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**
  - In a vacuum system \( \Delta V \)
  - \( P_{\text{ext}} = 0 \) and no work is done.

- **External force**
  - \( P_{\text{ext}} \) system \( \Delta V \)
  - \( w = - P_{\text{ext}} \Delta V \)

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

Open container
  - with \( P_{\text{ext}} = 1 \text{ atm} \)

\[ - P_{\text{ext}} \Delta V = w \]
\[ - (1 \text{ atm}) \Delta V = w \]
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.

We can show with calculations that for a reversible system
\[
w = -nRT \ln\left(\frac{V_{\text{final}}}{V_{\text{initial}}}\right)
\]
**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

\[ q \text{ is } + \quad \text{and reaction endothermic for heat entering system} \]

\[ q \text{ is } - \quad \text{and reaction exothermic for heat leaving system} \]

**Heat Capacity:** Different materials have different capacities for transferring heat energy. \( C = \frac{q}{\Delta T} \)

Two things matter

**Amount**

\[ q \rightarrow \Delta T = 1^\circ \]

**Kind of stuff**

\[ q \rightarrow \Delta T = 1^\circ \]

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

For example

Cu specific heat capacity is 0.38 J/g °C
H₂O specific heat capacity is 4.18 J/g °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

\[ \Delta E_{sys} = q + w \]

This amount cannot change (but q and w can)

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

\[ \Delta E_{sys} = - \Delta E_{surr\ calorimeter} = - C \Delta T_{H2O} + - C \Delta T_{calorimeter} \]

**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

\[ w = nRT \ln \left( \frac{V_f}{V_i} \right) \]

but \( \Delta E = 0 \)

so \( -w = q \)

**Example 2**
Irreversible process

\[ \Delta E = 0 \]

But \( w = 0 \) in vacuum expansion as well
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.

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

A useful equation for reaction and atmospheric pressure

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

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

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

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

So $\Delta H = q$ at constant $P$.

Drum roll please!!!

$\Delta E = q$ in a constant volume bomb calorimeter  
$\Delta H = q$ 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.