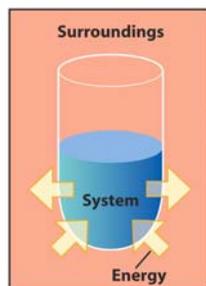


## LECTURE 23. INTERNAL ENERGY

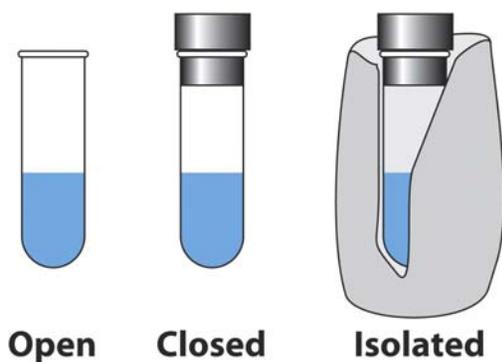
### Internal Energy

To begin, we need to distinguish concepts of system and state functions more precisely.



System + surroundings = universe  
Thermo studies the flow of energy  
in all forms between the chemical  
system and surroundings

To investigate the internal energy of the system, we need to think about different ways to create systems experimentally.



Open: the way we normally do reactions  
With constant pressure  
but change in volume

Closed: a bomb  
V is held constant and  
P changes. Heat flows

Isolated: V is constant and the  
vacuum prevents heat exchange

## Work and Internal Energy

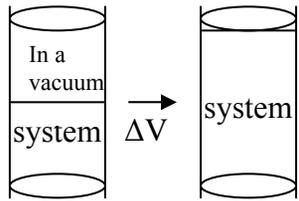
Work: we have discussed work in thermo as the result of gas molecules expanding against an external force.

$$w = - P \Delta V = -\Delta nRT$$

But the source of this expression, and its limitations, wasn't developed--until now:

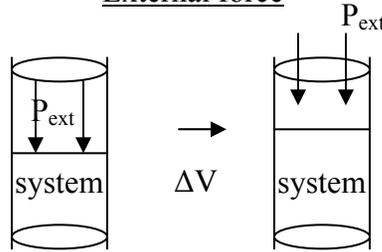
First consider the idea of a gas expansion (change in  $\Delta V$  of a gas) in the presence or absence of an external pressure

No external force



$P_{\text{ext}} = 0$  and no work is done.

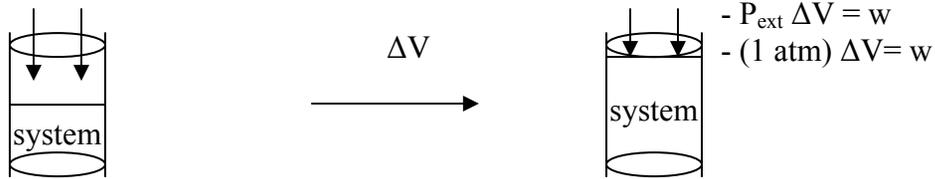
External force



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

Note that  $P_{\text{ext}}$  even happens in an open container because of the 1 atm of external pressure.

Open container  
with  $P_{\text{ext}} = 1 \text{ atm}$

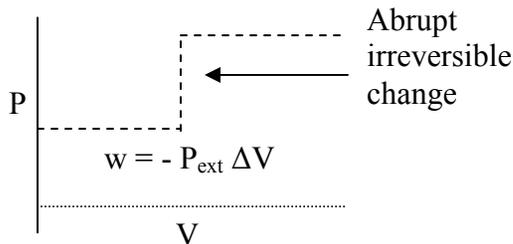


## Reversible vs. Irreversible work

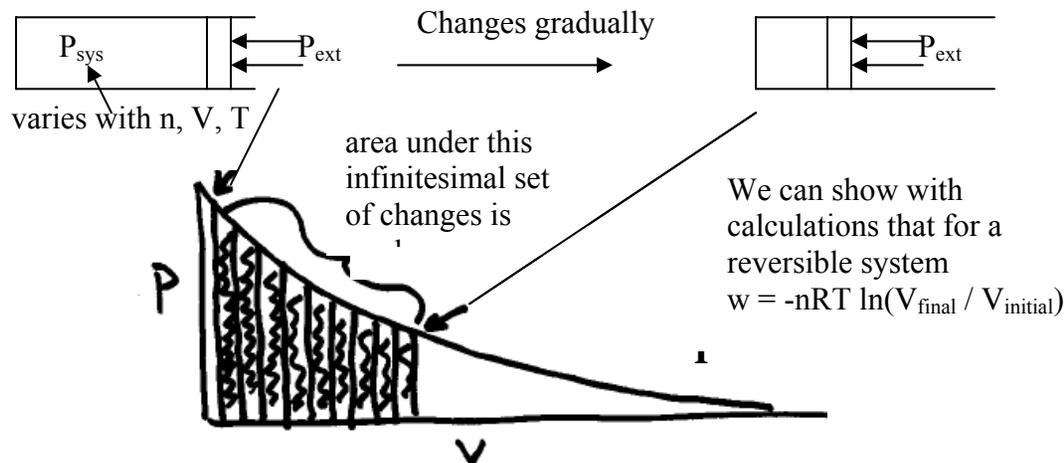
To this point we have considered only systems in which the external pressure is constant. Like atmospheric pressure, or the force created by putting a cap on the system. It is time for a change:

Definition:

**Irreversible work** is work done against an external, usually constant, pressure in which there is an abrupt change in the system pressure that does not match the external pressure.

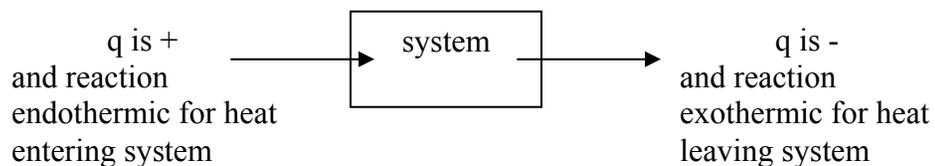


**Reversible work:** Imagine a changing external pressure, one in which  $P_{\text{int}}$  and  $P_{\text{ext}}$  are matched. This would permit a reaction to reverse itself by an infinitesimal change in  $P$ . We can create such a process with a piston that is varied so that  $P_{\text{ext}}$  changes gradually when system pressure changes, either because of changes in  $T$ ,  $n$ , etc.



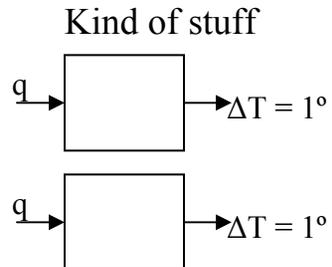
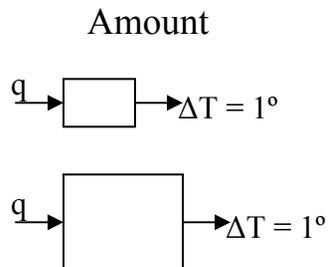
**Heat:** In addition to work, energy changes in a system can occur because of changes in temperature. This is heat energy,  $q$ .

Recall that by definition



**Heat Capacity:** Different materials have different capacities for transferring heat energy.  $C = q / \Delta T$

Two things matter



So raising temperature from heat depends on amount and kind of material

For example

Cu specific heat capacity is  $0.38 \text{ J/g } ^\circ\text{C}$

$\text{H}_2\text{O}$  specific heat capacity is  $4.18 \text{ J/g } ^\circ\text{C}$

## First Law and Calorimetry

Recall that we employed the first law of thermodynamics to help in devising a method for determining the heat capacity of food from calorimetry.

First law says: The total internal energy of an isolated system is conserved

$$\Delta E_{\text{sys}} = q + w \longleftarrow \text{This amount cannot change (but } q \text{ and } w \text{ can)}$$

So I can indirectly determine  $\Delta E_{\text{sys}}$  from amount of energy that goes from system to surroundings.

$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr calorimeter}} = -C\Delta T_{\text{H}_2\text{O}} + -C\Delta T_{\text{calorimeter}}$$

### State Functions: why $q$ and $w$ aren't state functions

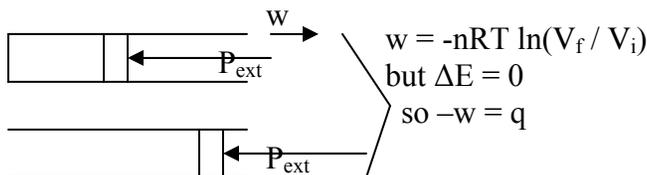
Recall that our definition of a state function was that its value depended solely on its final quantity minus the initial quantity.

$$\Delta E = E_f - E_i \quad \Delta T = T_f - T_i \quad \Delta H = H_f - H_i$$

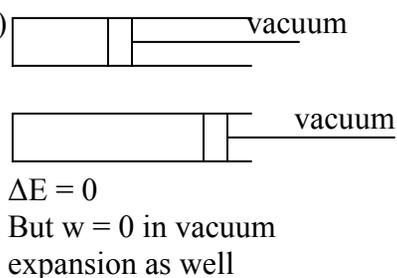
And the same for  $\Delta V$ ,  $\Delta P$ ,  $\Delta G$ ,  $\Delta S$ . All are state functions.

But  $q$  and  $w$  are not. Why? The reason is that the path does matter in the amount of  $q$  and  $w$  that result even if their total,  $\Delta E = q + w$ , isn't dependent on path.

#### Example 1 Reversible process



#### Example 2 Irreversible process



## Enthalpy

We sure have spent a lot of time on  $\Delta E$  and ignored  $\Delta H$  which seems odd because  $\Delta H$  is what we used to determine spontaneity from  $\Delta G = \Delta H - T\Delta S$ . Now it returns.

$\Delta E$  is really useful in closed environments because a sealed system has  $\Delta V = 0$  so  $w = 0$ . Therefore  $\Delta E = q$  in a bomb calorimeter.

But we do most experiments in open containers so there is expansion work,  $P\Delta V \neq 0$ . This means we need a way to keep track of both the internal energy of a system and the expansion work

$$\Delta H = \Delta E + P\Delta V$$

↑            ↑  
system    expansion  
energy    work

← A useful equation for  
reaction and  
atmospheric pressure

From here we can perform an exciting derivation of enthalpy at atm. pressure:

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = q + w + P\Delta V$$

$$\Delta H = q - P_{\text{ext}}\Delta V + P\Delta V \quad \text{but } P_{\text{ext}} = P_{\text{sys}} \text{ in open container}$$

$$\text{So } \Delta H = q \text{ at constant } P.$$

Drum roll please!!!

$$\Delta E = q \text{ in a constant volume bomb calorimeter}$$

$$\Delta H = q \text{ in a constant pressure Styrofoam cup container}$$

Relating  $\Delta H$  to  $\Delta E$

- No gas present,  $PV$  is negligible and  $\Delta H \sim \Delta E$
- Gas in reaction at constant pressure:  $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta nRT$   
And we see where the  $\Delta nRT$  work quantity.