## Chapter 3

# The First Law of Thermodynamics

**Min Soo Kim**

**Seoul National University**

# 3.1 Configuration work

**Configuration work = Work in a reversible process** $\delta$**W =** $\sum_i y_i dX_i$**, i=1, 2, ... n.**

Change in the volume (ΔV) of the cylinder housing of a piston is ΔV = AΔh as the piston moves.
The work performed by the surroundings on the system as the piston moves inward is given by $W = P_{ext}\Delta V$

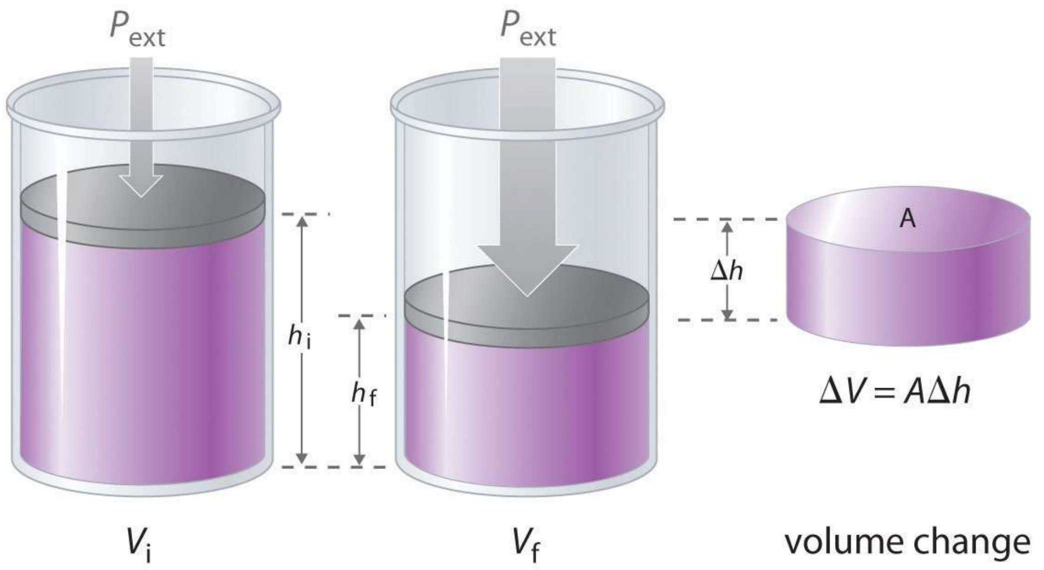



**Figure** 3.1 The work performed by the surroundings on the system [1]

[1] http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s22-01-thermodynamics-and-work.html

# 3.1 Configuration work

**Various examples of configuration work**

| System | Intensive Variable | Extensive Variable | $\delta W$ |
|---|---|---|---|
| Gas, liquid or solid | P (pressure) | V (volume) | $PdV$ |
| Film | Γ (surface tension) | A (area) | $\Gamma dA$ |
| Electrolytic cell | $\varepsilon$ (electromotive force) | q (charge) | $\varepsilon dq$ |
| Physical object | F (force) | s (distance) | $Fds$ |
| Dielectric material | E (electric field) | P (polarization) | $EdP$ |

**For isobaric process (P=constant)**

$$W = \int_{V_A}^{V_B} \delta W = \int_{V_A}^{V_B} P dV = P(V_B - V_A)$$

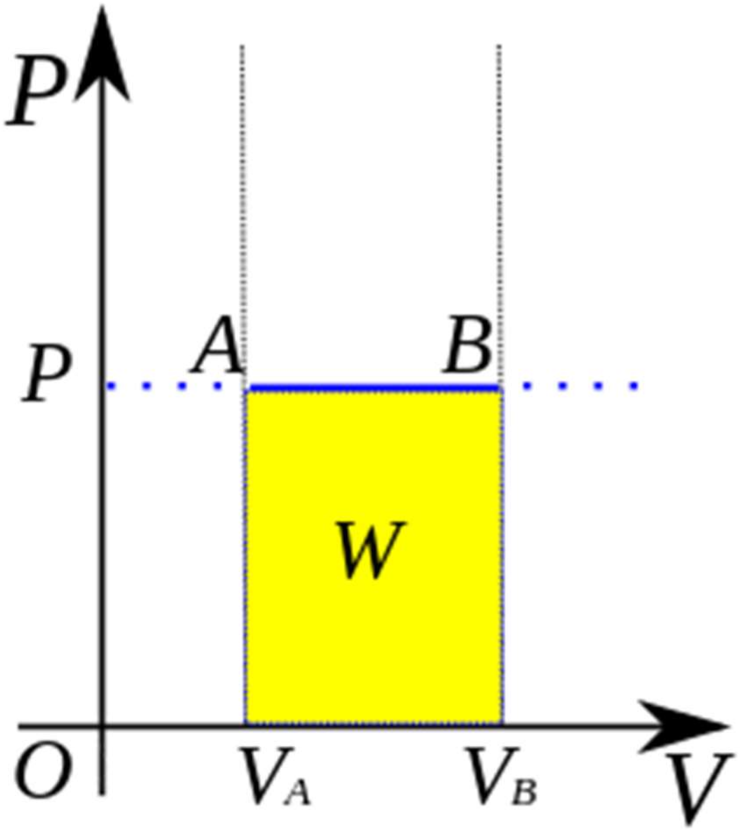



**Figure 3.2** The yellow area represents the work done [2]

[2] https://en.wikipedia.org/wiki/Isobaric_process#/media/File:Isobaric_process_plain.svg

## 3.1 Configuration work

**For isothermal process (ideal gas)**

$$W = \int_{V_A}^{V_B} PdV = \int_{V_A}^{V_B} \frac{n\bar{R}T}{V} dV = n\bar{R}T ln(\frac{V_B}{V_A})$$

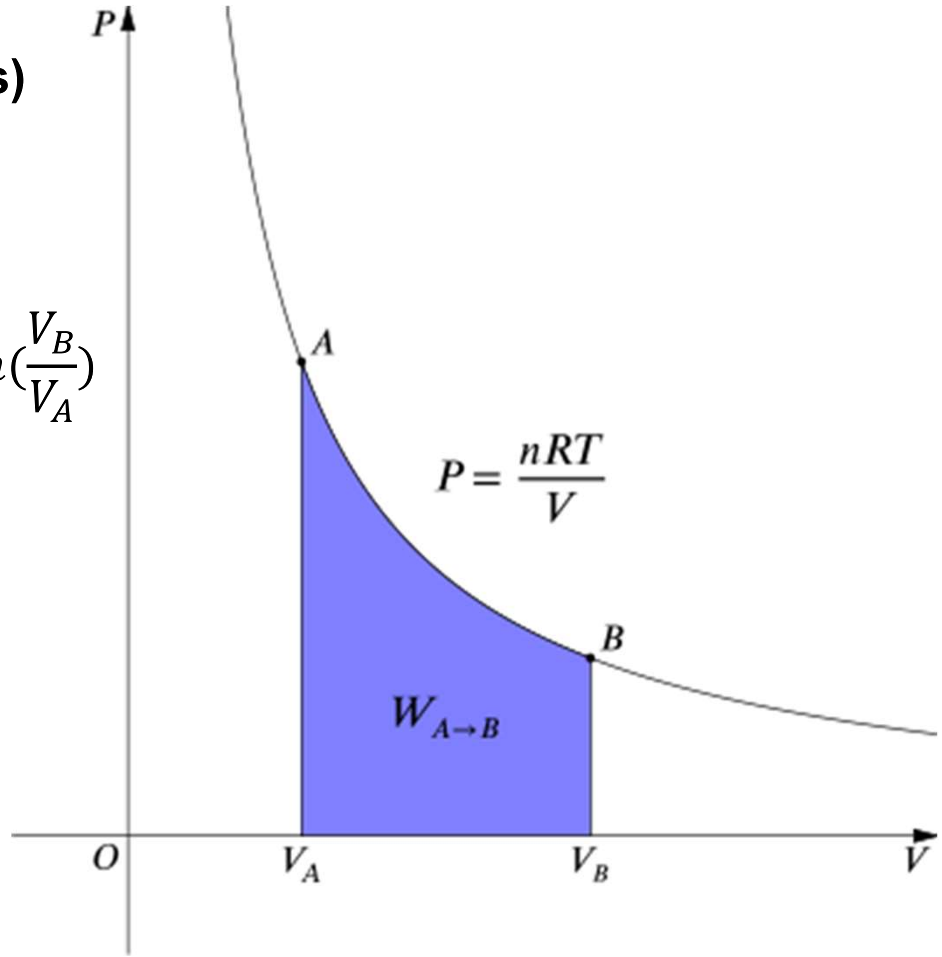
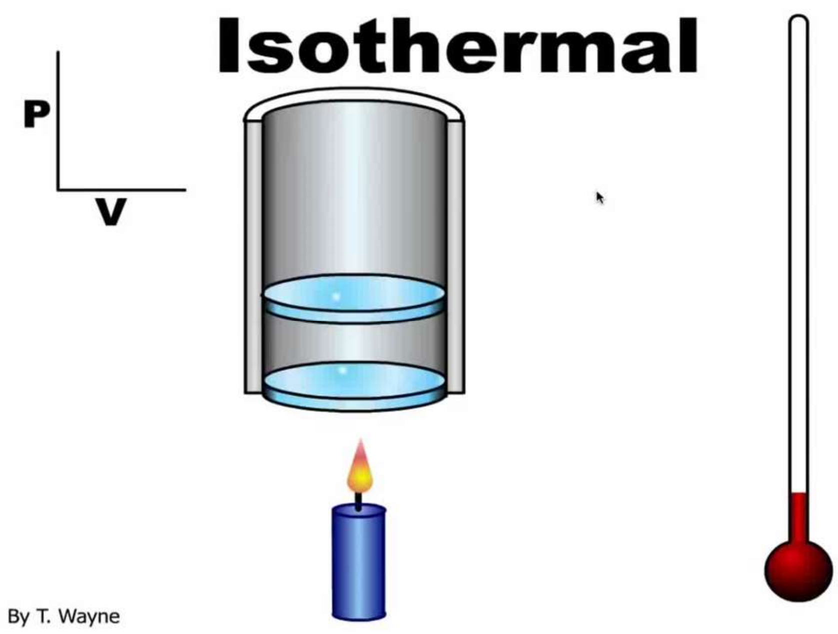


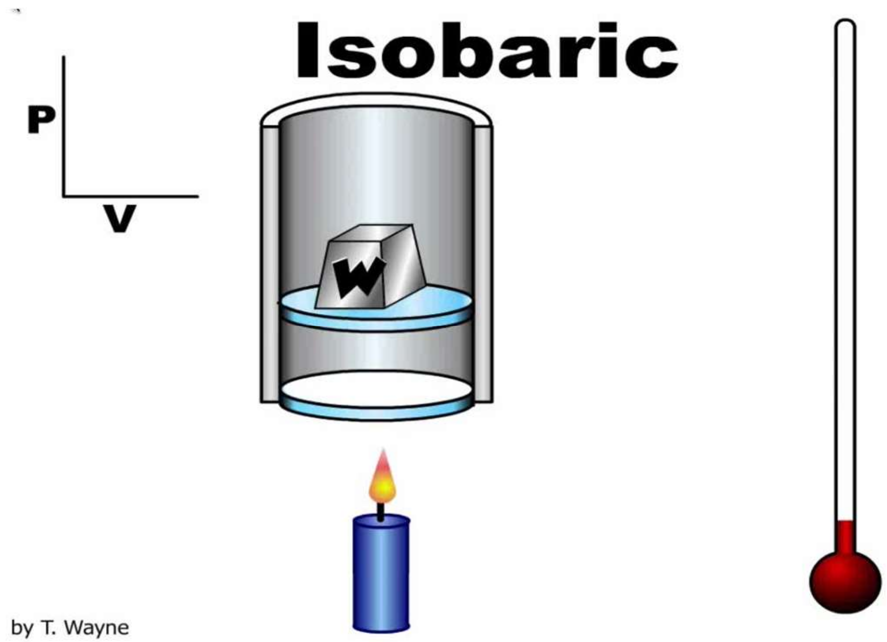

**Figure 3.3** The purple area represents the work for this isothermal change [3]

[3] https://en.wikipedia.org/wiki/Isothermal_process#/media/File:Isothermal_process.svg

# 3.1 Configuration work

**Video clips: isothermal and isobaric animation** [4], [5]




[4]https://www.youtube.com/watch?v=7doEaDtJtFs
[5]https://www.youtube.com/watch?v=CEBoFGkNaFQ

**Work is not a property of the system**:

W is not a state variable. Since $\int PdV$ is the area under the curve, different results are obtained for paths 1 and 2.

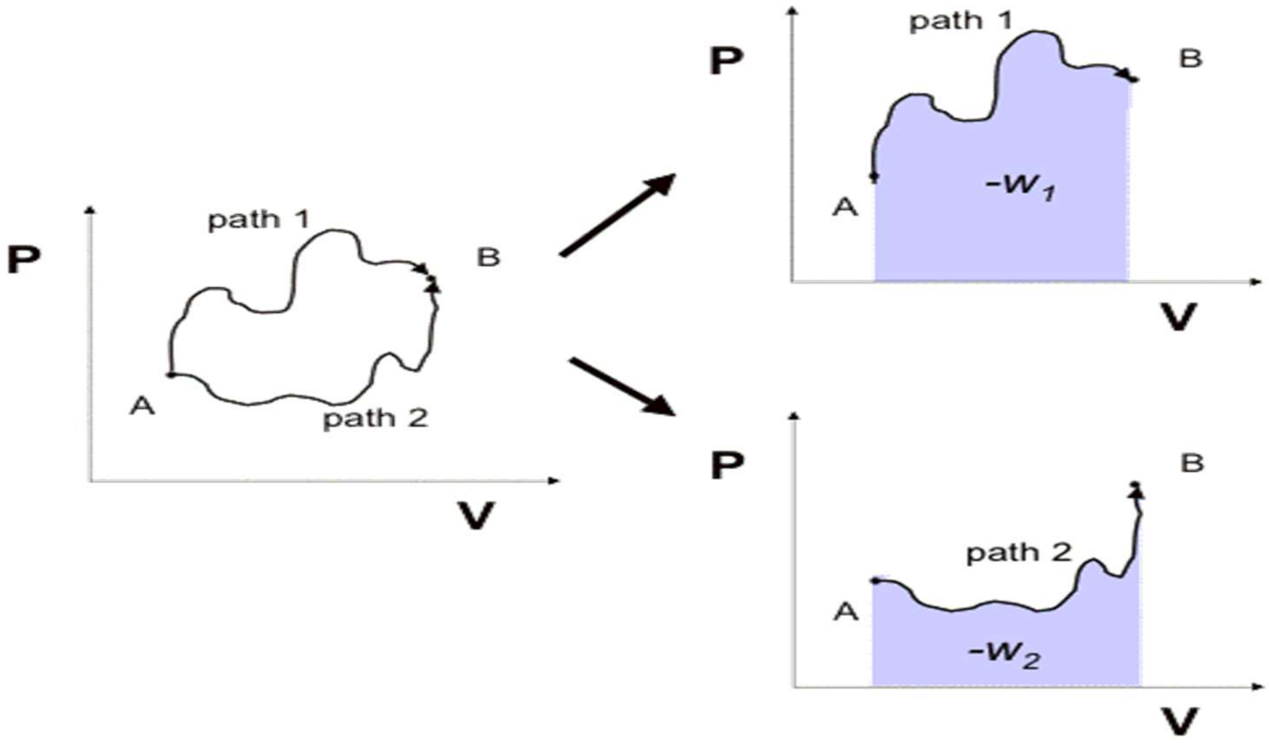


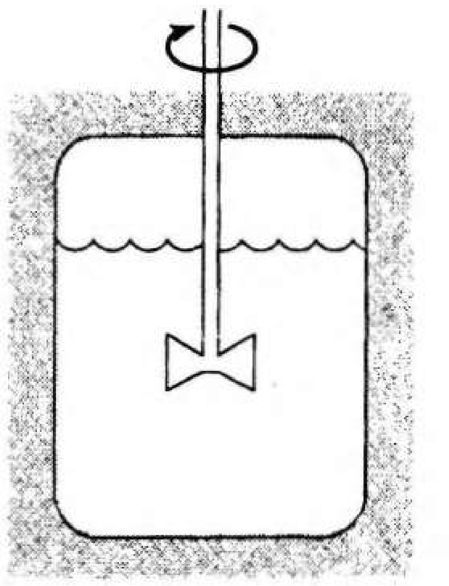

**Figure 3.4** Work is path-dependent: the area under path 1 is different from the area under path 2 [6]

[6] http://web.mit.edu/djirvine/www/3.012/3.012%20lectures/3.012%20lect03/3.012%20lect03.htm

# 3.2 Dissipative work

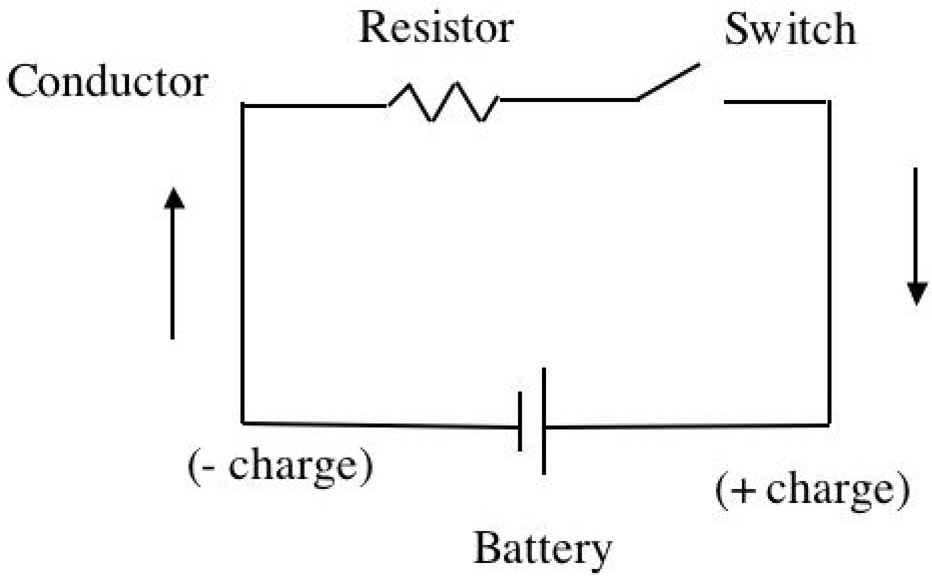
**Dissipative work is work done in an irreversible process**

A example of dissipative work is the work needed to maintain an electric current *I* in a resistor of resistance *R*



$$\delta W = -\tau d\theta$$

**Figure 3.5** Stirring work. A stirrer is immersed in a fluid and an external torque is applied.




$$\delta W = -I^2 R dt$$

**Figure 3.6** Electrical work. A current is passed through a resistor [7]

[7]http://educade.org/system/pictures/attachments/516f/3650/b381/5809/d300/0005/original/Basic_Electric_Board.png

# 3.3 Adiabatic work and internal energy

The total work done in all adiabatic processes between any two equilibrium states is **independent of the path**.

The work done on the system (with no heat flow) results in an increase in its **internal energy**

$$W_{ad} = \int_a^b \delta W_{ad}$$

$$dU = -\delta W_{ad}$$

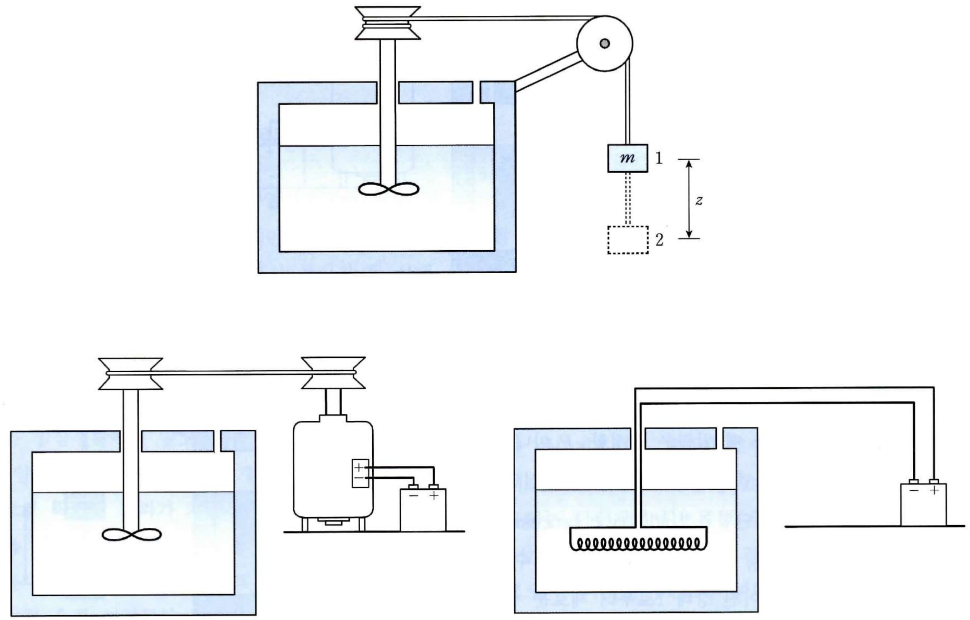



**Figure 3.7** Three different adiabatic processes from state a to state b

# 3.4 Heat

Under adiabatic conditions, for which $dU = -\delta W_{ad}$. If the conditions are not so specialized in general. Instead we may write the equation

$$dU = \delta Q - \delta W$$

Heat flow into the system is equal to the total work done by the system minus the adiabatic work done

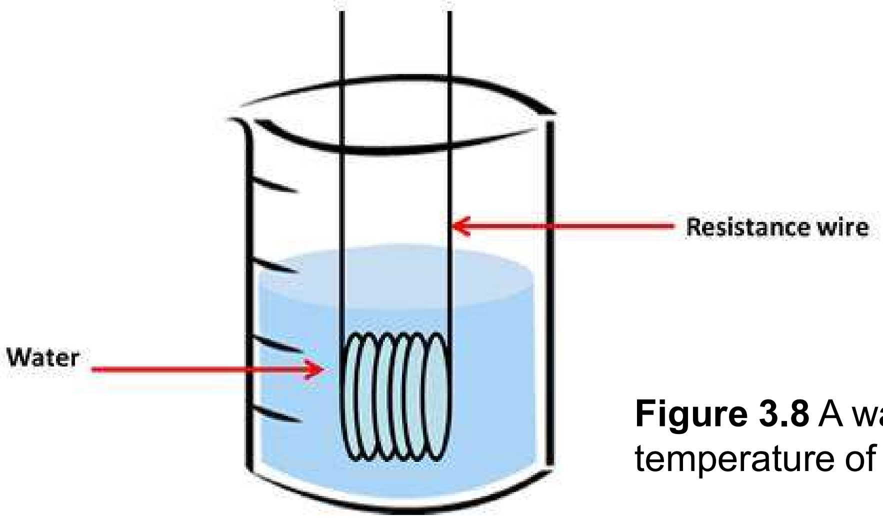



**Figure 3.8** A way of raising the temperature of water by electrical work [8]

[8]http://physics.taskermilward.org.uk/KS4/core/heat_transfer/specific_heat_capacity/NichromeWireInWater.jpg

# 3.4 Heat

In words, the first law states that

The heat supplied is equal to the increase in internal energy of the system plus the work done by the system. Energy is conserved if heat is taken into account

Note that heat is not a property (state variable) of the system; only the internal energy is.
It can be shown that the quantity $\delta Q$ exhibits the properties that are commonly associated with heat.

These properties are summarized as follows.
1. The addition of heat to a body changes its state.
2. Heat may be conveyed from one body to another by conduction, convection, or radiation.
3. In a calorimetric experiment by the method of mixtures, heat is conserved, if the experimental bodies are adiabatically enclosed.

# 3.4 Heat

**Modes of heat energy transfer: Conduction, Convection, Radiation**

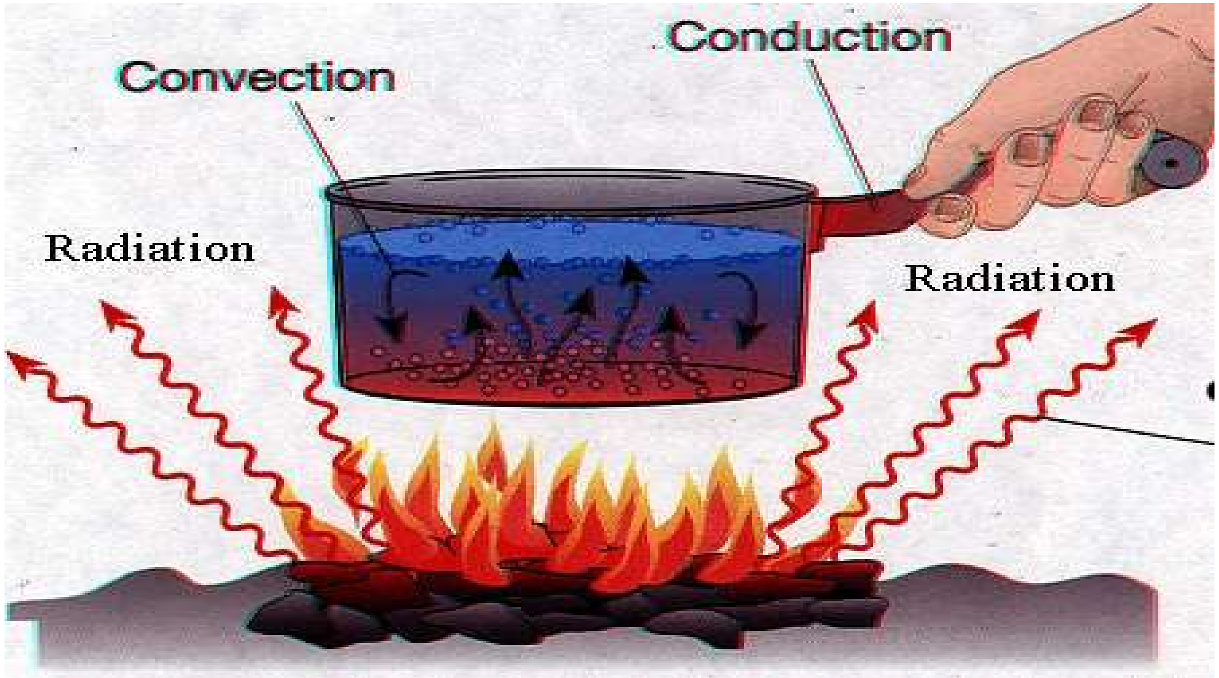



**Figure 3.9** Modes of heat energy transfer [9]

[9] https://2.bp.blogspot.com/-VEB7KL43kEc/V3FURhV8aYI/AAAAAAAABS0/lpR2nr6WP5423kiDgdY2_H7NkC6pKmS6gCLcB/s1600/heattransfer.jpg

# 3.7 Summary of the first law

1. Energy is conserved. Heat is energy transferred to a system causing a change in its internal energy minus any work done in the process.

2. The quantity U is a generalized store of energy possessed by a thermodynamic system which can be changed by adding or subtracting energy in any form.

3. The internal energy U is a state variable: it is extensive.

4. The first law can be expressed in differential form as

$$\delta Q = dU + \delta W$$

5. For a reversible process, $\delta W$ is solely configuration ("PdV") work, so that

$$\delta Q = dU + PdV$$