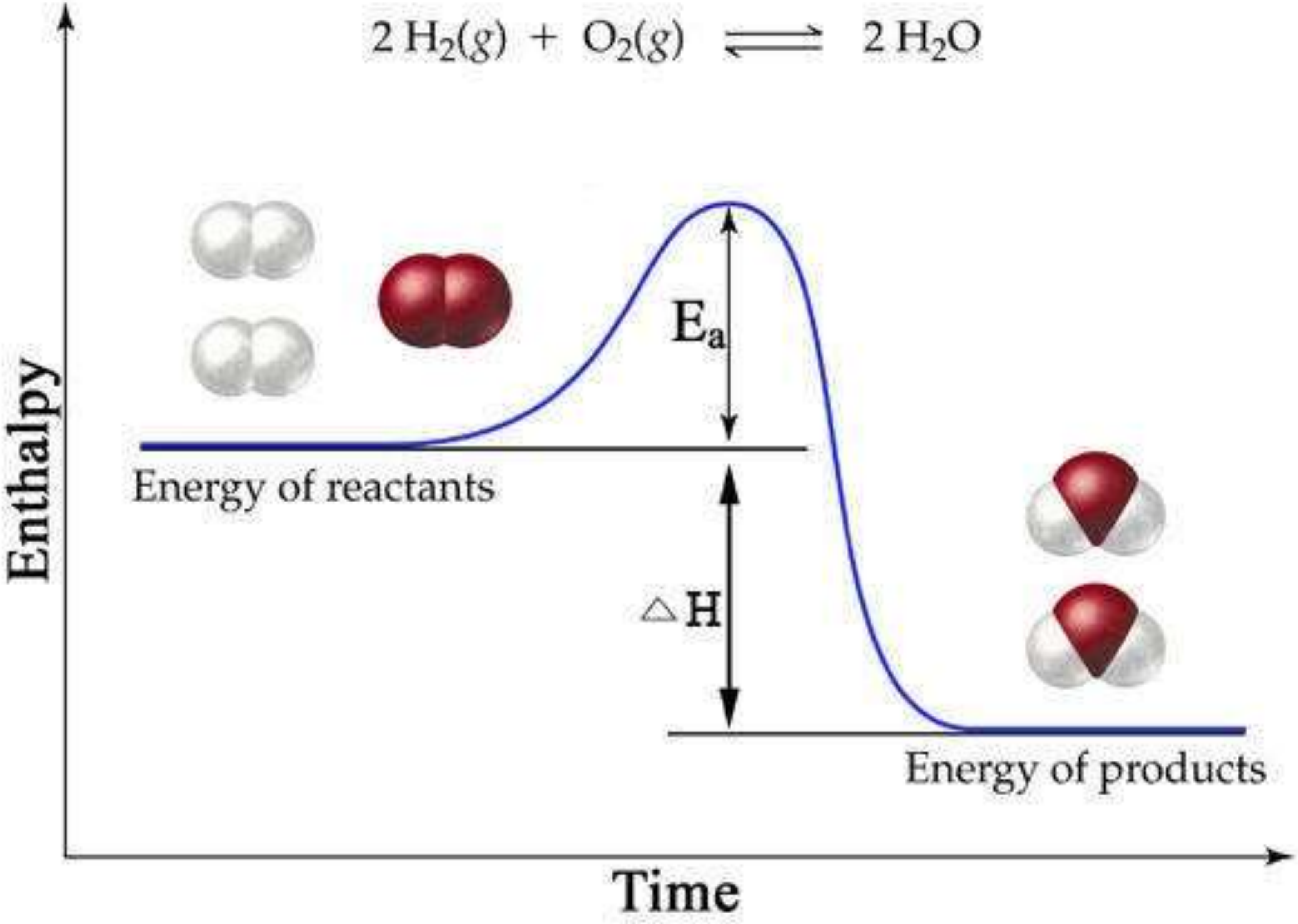
Free energy as a source of work

- Change in free energy indicates that the reaction could be used to perform useful work
- If $\Delta G^{\circ} < 0$, we can do work
- If $\Delta G^{\circ} > 0$, we need to do work to make the reaction occur

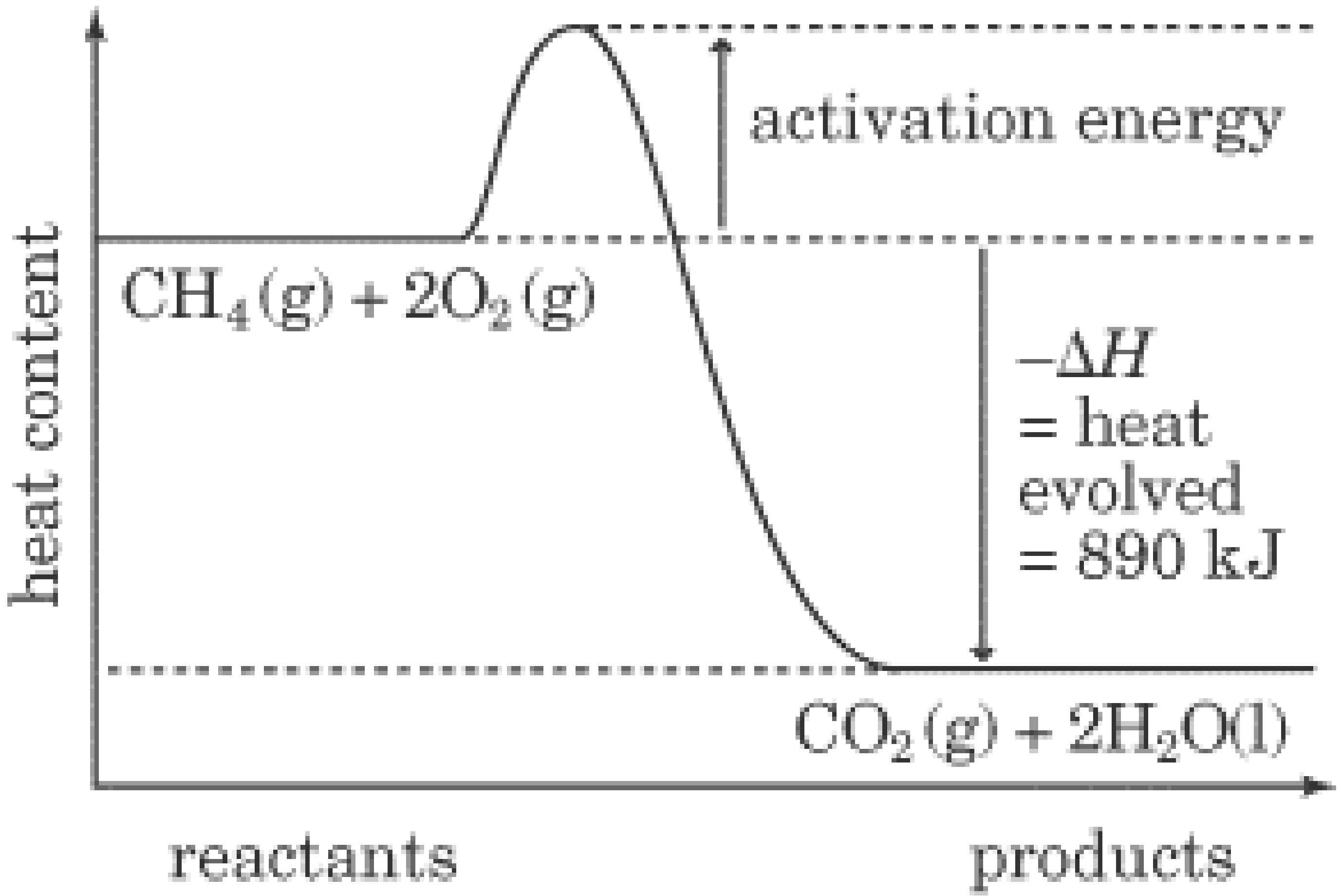

Reactants
C
ΔG = ΔH − TΔS
+
−
favorable enthalpy -ΔH
unfavorable entropy - ΔS
ΔG = ΔH − TΔS
−
+
Products
Reactants
D
ΔG = ΔH − TΔS
+
−
unfavorable enthalpy +ΔH
favorable entropy +ΔS
ΔG = ΔH − TΔS
−
+
Products

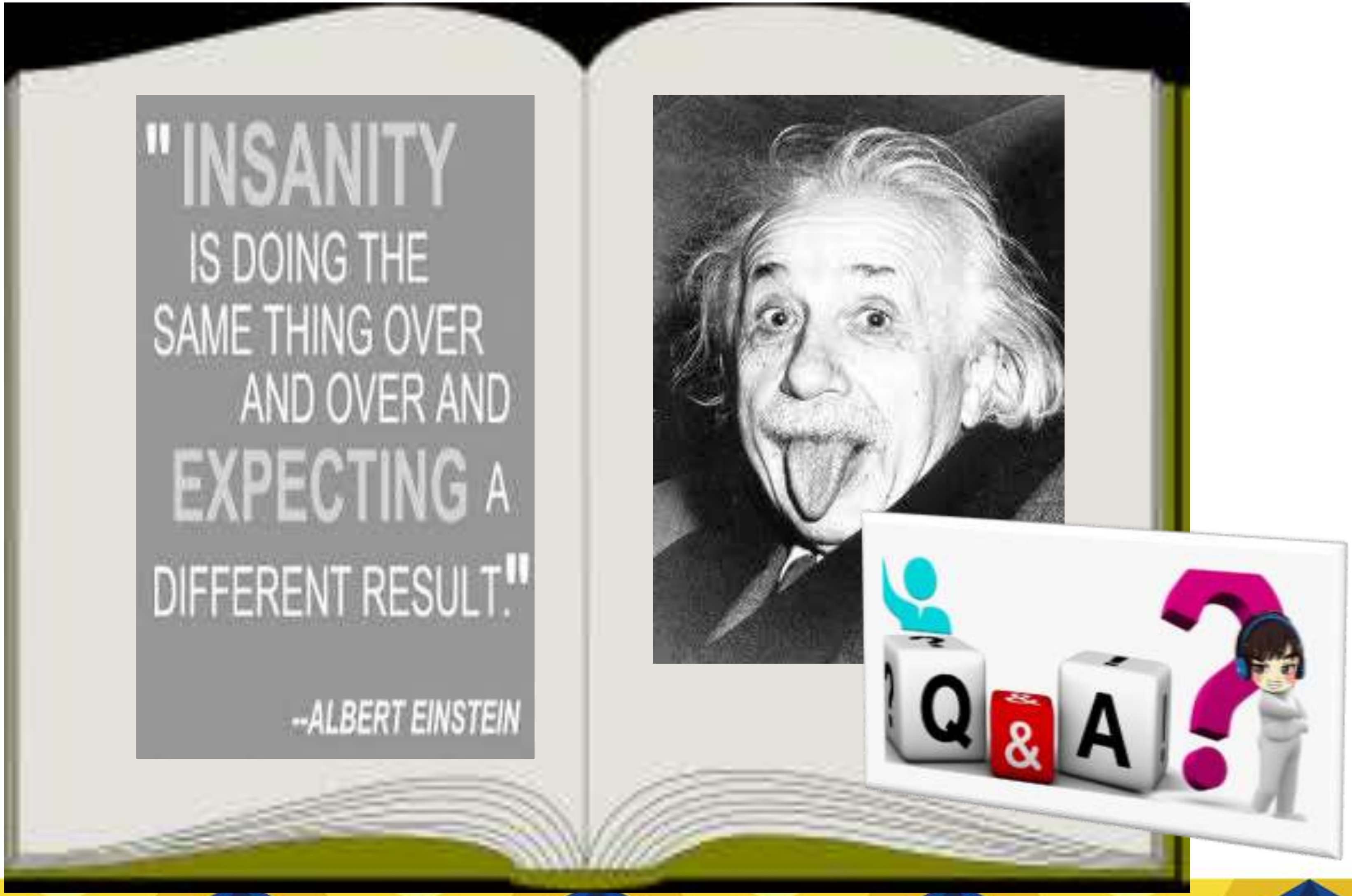
What kind of work?

- Movement (flagella, muscles)
- Chemical work:
  - Transport molecules against concentration gradients
  - Transport ions against potential gradients
- To drive otherwise endergonic reactions
  - by direct coupling of reactions
  - by depletion of products


$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O$
Enthalpy
E_a
Energy of reactants
$\triangle H$
Energy of products
Time

exothermic reaction




"INSANITY
IS DOING THE
SAME THING OVER
AND OVER AND
EXPECTING A
DIFFERENT RESULT."
--ALBERT EINSTEIN
Q & A