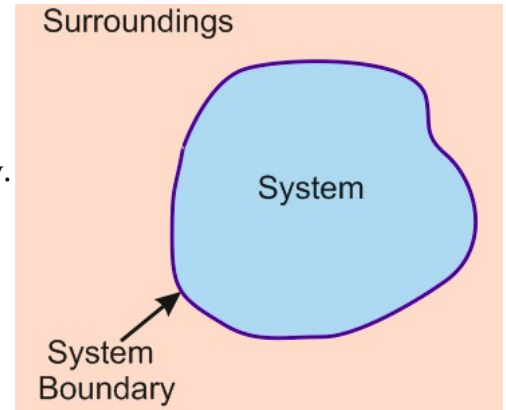


# Heat and 1<sup>st</sup> Law of Thermodynamics

## Thermodynamic System

A *system* is a region of interest with a well defined *boundary*. The region outside the boundary is called the *surrounding* or *environment*. The system can contain any sort of matter and radiation, same for the surrounding. The boundary can be a realistic physical quantity or it can be just defined geometrically.



## Examples

System: the classroom (with all the students and equipment in it). Boundary: the walls, doors and windows of the classroom. Surrounding: everything outside the classroom.

System: the physics Dept (with all the classrooms and hallways and people in it). Boundary: the outside walls and roof. Surrounding: everything outside the building.

System: a *He* balloon in a classroom. Boundary: the balloon itself made of rubber. Surrounding: everything outside of the balloon.

From these examples you can see how a system can contain subsystems. Defining a system means to define its boundary.

A thermodynamic system is described by its macroscopic *state variables* (or *state functions*) like the temperature, volume, pressure, internal energy, entropy (defined in the following paragraphs), etc. A state variable depends only on the actual state of the system and not on how the system has reached that particular state, i.e. is path independent.

## Internal Energy

The internal energy  $U$  of a thermodynamic system is the total energy of the system. It is the sum of all forms of energy within its boundary. In the case of a real gas depends on several factors as

- the kinetic energy of all molecules.
- the potential energy of bounding energies (electromagnetic)
- internal friction
- mass
- (others factors)

## Internal Energy of Ideal Gas

The internal energy  $U$  of an ideal gas is simply given by the total kinetic energy of all its  $N$  particles.

$$U = N \frac{1}{2} m \overline{v^2} = \frac{3}{2} N k_B T$$

using  $N k_B = N \frac{R}{N_A} = \frac{N}{N_A} R = n R$  then

$$U = \frac{3}{2} nRT$$

### *Example*

What is the internal energy of one mole of nitrogen at 20°C?

$$U = N \frac{3}{2} k_B T = \frac{3}{2} nRT = \frac{3}{2} (1 \text{ mole})(8.31 \text{ J/mole} \cdot \text{K})(293 \text{ K}) = 3.65 \times 10^3 \text{ J}$$

## **Heat**

The *heat*  $Q$  is the energy transferred between a system and its environment.

When heat is transferred from one system to another, then the internal energy of one system will increase and the internal energy of the other system will decrease.

### Units of heat

A calorie is the energy required to raise the temperature of 1 g of water from 14.5°C to 15.5°C.

$$1 \text{ cal} = 4.186 \text{ J}$$

One *food calorie* = 1 Calorie = 1 kCal = 1000 calories. (Capital  $C$  for food calorie).

### *Example*

If you consume 2000 Calories of food in a day, then the energy you are consuming is

$$2000 \text{ Calories} \times 1000 \text{ cal/Cal} \times 4.186 \text{ J/cal} = 8.37 \times 10^6 \text{ J}$$

## Heat Capacity and Specific heat

The *heat capacity*  $C$  of a substance is the proportionality constant which gives the amount of heat  $Q$  required to raise the temperature of that substance by  $\Delta T$

$$Q = C \Delta T$$

In the SI system, the units of  $C$  are  $J/^\circ\text{C}$ .  $C$  is also often expressed in  $\text{cal}/^\circ\text{C}$ .

Whereas the heat capacity  $C$  depends on the amount of the material, the *specific heat*  $c$  is an intrinsic property of the material independent of the amount.

Specific heat is defined as

$$c = \frac{Q}{m\Delta T} \quad \text{or} \quad c = \frac{C}{m}$$

Units are  $\text{J}/\text{kg}\cdot^\circ\text{C}$  or  $\text{cal}/\text{g}\cdot^\circ\text{C}$ . By definition of the calorie, for water  $c = 1 \text{ cal}/\text{g}\cdot^\circ\text{C} = 4186 \text{ J}/\text{kg}\cdot^\circ\text{C}$ . Most substances have a smaller specific heat than that of water. From the above equation, the heat required to raise the temperature of a substance of mass  $m$  by  $\Delta T$  is

$$Q = mc \Delta T$$

### Example

How much heat is required to raise the temperature of 100 g of water from  $20^\circ\text{C}$  to  $50^\circ\text{C}$ ?

$$Q = (0.1 \text{ kg})(4186 \text{ J}/\text{kg}\cdot^\circ\text{C})(30^\circ\text{C}) = 12.6 \times 10^3 \text{ J}$$

## Latent heat

Latent heat refers to the energy required to cause the *phase change* of a substance without changing the temperature. Examples of phase change of a substance are:

Phase change	description	Latent heat
Melting	solid to liquid	fusion
Freezing	liquid to solid	fusion
Vaporization	liquid to gas	vaporization
Condensation	gas to liquid	vaporization

There are two latent heats for a given substance:

$L_F$  (*latent heat of fusion*): energy per unit mass to melt a solid or freeze a liquid.

$L_V$  (*latent heat of vaporization*): energy per unit mass to boil a liquid or condense a gas.

$$L_F = \frac{Q}{m} \quad L_V = \frac{Q}{m} \quad [\text{cal/g, or J/kg}]$$

The equation is the same but the numeric values are not. For ice melting into water  $L_F = 80 \text{ cal/g}$  and for water transforming into vapor  $L_V = 540 \text{ cal/g}$ . This implies that for a fixed mass of water, more energy is required to vaporize it than to turn it into ice.

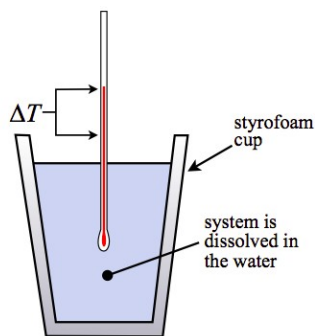
### Example

How much energy is required to convert 200 g of ice that is initially at  $0^\circ\text{C}$  to steam?

$$\begin{aligned} Q &= Q(\text{to melt ice}) + Q(\text{to warm water}) + Q(\text{to boil water}) \\ &= mL_f + mc(100^\circ\text{C} - 0^\circ\text{C}) + mL_v \\ &= (200\text{ g})(80\text{ cal/g}) + (200\text{ g})(1\text{ cal/g}\cdot^\circ\text{C})(100^\circ\text{C}) + (200\text{ g})(540\text{ cal/g}) \\ &= 16000\text{ cal} + 20000\text{ cal} + 108000\text{ cal} = 144000\text{ cal} \end{aligned}$$

### Calorimetry

A *calorimeter* is a device in which the exchange of heats between various materials is studied. A simple calorimeter is a container with a thermometer as for example a Styrofoam cup.



If the calorimeter is perfectly insulated (no heat is exchanged with the surrounding) we have

$$\sum_i Q_i = 0$$

where  $Q_i$  is either the specific heat  $Q = mc\Delta T$ , or latent heat  $Q = mL$

In the case of specific heat  $\Delta T = (T_f - T_i)$  is the difference between the final and initial temperatures, which can be either positive or negative. It follows the  $Q_i$  are positive for materials absorbing heat and are negative for materials losing heat. Similarly for the latent heat  $Q_i$  which is positive if heat is absorbed and negative when heat is removed

### Example

A 360 g piece of steel is dropped into 425 mL of water at 24 °C. The final temperature of water is measured to be 42.7 °C.  $c_w = 4.184 \text{ J/g}^\circ\text{C}$  and  $c_{steel} = 0.499 \text{ J/g}^\circ\text{C}$ . What is the initial temperature of steel?

Since water temperature increases, water absorbs heat from steel.

$$Q_{water} + Q_{steel} = 0$$

where  $Q_{water}$  is positive and  $Q_{steel}$  is negative,

$$c_w m_w (T_f - T_{i,w}) + c_{steel} m_{steel} (T_f - T_{i,steel}) = 0$$

solving for the initial temperature of steel

$$T_{i,steel} = \frac{(4.184 \text{ J/g}^\circ\text{C})(425 \text{ g})(42.7^\circ\text{C} - 24.0^\circ\text{C})}{(0.449 \text{ J/g}^\circ\text{C})(360 \text{ g})} + 42.7^\circ\text{C} = 248^\circ\text{C}$$

### Example

A cube of ice of mass  $m_i = 0.3 \text{ kg}$  at temperature of  $-20^\circ\text{C}$  is added to  $m_w = 8.2 \text{ L}$  of water at temperature  $12^\circ\text{C}$ . Write the equation to find the final equilibrium temperature  $T_e$  of ice and water.

$$Q_I + Q_{FW} + Q_{IW} + Q_W = 0$$

$Q_I$  is the heat necessary to bring  $m_i$  to  $T = 0^\circ\text{C}$  (positive).

$Q_F$  is the heat absorbed by  $m_i$  to melt into water (positive).

$Q_{IW}$  is the heat absorbed by the ice melted-into water to  $T_e$  (positive).

$Q_W$  is the heat lost by the initial amount of water  $m_w$  (negative).

Combining the terms

$$m_i c_i (0^\circ\text{C} - (-20^\circ\text{C})) + m_i L_f + m_i c_w (T_e - 0^\circ\text{C}) + m_w c_w (T_e - 12^\circ\text{C}) = 0$$

which can be solved for  $T_e$ .

## Heat transfer

There are different mechanisms by which heat is transferred between physical systems.

### Conduction

Two objects with different temperatures are in physical contact. The object at higher temperature has molecules with greater vibration speed. The collisions between the molecules of the two objects increase the speed of vibration of the object at lower temperature. This results in heat being transferred to the object at lower temperature.

### Radiation

All objects emit heat in the form of electromagnetic radiation. The rate depends on the temperature of the object and the surface area. It also depends on the nature of the surface. The rate of energy transfer (power) is given by Stefan's law:

$$P = \sigma A e T^4$$

$\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$  is a universal constant.

$A$  = surface area of object.

$T$  = absolute temperature (Kelvin).

$e$  = emissivity. This depends on the nature of the surface and how well it radiates.  $e$  is unit-less and its numerical value has range  $0 < e < 1$ .

An object that is a good absorber is also a good radiator. A perfect radiator (or absorber) is called a 'black-body' and has emissivity  $e = 1$ .

An object will also absorb energy by radiation from its surroundings. If the surrounding temperature is  $T_0$ , then the net energy radiated by the object with temperature  $T$  is

$$P = \sigma A e (T^4 - T_0^4)$$

### Convection

It's the transfer of heat from one system to another because of the movement of the fluid present between them. For example if you place your hand (system 1) above a stove (system 2) without touching it, your hand gets hot: the heat reaches your hand as it travels through the air (fluid) because of the motion of the air molecules.

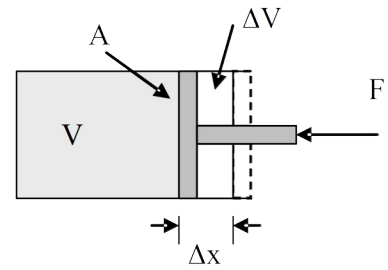
## Work and heat in thermodynamics processes

A gas in a cylinder can be compressed by pushing on a piston, as shown to the right. The work *done on* the gas during an infinitesimal volume change is given by

$$dW = Fdx = P Adx = P dV$$

The net work done during a finite volume change is

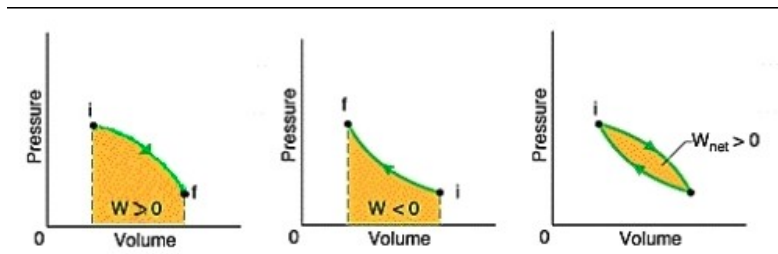
$$W = \int_{V_i}^{V_f} P dV$$



If the gas is compressed, then  $\Delta V$  is negative and the work *done on* the gas is negative.

If the gas expands, then  $\Delta V$  is positive and the work is *done by* the gas is positive.

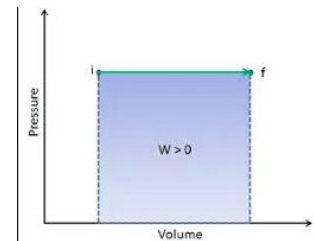
The work done on the substance is the area under the  $P$  versus  $V$  curve



### Isobaric process

In an *isobaric* process the pressure is constant. Thus, the work done is

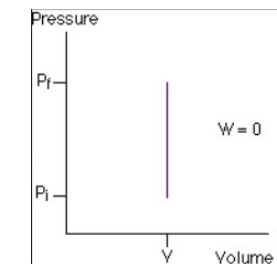
$$W = P\Delta V = P(V_f - V_i) .$$



### Isovolumeric process

In an isovolumeric (isochoric) process the volume is constant. Thus,

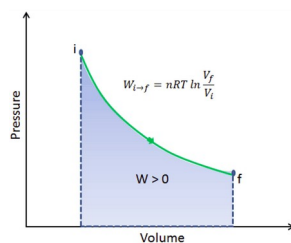
$$W = P\Delta V = 0 .$$



### Isothermal process

The work done during an isothermal (constant temperature) process is

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right) .$$



## First Law of Thermodynamics

The first law of thermodynamics relates the change of the internal energy of a system to the heat absorbed/released and the work done on/by a system. It is essentially a statement of conservation of energy.

$$\Delta U = U_f - U_i = Q_{NET} - W_{NET}$$

where

$$Q_{NET} = \sum_i Q_i$$
$$W_{NET} = \sum_i W_i$$

$Q_i$  positive if heat is *absorbed* and is negative if heat is *lost* by the system.

$W_i$  positive if *done by* the system and negative if *done on* the system.

Or in term of infinitesimals

$$dU = dQ - dW$$

Note: some textbooks (see chemistry or engineering) prefer the opposite signs convention for the work, resulting in the first law of thermodynamics written as  $dU = dQ + dW$ .

### Example

A system absorbs 40 J of heat and releases in the surrounding 25 J of heat. It also does 10 J of work and a work of 4 j is done on the system.

Calculate the net heat exchanged and the new work.

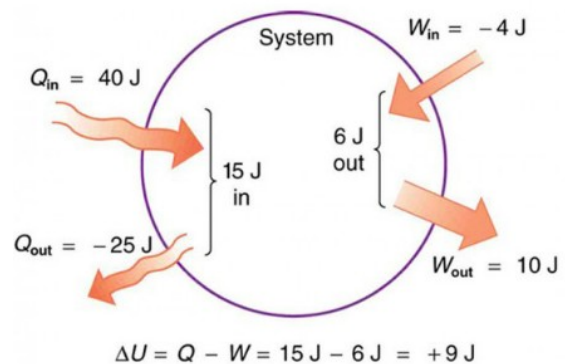
$$Q_{NET} = Q_{in} + Q_{out} = 40 J - 25 J = 15 J$$

$$W_{NET} = W_{in} + W_{out} = -4 J + 10 J = 6 J$$

Calculate the change in the internal energy

$$\Delta U = 15 J - 6 J = +9 J$$

The system energy increases by 9 J.



### Adiabatic process

A process for which no heat flows into or out of a system:  $Q_{NET} = 0$ .



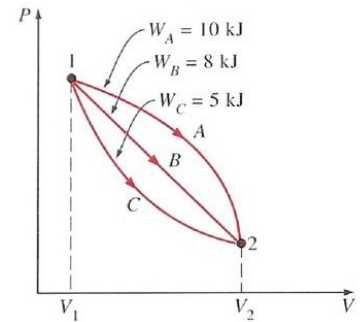
For an adiabatic process,  $\Delta U = -W$ . Thus, in an adiabatic expansion the internal energy decreases and in an adiabatic compression the internal energy increases.

For an ideal gas, the internal energy just depends on  $T$ . Thus, for a ideal gas undergoing an *isothermal* process, we have  $\Delta U = 0$  and  $Q = W$ .

While  $Q_i$  and  $W_i$  depend on the path  $\Delta U$  does not.

The  $W_i$  are path dependent

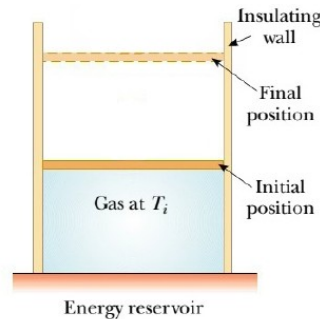
The figure to the right shows three thermodynamic processes which take a gas from the initial  $(P_1, V_1)$  to the final  $(P_2, V_2)$ . Since the three curves have the same  $(P_1, V_1)$  and  $(P_2, V_2)$  the change of internal energy is equal for each path. The work calculated (the area under the curve) is *path dependent* since it depend on the curve.



The  $Q_i$  are path dependent

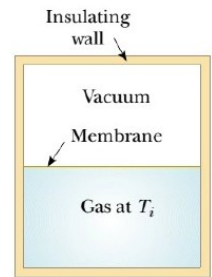
The figure below displays two processes of a gas from the same initial states  $(P_1, V_1)$  to the same final states  $(P_2, V_2)$ . In both cases the change of internal energy is the same. The heat is *path dependent* since it depends on the transformation. For example the following two transformations require a different amount of heat.

On the left: heat is added to the gas which expands the piston. Temperature is maintained at constant temperature by the energy reservoir



$$Q > 0$$

On the right: The membrane is broken, the gas expands freely at constant temperature. The process as adiabatic.



$$Q = 0$$

*Example*

A gas undergoes two processes from the same initial state  $(P_1, V_1)$  to the same final states  $(P_2, V_2)$ , even if net work and net heat are different, the change of internal energy must be the same

$$\Delta U_1 = Q_1 - W_1 = 30J - 12J = 18J$$

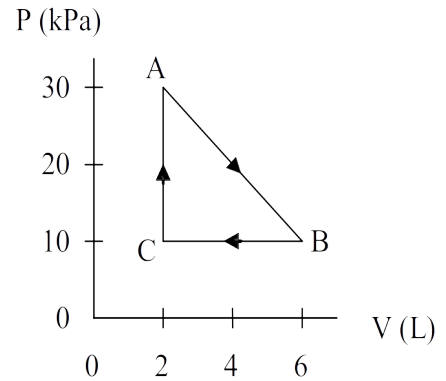
$$\Delta U_2 = Q_2 - W_2 = 23J - 5J = 18J$$

## Thermodynamics cycle

If a system goes through a cycle and returns to its original state, then  $\Delta U = 0$  and  $Q_{NET} = W_{NET}$ .  
*Example (cyclic process)*

An ideal gas goes through the cyclic process  $A \rightarrow B \rightarrow C \rightarrow A$  as shown to the right. The temperature of the gas at A is 600K. Calculate the work done on the gas, the heat absorbed by the gas, and the change in internal energy for each process and for the total cycle.

From the ideal gas equation,  $PV = nRT$ , we can calculate that  $T_B = 600\text{K}$  and  $T_C = 200\text{K}$ . Since the gas is a ideal, then we have  $U = 3/2 nRT$ . Also  $1 \text{ liter} = 10^{-3} \text{ m}^3$ .



$A \rightarrow B$ :

Since the gas is expanding, then the work done by the gas is positive

$$W_{AB} = \text{area under } PV \text{ curve} = \frac{1}{2} (2 \times 10^4 \text{ Pa})(4 \times 10^{-3} \text{ m}^3) + (10^4 \text{ Pa})(4 \times 10^{-3} \text{ m}^3) = 80 \text{ J}$$

$$\Delta U_{AB} = \frac{3}{2} nR\Delta T_{AB} = 0 \quad (T_A = T_B)$$

From the 1<sup>st</sup> law,  $Q_{AB} = \Delta U_{AB} + W_{AB} = 0 + 80 \text{ J} = 80 \text{ J}$  (heat is *absorbed*)

$B \rightarrow C$ :

Since the gas is being compressed, work is done *on* the gas. The change in volume  $\Delta V$  is negative, and so the work given by the area under  $PV$  curve is

$$W_{BC} = P\Delta V = (1 \times 10^4 \text{ Pa})(-4 \times 10^{-3} \text{ m}^3) = -40 \text{ J}$$

$$\begin{aligned} \Delta U_{BC} &= \frac{3}{2} nR\Delta T_{BC} = \frac{3}{2} nR(T_C - T_B) = \frac{3}{2} P_C V_C - \frac{3}{2} P_B V_B \\ &= \frac{3}{2} (1 \times 10^4 \text{ Pa})(2 - 6) \times 10^{-3} \text{ m}^3 = -60 \text{ J} \end{aligned}$$

$$Q_{BC} = \Delta U_{BC} + W_{BC} = -60 \text{ J} + (-40) \text{ J} = -100 \text{ J} \quad (\text{heat is } \textit{released})$$

$C \rightarrow A$ :

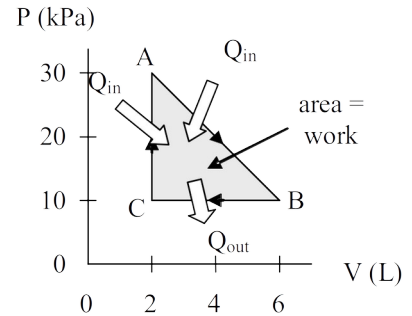
This is an isovolumeric process, so  $W_{CA} = 0$ .

$$\begin{aligned} \Delta U_{CA} &= \frac{3}{2} nR\Delta T_{CA} = \frac{3}{2} nR(T_A - T_C) = \frac{3}{2} P_A V_A - \frac{3}{2} P_C V_C \\ &= \frac{3}{2} (3 \times 10^4 \text{ Pa} - 1 \times 10^4 \text{ Pa})(2 \times 10^{-3} \text{ m}^3) = 60 \text{ J} \end{aligned}$$

$$Q_{CA} = \Delta U_{CA} + W_{CA} = 60 \text{ J}$$

Summary results:  $\Delta U = Q_{NET} - W_{NET} = 0$

	$A \rightarrow B$	$B \rightarrow C$	$C \rightarrow A$	$NET$
$W (J)$	+80	-40	0	40
$Q (J)$	80	-100	60	40
$\Delta U (J)$	0	-60	60	0



Note that the net work done in the cycle is the enclosed area. The positive value means that the gas does work on its environment during the cycle. Since the gas returns to its original state, the net change in internal energy is zero. The net heat absorbed is equal to the net work done by the gas. Heat is absorbed during the processes  $A \rightarrow B$  and  $C \rightarrow A$  and rejected during the process  $B \rightarrow C$ .

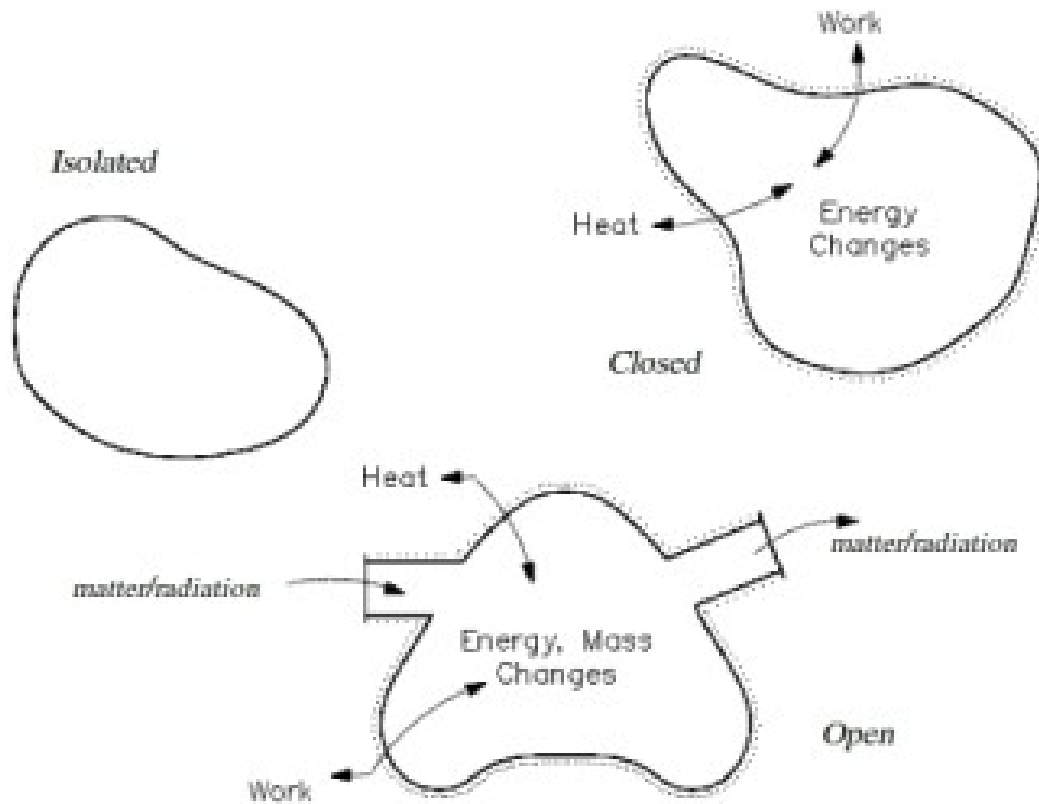
For the above cyclic process, the efficiency (see next chapter) can also be calculated:

$$Q_{in} = Q_{AB} + Q_{CA} = 80J + 60J = 140J$$

$$W(\text{net}) = 40J \text{ (done by the gas)}$$

$$e = \frac{W}{Q_{in}} = \frac{40J}{140J} = 0.286 = 28.6\%$$

## Classification of Thermodynamic Systems



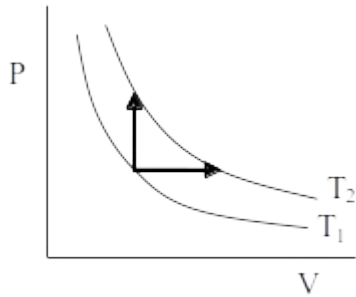
*Isolated* system: not material or radiation\* is exchanged with the surrounding. No work is done by the system or on the system and no heat enters or leave the system. Since  $Q = 0$  and  $W = 0$  then  $\Delta U = 0$  and the internal energy remains constant.

*Closed* system: not material or radiation is exchanged with the surrounding. Work can be done on the system or is done by the system, heat can enters or leave the system.

*Open* system: material or radiation can be exchanged with the surrounding. Work can be done on or is done by the system, heat can enters or leave the system.

\* this radiation is non-thermal. For isolated and closed the non-thermal radiation cannot be exchanged. If heat can be exchanged (closed and open system) then the thermal radiation can be exchanged with the enviromet.

## Specific Heat of an Ideal Gas



For gases, it is conventional to refer to the *molar* specific heat, which is the heat absorbed per *mole* per unit temperature rise. The molar specific heat, and thus the heat absorbed for a given temperature rise, depends on whether the pressure or the volume is held constant as the temperature increases.

$$Q = nc_v \Delta T \text{ (constant volume)}$$

$$Q = nc_p \Delta T \text{ (constant pressure)}$$

From the 1<sup>st</sup> law of thermodynamics, no work is done in a constant volume process. Thus,

$$\Delta U = Q \text{ (constant volume)}$$

For a *monatomic* gas the internal energy is the total translational kinetic energy. Then

$$U = E = \frac{3}{2} nRT, \Delta U = \frac{3}{2} nR \Delta T, \text{ and}$$

$$\frac{3}{2} nR \Delta T = nc_v \Delta T, \text{ or } c_v = \frac{3}{2} nR$$

For a constant pressure process,  $\Delta W = -P\Delta V = -nR\Delta T$ . So,

$$\Delta U = Q + W = Q - P\Delta V = Q - nR\Delta T,$$

or 
$$Q = \Delta U + nR\Delta T = \frac{3}{2} nR \Delta T + nR \Delta T = \frac{5}{2} nR \Delta T.$$

Then 
$$c_p = \frac{Q}{n\Delta T} = \frac{5}{2} nR \text{ and } c_p = c_v + R$$

During a constant volume process, no work is done so all the heat absorbed goes into increasing the internal energy and the temperature. During a constant pressure process, the gas expands and reduces the internal energy by doing work. Thus, more heat can be absorbed for a given temperature change.

## Specific Heat of Diatomic Gases

Previously, it was shown that

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

Since  $\frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{v_x^2} + \frac{1}{2}m\overline{v_y^2} + \frac{1}{2}m\overline{v_z^2}$ , this means that the average kinetic energy is  $\frac{1}{2}k_B T$  per term or per degree of freedom. A diatomic molecule is somewhat like two masses connected by a spring. The molecule can rotate about its center of mass and the atoms can vibrate back and forth along the line connecting them. Since the rotational inertia about an axis connecting the atoms is extremely small, there are two energy terms corresponding to rotation about the other two perpendicular axes (two degrees of freedom). The average kinetic energy of each of these terms is  $\frac{1}{2}k_B T$  and the total average rotational energy is  $k_B T$ . The vibrational energy of the mass-spring system consists of a kinetic energy and a potential energy term (also two degrees of freedom). Each of these terms has an average of  $\frac{1}{2}k_B T$  and the total average vibrational energy is  $k_B T$ .

Because of these additional degrees of freedom, the specific heat of a diatomic molecule is greater than that of a monatomic molecule ( $\frac{1}{2} R$  for each degree of freedom). The rotational and vibrational energies of a molecule are quantized. That is, only certain discrete energies are allowed. In order to excite these rotational and vibrational levels, the gas must be at a sufficiently high temperature. At low temperatures, only translational motions can occur. At higher temperatures, the molecular collisions are sufficient to excite the rotational levels. At still higher temperatures, the vibrational energy levels can be excited. Thus, the specific heat of a diatomic molecule will increase with temperature, giving evidence of the quantum nature of the energies.