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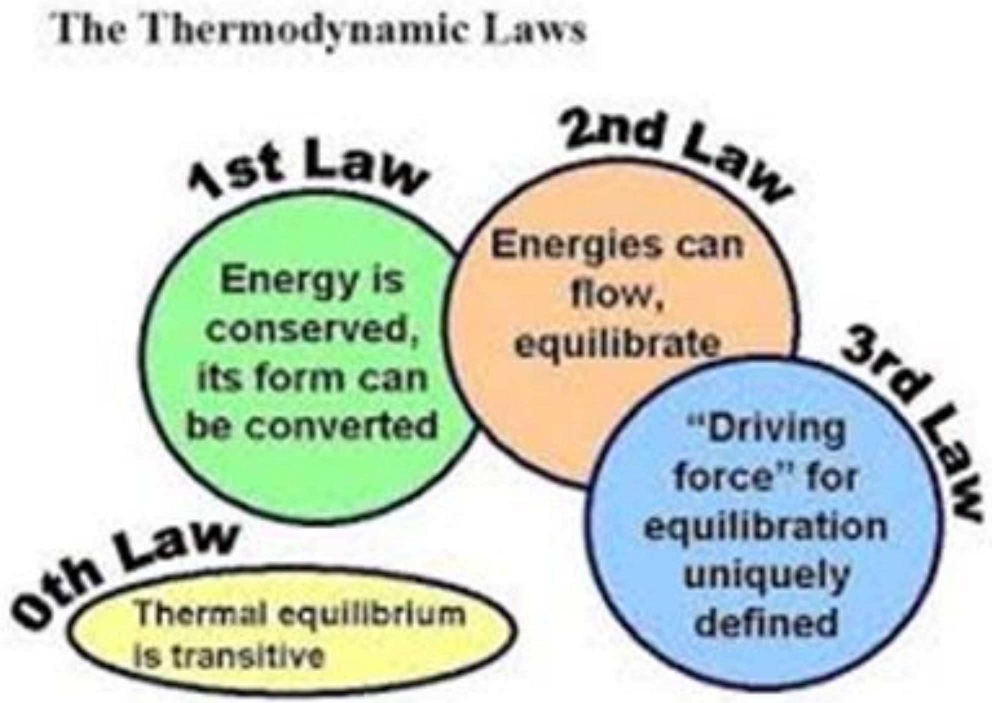
Thermodynamics
Part 2

Learning objectives

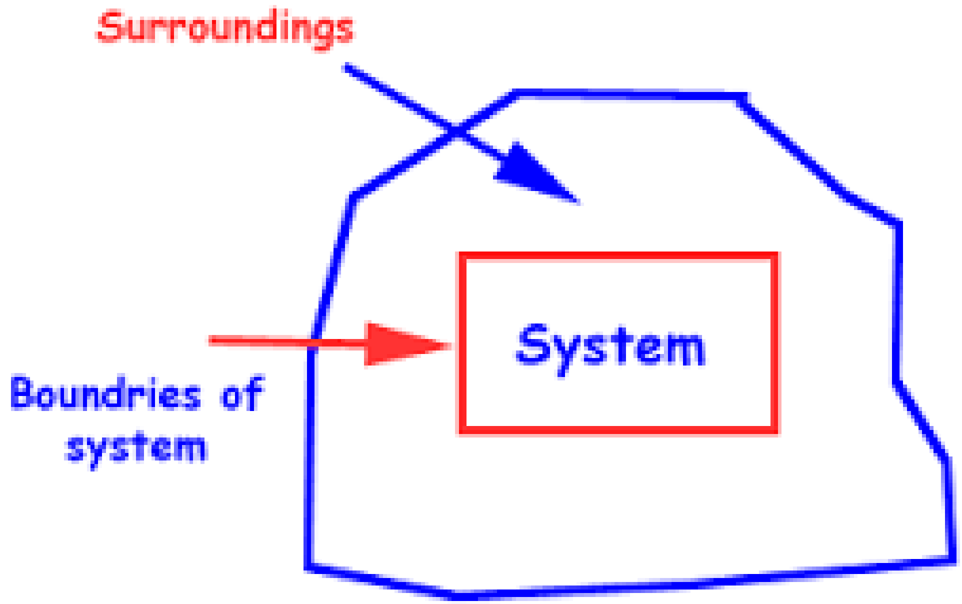
- Understand the theory of thermodynamics and its use for describing energy-related changes in reactions.
- Understand the first law of thermodynamics and its use..

,The word ‘**thermodynamics**’ means study of flow of heat .It was derived from the Greek words thermo (heat) ,dynamic (power or force) Thermodynamics deals with the quantitative relationships of interconversion of the various forms of energy, including mechanical, chemical, electric, and radiant energy .Thermodynamics is based on **three “laws”** or facts of experience that have never been proven in a direct way, in part due to the ideal conditions for which they were derived.



System, surroundings and boundary

- **System:** A quantity of matter or a region in space chosen for study.
- **Surroundings**: The mass or region outside the system
- **Boundary**: The real or imaginary surface that separates the system from its surroundings



The three types of systems that are frequently used to describe thermodynamic properties.

- **an open system** in which energy and matter can be exchanged with the surroundings.
- **closed systems**, in which there is **no** exchange of matter with the surroundings, that is, the system's mass is constant. However, energy can be transferred by work or heat through the closed system's boundaries
- last a system in which neither matter nor energy can be exchanged with the surroundings; this is called an **isolated system**

Physical properties of a system-

1.Intensive properties- e.g. – temperature, pressure, viscosity, surface tension, refractive index, specific heat, density, etc.

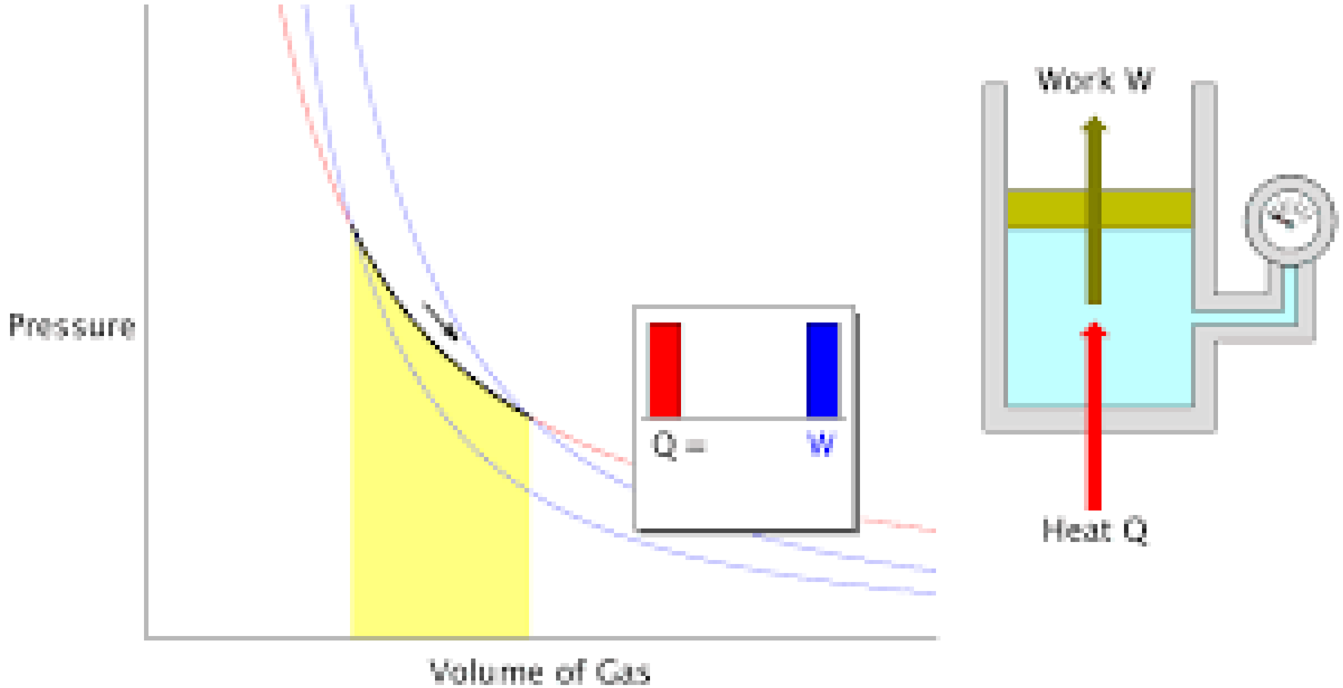
2.Extensive properties- e.g.- mass, volume, energy, heat capacity, entropy, Gibb’s free energy, ect.

Thermodynamic process

✓ -Isothermal process &Adiabatic process

✓ -Reversible process

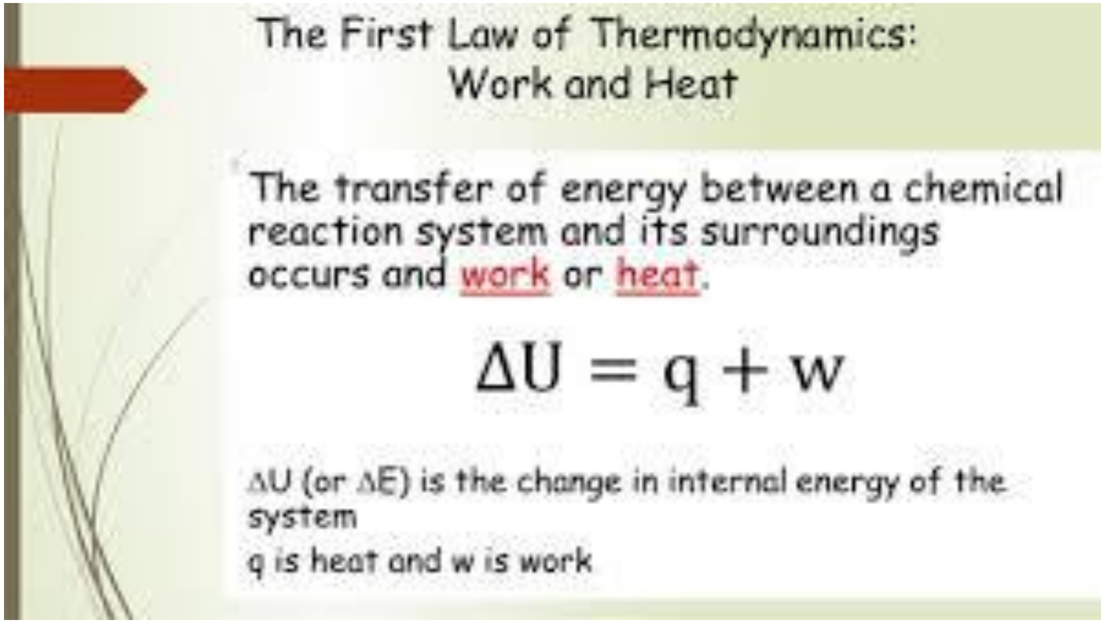
Work (W) and heat (Q) also have precise thermodynamic meanings
Work is a transfer of energy that can be used to change the height of a weight somewhere in the surroundings
and **heat** is a transfer of energy resulting from a temperature difference between the system and the surroundings. It is important to consider that both work and heat appear only at the system's boundaries where the energy is being transferred



Law's of thermodynamics

First law of thermodynamics or law of **conservation of energy-**.
"Energy can neither be created nor destroyed although it can be transformed from one form to another". OR "The total amount of the energy of the universe is a constant. Such As Mechanical Energy, Heat, Light, Chemical Energy, And Electrical Energy.

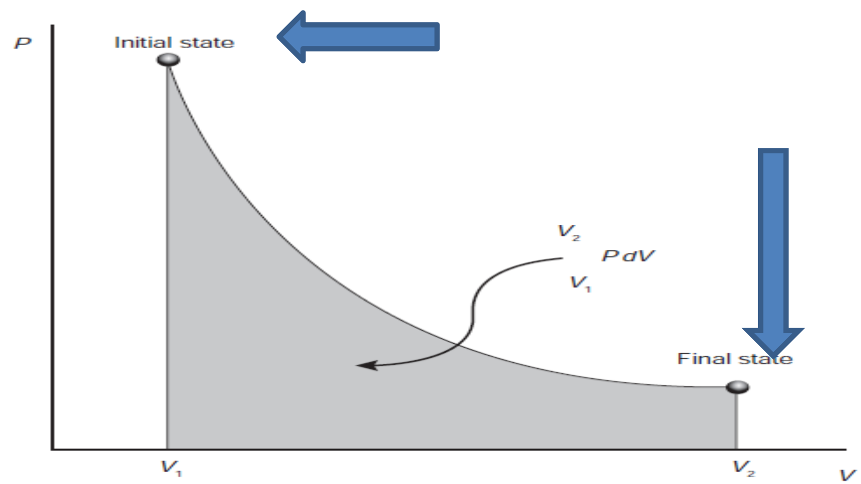
- **Energy** Is the ability to bring about change Or to do work.
- **Thermodynamics** Is The Study of energy



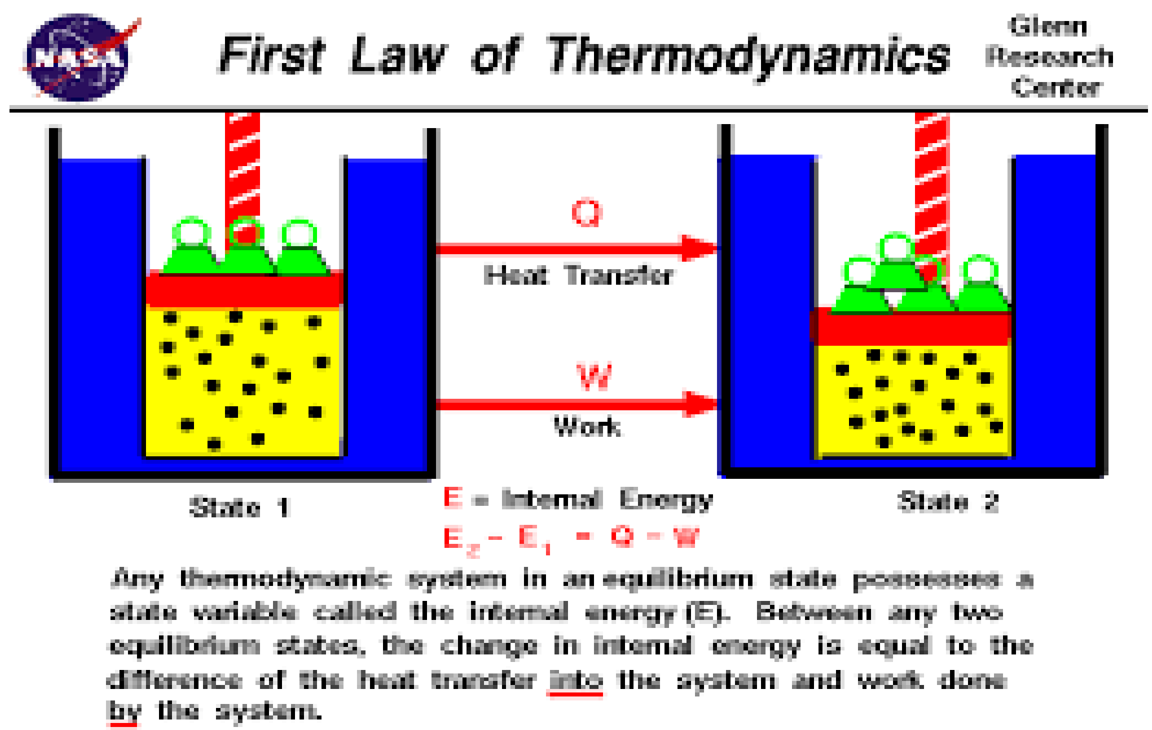
According to the **first law,** the effects of **Q** and **W** in a given system during a transformation from an **initial** thermodynamic state to a **final** thermodynamic state are related to an intrinsic property of the system called the **internal energy**, defined as

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

where **E2** is the internal energy of the system in its final state and **E1** 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 **E** is related to **Q** and **W** transferred between the system and its surroundings.

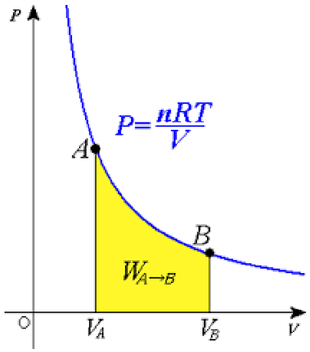


The term **thermodynamic state** means the condition in which the measurable properties of the system have a definite value. The state of 1 g of water at E1 may be specified by the conditions of, say, 1 atm pressure and 10°C, and the state E2 by the conditions of 5 atm and 150°C. Hence, the states of most interest to the chemist ordinarily are defined by specifying any two of the three variables, temperature (T), pressure (P), and volume (V); however, additional independent variables sometimes are needed to specify the state of the system.



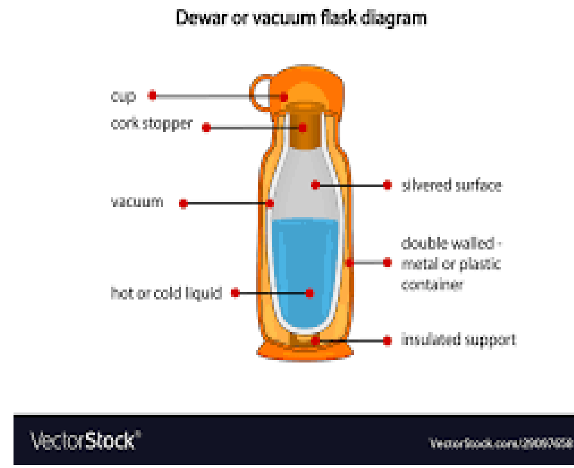
The ideal gas law and the van der Waals equation Thus, V, P, and T are variables that define a state, so they are called **state variables**. The variables of a thermodynamic state are independent of how the state has been reached.

A feature of the change of **internal energy**,Δ***E***, discovered by the first law is that it depends only on the **initial** and **final** thermodynamic states, that is, it is a variable of state; it is a thermodynamic property of the system. On the other hand, both ***Q*** and ***W*** depend on the manner in which the change is conducted. Hence, ***Q*** and ***W*** are not variables of state or thermodynamic properties; they are said to depend on the "path" of the transformation



Isothermal process & Adiabatic process

When the temperature is kept constant during a process, thereaction is said to be conducted **isothermally**. An isothermal reaction may be carried out by placing the system in a large constant-temperature bath so that heat is drawn from or returned to it without affecting the temperature significantly.

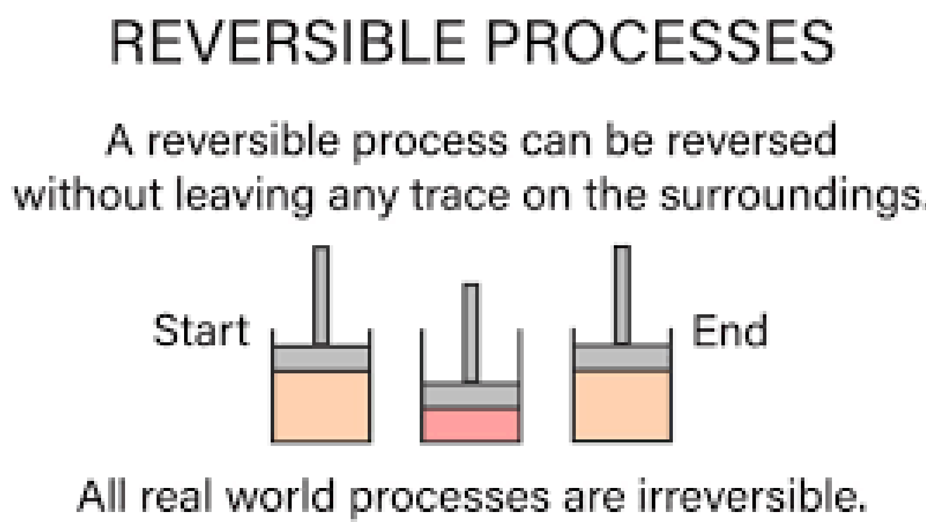


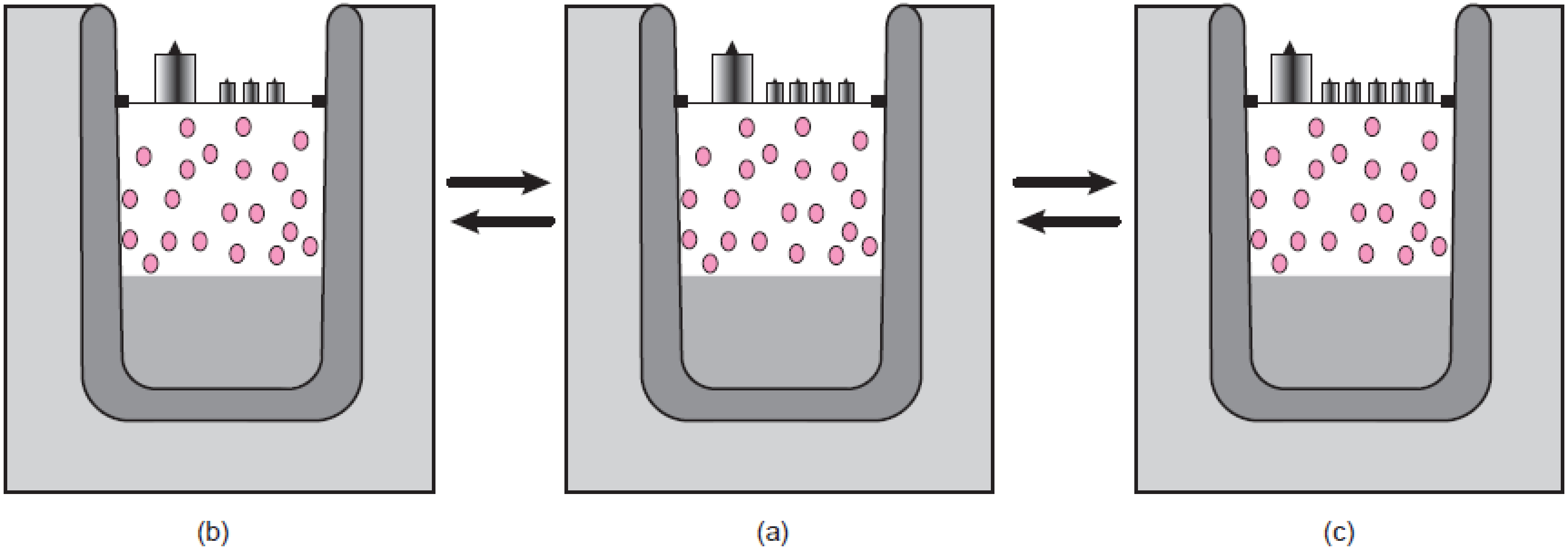
When heat is neither lost nor gained during a process, the reaction is said to occur ***adiabatically*.** A reaction carried on inside a sealed Dewar flask or “vacuum bottle” is adiabatic because the system is thermally insulated from its surroundings. In thermodynamic terms, it can be said that an adiabatic process is one in which $dq = 0$, and the first law under adiabatic conditions reduces to

$$dE = \text{đ}q + \text{đ}w \quad \Longrightarrow \quad \text{đ}w = dE$$

Reversible Processes

In simple words the process which can be revered back completely is called a reversible process. This means that the final properties of the system can be perfectly reversed back to the original properties. The process can be perfectly reversible only if the changes in the process are infinitesimally small. In practical situations it is not possible to trace these extremely small changes in extremely small time, hence the reversible process is also an ideal process. The changes which occur during reversible process are in equilibrium with each other.





reversible process: evaporation and condensation of water at 1 atm in a closed system.

(a) System at equilibrium with P ex=1 atm;

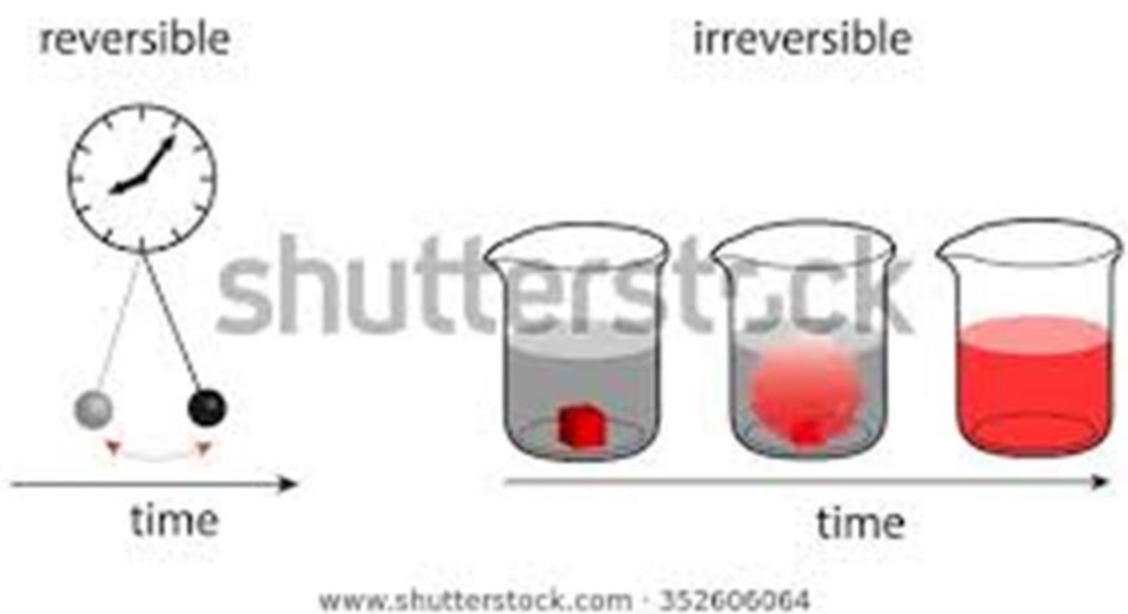
(b) expansion is infinitesimal;

(c) compression is infinitesimal.

water at its boiling point contained in a cylinder fitted with a weightless and frictionless piston **(a).** The apparatus is immersed in a constant-temperature bath maintained at the **same temperature** as the water in the cylinder. By definition, the vapor pressure of water at its boiling point is **equal to the atmospheric pressure**, by a set of weights equivalent to the atmospheric pressure of 1 atm; therefore, the temperature is 100◦C. The process is **an isothermal** one, that is, it is carried out at constant temperature. **Now**, if the external pressure is **decreased** slightly by removing one of the infinitesimally small weights (**b**), the volume of the system increases and the vapor pressure **falls** infinitesimally. Water then evaporates to maintain the vapor pressure constant at its original value, and heat is extracted from the bath to keep the temperature constant and bring about the vaporization. During this process, a heat exchange between the system and the temperature bath will occur.

if the external pressure is **increased** slightly by adding an infinitesimally small weight (**c**),the system is compressed and the vapor pressure also **rises** infinitesimally. Some of the water condenses to reestablish the equilibrium vapor pressure, and the liberated heat is absorbed by the constant-temperature bath.

If the pressure on the system is increased or decreased rapidly or if the temperature of the bath **cannot adjust** instantaneously to the change in the system, the system is not in the same thermodynamic state at each moment, and the process is irreversible.



the maximum work done in the expansion as well as the heat absorbed because

$$Q = E - W$$

E 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 because from **Boyle's law**, $V2/V1 = P1/P2$ at constant temperature. Therefore, equation can be

$$W_{max} = -nRT \ln \frac{V_2}{V_1}$$

$$W_{max} = -nRT \ln \frac{P_1}{P_2}$$

Example1

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 is about 9720 cal/mole. What are the values of the three first-law terms **Q**, **W,** and **ΔE**?

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

The work **W** performed against the constant atmospheric pressure is obtained by using equation

$$\mathbf{W = -nRT \ln(V2/V1).}$$

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:

$$PV = nRT$$ ideal gas law

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

It is now possible to obtain the work,

$$W = -(1 \text{ mole})(1.9872 \text{ cal/K mole})(398.15 \text{ K}) \ln(30.6/0.018)$$
$$W = -5883 \text{ cal}$$

The internal energy change ΔE is obtained from the first-law expression,

$$\Delta E = 9720 - 5883 = 3837 \text{ cal}$$

The remaining 3837 cal increases the **internal energy** of the system. This quantity of heat supplies **potential energy** to the vapor molecules, that is, it represents the work done against the non covalent forces of attraction

Example2

Calculate the work done when 1.0 mole water at 373K vaporizes against an atmospheric pressure of 1.0 atmosphere. Assume ideal gas behavior.

ANSWER

Volume of water **before** vaporization,

Volume of water $=\dfrac{18g}{1g/ml}$

V1=18ml

Volume of water **after** vapourization,

$$PV = nRT$$

$V_2=\dfrac{1.0\times 0.0821\times 373}{1.0}$=30.6 liter

V1 is negligible w.r.t. V2

w=−P ×ΔV=−(1.0)×(30.6)liter−atm

=−30.6

Example3

One mole of a gas occupying $3dm^3$ expands against constant external pressure of 1atm to a volume of 13 dm^3. The work done

A- -10atm dm^3

B- -20atm dm^3

C- -39atm dm^3

D- -48atm dm^3

ANSWER

W =−P×ΔV

=−1×(13−3)=−10atm dm^3

Example4

-Why is alcohol used in thermometers for measuring very low temperatures, whereas mercury is used for high temperatures?

❑ The Alcohol Thermometer

This was the first to be invented and it is still in use today. The column of alcohol is quite wide, coloured (usually red) to make it easy to read. It is often used for measuring air temperatures which range between - 20°C and +50°C. This is fine because alcohol freezes at - 80°C and boils at +78°C.

❑ The Mercury Thermometer

This is the most commonly used laboratory thermometer because temperatures above +78°C often need to be measured. Mercury freezes at - 39°C, so for very low temperatures it is not so useful. Mercury boils at + 357°C which is the upper limit of the thermometer

Example5

Calculate the work to vaporize 1.73 moles of water at 0.68 atm pressure and a temperature of 373K. Assume that the vapor behaves as an ideal gas.

ANSWER

Volume of water $= \frac{1.73 \text{ moles}}{18 Mwt} =$ 0.096ml

$$PV = nRT$$

V2$= \frac{1.73 \times 0.0821 \times 373}{0.68 atm} =$77.909 liter

W=P ΔV

W=77.9X0.68=52.97liter .atm


THANK
YOU