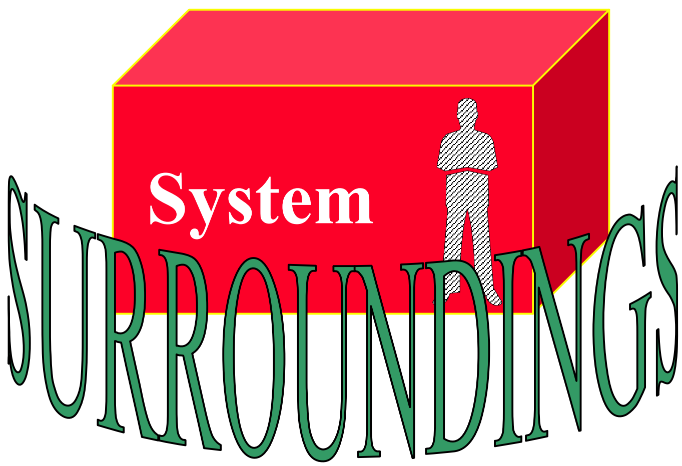
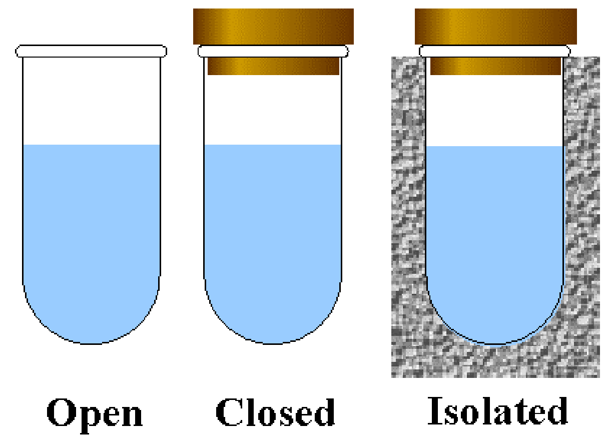
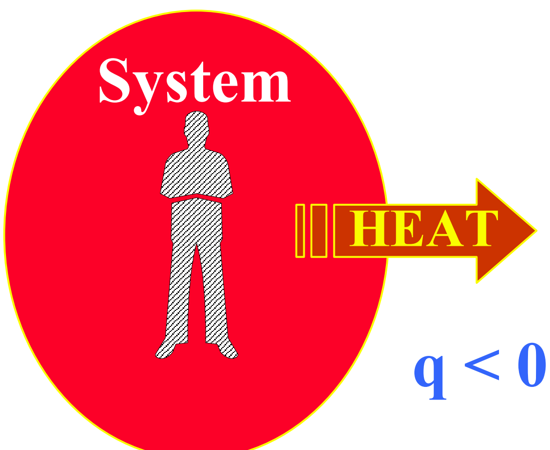
Thermodynamics: The First Law

Atkins, Chapter 2



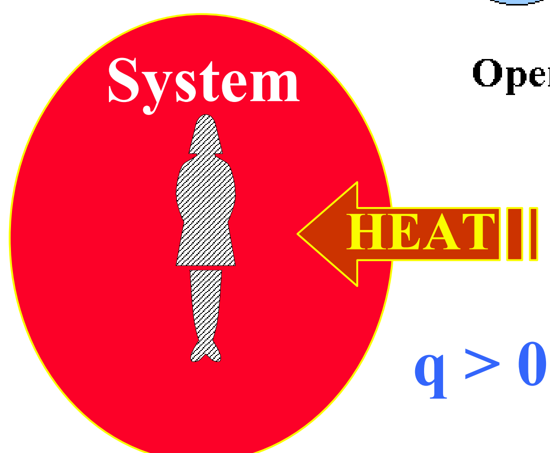
- <u>Open System:</u> Mass, heat, energy flow freely
- <u>Closed System:</u> Heat, energy flow freely
- <u>Isolated System:</u> No mass, heat, or energy flow





$q < 0$

Exothermic



$q > 0$

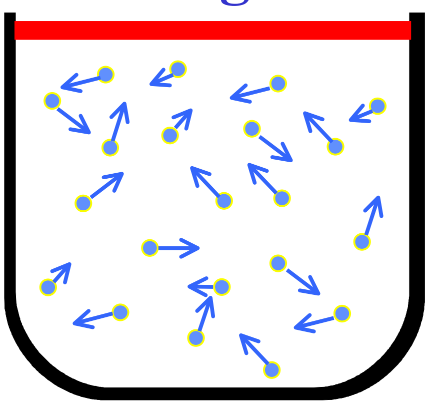
Endothermic

Internal Energy U

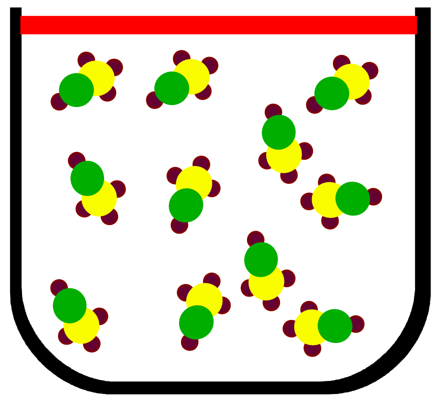
Internal Energy U:

The sum of all of the kinetic and potential energy contributions to the energy of all the atoms, ions, molecules, etc. in the system

He gas

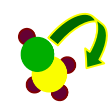


Methanol Gas

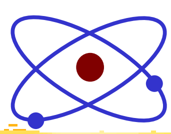


Translational Energy

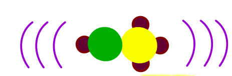
Rotational Energy



Electronic Energy



Vibrational Energy



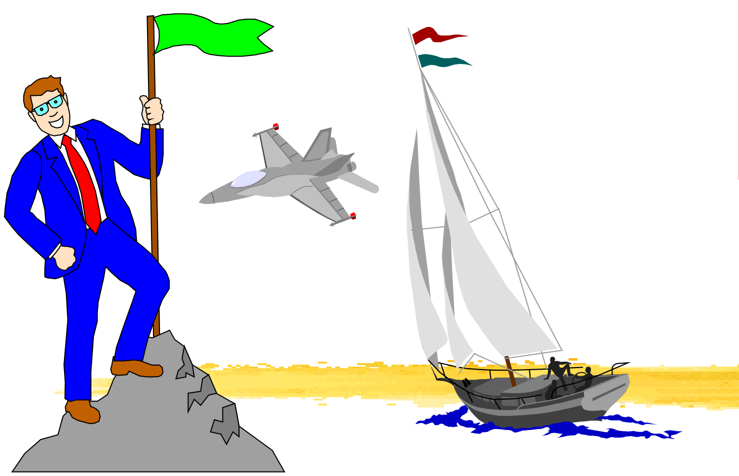
Nuclear Energy

Bond Energy

The First Law of Thermodynamics: Internal Energy is Conserved

- The change in internal energy (ΔU) of a closed system is equal to the sum of the heat (q) added to it and the work (w) done upon it
- The internal energy of an isolated system is constant

$\Delta U = q + w$	For a Closed System
$\Delta U = 0$	For an Isolated System



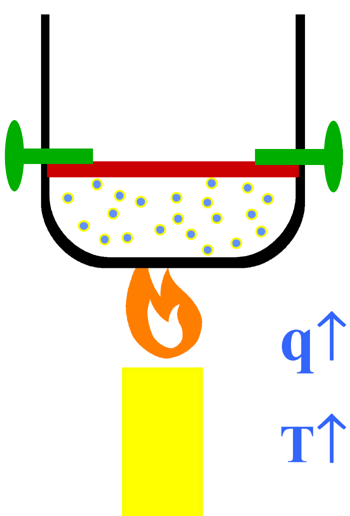
Internal energy U is a state function
$\Rightarrow$ Quantity is independent of path

Volume, Temperature, Pressure, and Quantity are other examples of state functions

Internal Energy can be exchanged with the surroundings as heat or work

$\boxed{\Delta U = q + w}$

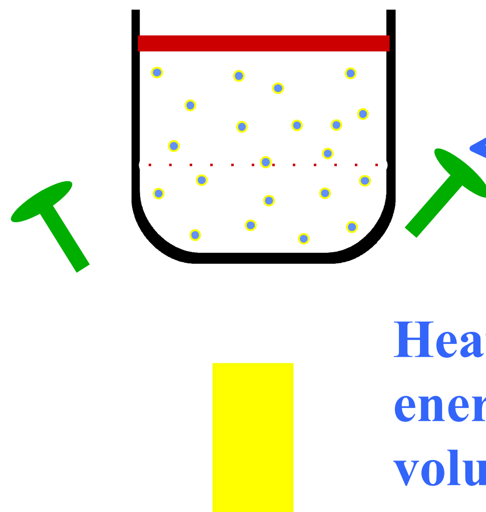
Closed system, constant volume



$q\uparrow$ heat introduced

$T\uparrow$

Closed system, expansion against external pressure

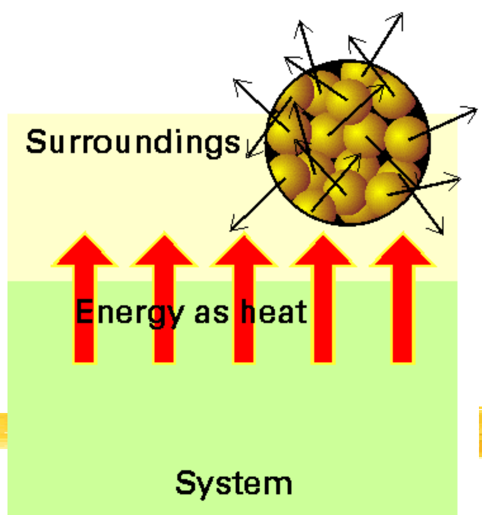


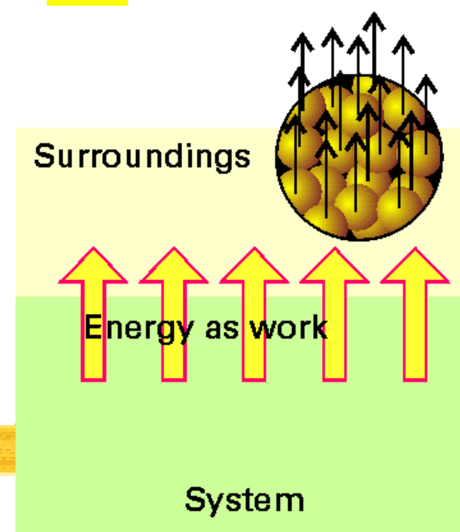
Heat is stored as internal energy and released as volume-pressure work [J]

$w = -Fdx = -p\Delta V$

$w = 0$; no work done

$\boxed{\Rightarrow \Delta U = q_v}$





$$\boxed{\begin{aligned}\Delta U &= q + w \\ &= q - p_{ex}\Delta V\end{aligned}}$$

Internal Energy and Enthalpy

Enthalpy definition: $\boxed{H = U + pV}$

Most convenient for processes at constant pressure:

- Cooking dinner
- Drying the laundry
- Digesting dinner
- Synthesizing a compound in lab

At constant pressure, if only pV work is done:

$$\Delta U = q + w = q_p - \int_{V_1}^{V_2} p\, dV$$

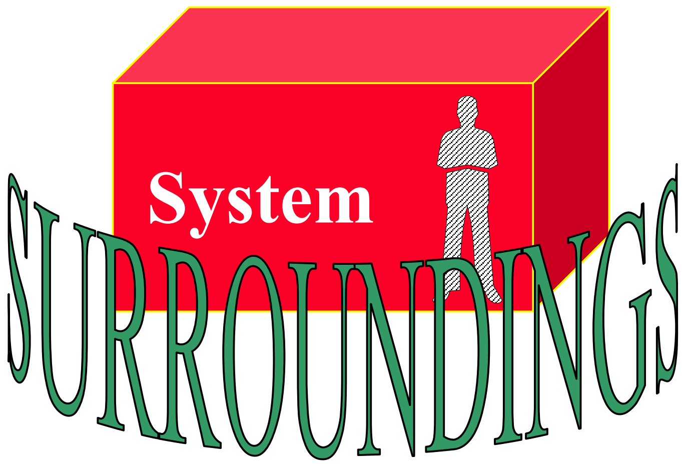
$$= q_p - p\int_{V_1}^{V_2} dV = q_p - p(V_2 - V_1) = q_p - p\Delta V$$

p independent of V

$$\boxed{\Delta H = \Delta U + p\Delta V = q_p}$$

Enthalpy is the heat transferred in a process at constant pressure (assuming only pV work)

Enthalpy



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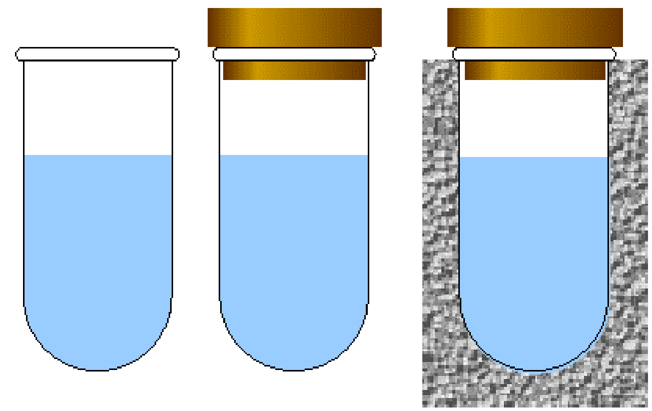
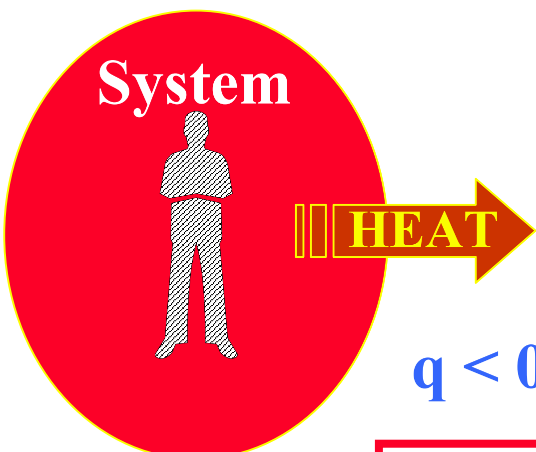
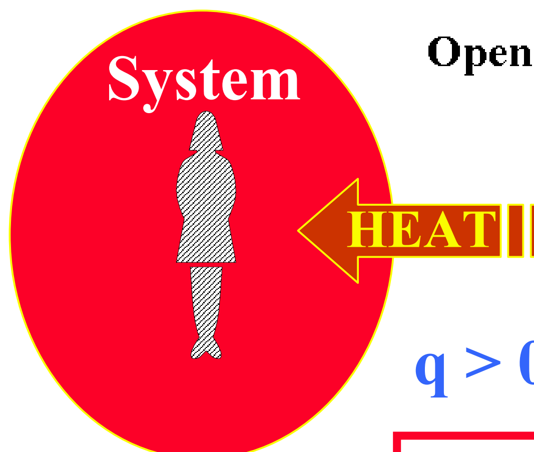


Open Closed Isolated



$q < 0$

Exothermic $\boxed{\Delta H < 0}$



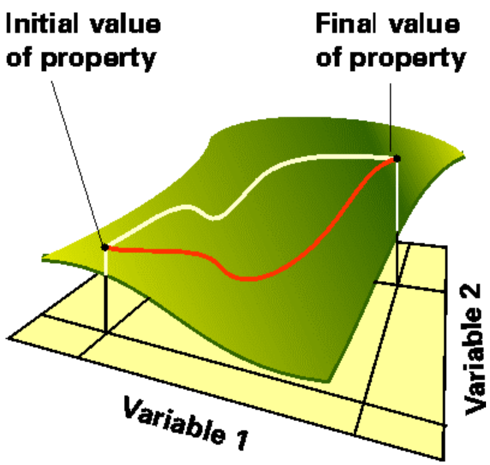
$q > 0$

Endothermic $\boxed{\Delta H > 0}$

Enthalpy and Internal Energy are State Functions

We only need be concerned with the change in enthalpy (ΔH) or change in internal energy (ΔU), not the path of how we got there

$\Rightarrow$ We can arbitrarily assign **H = 0 for each element in its standard state = state of aggregation at p = 1 bar, T = 298.15 K**



$\Delta_f H^\phi$ = standard molar enthalpies of formation

Standard Formation Reaction: Formation of one mole of a substance from the elements in their standard states.

$CS_{2\,(l)}$ +87.86 kJ/mol — $C_{(graphite)} + 2\ S_{(s,\ rhombic)} \rightarrow CS_{2(l)}$

$C_{(graphite)}$, $O_{2\,(g)}$, $C_{(graphite)}$, $S_{(s,\ rhombic)}$ — 0

$CO_{(g)}$ -110.52 kJ/mol — $C_{(graphite)} + 1/2\ O_{2\,(g)} \rightarrow CO_{(g)}$

$CO_{2\,(g)}$ -393.51 kJ/mol — $C_{(graphite)} + O_{2\,(g)} \rightarrow CO_{2(g)}$