The First Law of Thermodynamics

energy cannot be created or destroyed. it can be transformed from one kind into another, But the total energy of a system and its immediate surroundings remains constant during any operation.

- ***The change in the internal energy of a system (ΔE) depends only on***
  - ***a) the amount of heat (q) gained or lost by the system***
  - ***b) the work (w) done on or by the system.***

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

$$\Delta E = q - p\,\Delta V$$

where E_2 is the internal energy of the system in its final state and E_1 is the internal energy of the system in its initial state, q is the heat, and W is the work. The change in internal energy ΔE is related to q and W transferred between the system and its surroundings

- ❖ **If a system's volume is constant, and heat is added, its internal energy increases.**

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

- ❖ **If a system does work on the external world, and no heat is** added, its internal energy decreases

$$\Delta E = E_2 - E_1 = -W$$

Applications/Processes of Thermodynamics

The *First Law* works differently for a process in which the volume stays constant than for a process in which the pressure stays constant

Isochoric Process

The volume of the system remains constant ($\Delta V = 0$). On a pV diagram, this type of process would be represented by a vertical line. Therefore, there is no area under the curve.

Since there is no change in volume, $w = 0$. So the internal energy of the system depends only on heat transfer.

$$\Delta U = q_V$$

Isobaric Process

The system's pressure is fixed ($\Delta p = 0$). It is represented by a horizontal line on a pV diagram.

Both w and q will still exist for this process.

$$\Delta U = q + w$$

Adiabatic Process

There is no transfer of heat to or from the system, $\Delta q = 0$, though other characteristics such as the pressure, volume, and temperature of the system may vary. The curve of an adiabatic process on a pV diagram depends on the changes in the system.

$$\Delta U = w_{ad}$$

Isothermal Process

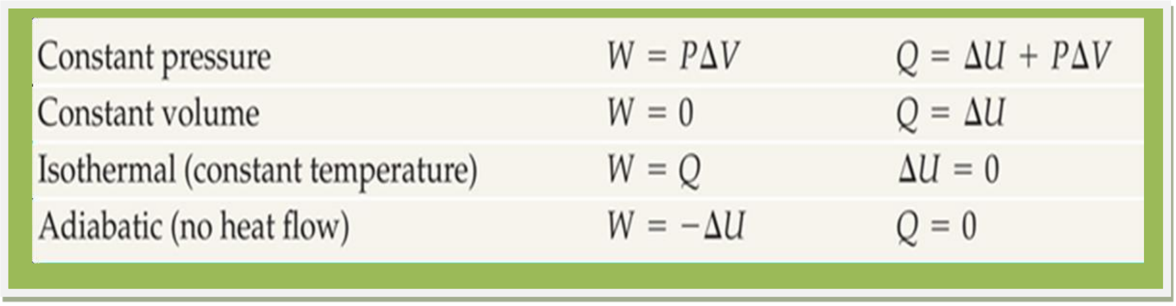
The system's temperature is fixed ($\Delta T = 0$). It is represented by a pV diagram and energy stays constant ($\Delta U = 0$)

$$q = -w$$

Cyclic Process

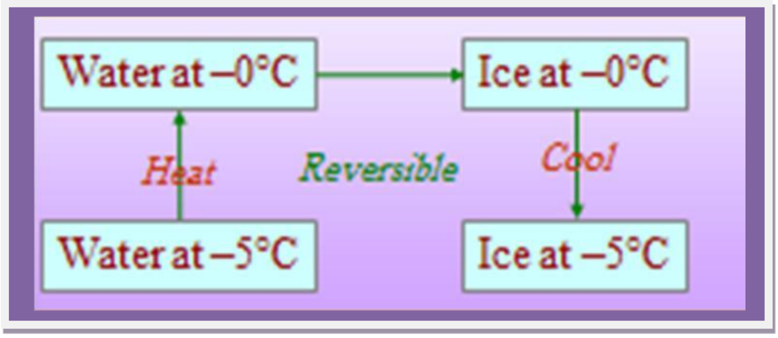
Certain processes have the same initial and final states (e.g., engines). This is represented by a closed path and $\Delta U = 0$

$$q = -w$$



Constant pressure	$W = P\Delta V$	$Q = \Delta U + P\Delta V$
Constant volume	$W = 0$	$Q = \Delta U$
Isothermal (constant temperature)	$W = Q$	$\Delta U = 0$
Adiabatic (no heat flow)	$W = -\Delta U$	$Q = 0$

***Reversible Processes*:-** is one where an infinitesimal change in the conditions of the surroundings leads to a 'reversal' of the process. (The system is very close to equilibrium and infinitesimal changes can restore the system and surroundings to the original state).



The work in an isothermal reversible process is in its maximum value.

$$W_{\max} = -nRT \ln \frac{V_2}{V_1} \qquad (3\text{–}10)$$

- ✓ in expansion, $V_2 > V_1$, and $\ln(V_2/V_1)$ is a positive quantity; therefore, the work is done by the system (w= -), so that its energy decreases (negativesign)
- ✓ in compression $V_2 < V_1$, and $\ln(V_2/V_1)$ is negative, work is done on the system (w=+), so that its energy increases (positive sign). The process itself determines the sign of W and ΔE.

Equation **(**3-10**)** gives the maximum work done in the expansion as well as the heat absorbed, because $Q = \Delta E - W$

ΔE is equal to zero for an ideal gas in an isothermal process.

The maximum work in an isothermal reversible expansion may also be expressed in terms of pressure

$$W_{\max} = -nRT \ln \frac{P_1}{P_2} \qquad (3\text{–}11)$$

Example

One mole of water in equilibrium with its vapor is converted into steam at 100°C and 1 atm. The heat absorbed in the process (i.e., the heat of vaporization of water at 100°C) is about 9720 cal/mole. What are the values of the three first-law terms *Q*, *W*, and Δ*E*?

The amount of heat absorbed is the heat of vaporization, given as 9720 cal/mole. So that Q = 9720cal/mole

The work W performed against the constant atmospheric pressure is obtained by using equation (3-10), $W = -nRT \ln(V_2/V_1)$. Now, V_1 is the volume of 1 mole of liquid water at 100°C, or about 0.018 liter. The volume V_2 of 1 mole of steam at 100°C and 1 atm is given by the gas law, assuming that the vapor behaves ideally:

$$V_2 = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.6 \text{ liters}$$

It is now possible to obtain the work,
W = -(1 mole)(1.9872 cal/K mole)(373.15 K) ln (30.6/0.018) = -5515.73 cal
The internal energy change Δ*E* is obtained from the first-law expression,
Δ*E* = 9720 – 5515.73 = 4204.27 cal

Example

What is the maximum work done in the isothermal reversible expansion of 1 mole of an ideal gas from 1 to 1.5 liters at 25°C?

The conditions of this problem are similar to those of *Example 3–2*, except that equation (3-10) can now be used to obtain the (maximum) work involved in expanding reversibly this gas by 0.5 liters; thus,
W = -(1 mole)(8.3143 joules/K mole)(298.15 K) ln (1.5/1.0)
W = -1005.3 joules

Heat capacity

- **The heat capacity is the energy required to raise the temperature of an object by 1^oC.**
- **The heat capacity depends on the mass of the object and the ability of the object to resist the flow of heat into or out of the object.**
- **$Q = mc_x\Delta T$**
- The constant $\mathbf{c_x}$ is called the specific heat of substance x, (SI units of J/kg·K)
- Heat capacity at constant Volume (C_V):
- Heat capacity at constant Pressure (C_P):
- Units: Joules/Kelvin/mole, J/K/mole, J/°C/mole, J/°C/g.
- **Both C_V and C_P can be calculated for a monatomic ideal gas using the**

$$\boxed{\begin{aligned} C_V &= \tfrac{3}{2}R \\ C_P &= \tfrac{5}{2}R \\ C_P - C_V &= R \end{aligned}}$$

first law of thermodynamics ***Specific heats for ideal gases must be quoted either at constant pressure or at constant volume. For a constant-volume process***

$$Q_V = nC_V\Delta T$$

Specific Heats for an Ideal Gas at Constant Pressure

$$Q_P = nC_P\Delta T$$

Changes of State at Constant Pressure

When the work of expansion is done at *constant pressure*, $W = -P\,\Delta V = -P(V_2 - V_1)$ by equation (**3–7**), and under these conditions, the first law can be written as

$$\Delta E = Q_P - P(V_2 - V_1) \qquad \textbf{(3–18)}$$

where Q_P is the heat absorbed at constant pressure. Rearranging the equation results in

$$\begin{aligned} Q_P &= E_2 - E_1 + P(V_2 - V_1) \\ &= (E_2 + PV_2) - (E_1 + PV_1) \qquad \textbf{(3–19)} \end{aligned}$$

The term $E + PV$ is called the ***enthalpy, H***. The increase in enthalpy, ΔH, is equal to the heat absorbed at constant pressure by the system. It is the heat required to increase the internal energy and to perform the work of expansion, as seen by substituting H in equation **(**3-19**)**,

$$Q_P = H_2 - H_1 = \Delta H \qquad \textbf{(3–20)}$$

and writing equation **(**3-18**)** as

$$\boxed{\Delta H = \Delta E + P\Delta V \qquad \textbf{(3–21)}}$$

change in enthalpy between products and reactants,

$$\Delta H = H_{products} - H_{reactants}$$

$$\Delta C_P = (C_P)_{\text{products}} - (C_P)_{\text{reactants}}.$$