VIVEKANANDA COLLEGE, THAKURPUKUR

NAAC Accredited Grade—A

STUDY MATERIAL

Subject : GE2 - Chemistry

Course Title : Chemical Thermodynamics

Topic : Chemical Thermodynamics: Intensive and extensive variables; state and path functions; isolated, closed and open systems; zeroth law of thermodynamics; Concept of heat, work, internal energy and statement of first law; enthalpy, H; relation between heat capacities, calculations of q, w, ΔU and ΔH for reversible, irreversible and free expansion of gases.

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Introduction:

Thermodynamics is the branch of physics that deals with the relationships between heat and other forms of energy. In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter. Thermodynamics, then, is concerned with several properties of matter; foremost among these is heat. Heat is energy transferred between substances or systems due to a temperature difference between them, according to Energy Education. As a form of energy, heat is conserved, i.e., it cannot be created or destroyed. It can, however, be transferred from one place to another. Heat can also be converted to and from other forms of energy. For example, a steam turbine can convert heat to kinetic energy to run a generator that converts kinetic energy to electrical energy. A light bulb can convert this electrical energy to electromagnetic radiation (light), which, when absorbed by a surface, is converted back into heat.

Intensive and extensive variables:

An *intensive property* is a bulk property, meaning that it is a local physical property of a system that does not depend on the system size or the amount of material in the system. Examples of intensive properties include temperature, T; refractive index, n; density, ρ; and hardness of an object, η.

By contrast, *extensive properties* such as the mass, volume and entropy of systems are additive for sub-systems because they increase and decrease as they grow larger and smaller, respectively.[

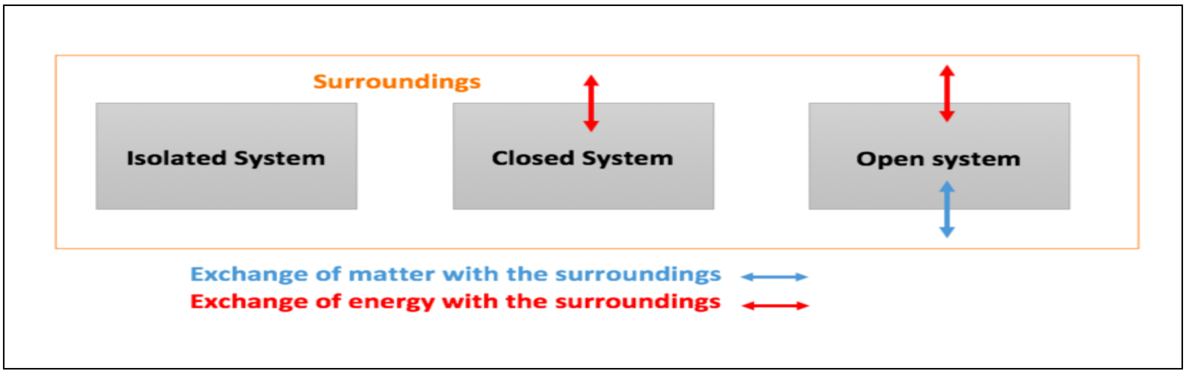
State functions and path functions:

A state function is a property describes a particular state, without depending on the path taken to reach this state. In contrast, functions whose value depends on the path taken to get between two states are called path functions.

To understand the difference between the two, think of two cities, A and B, that are 100km100km away from each other along a straight line. Roads are rarely built in long straight lines, we may have two roads linking A and B, with lengths 150km150km and 200km200km. So, while the displacement between the two towns is the same for each route (it is a state function), the distance you need to travel to get from A to B depends on which road you take (it is a path function).

Isolated, closed and open systems:

An open system is one that allows energy and matter exchange. If it does not, then it is either a closed system or an isolated system. If the system allows neither energy or matter transfer, then it is an isolated system. However, if it allows only energy transfer, it is a closed system.

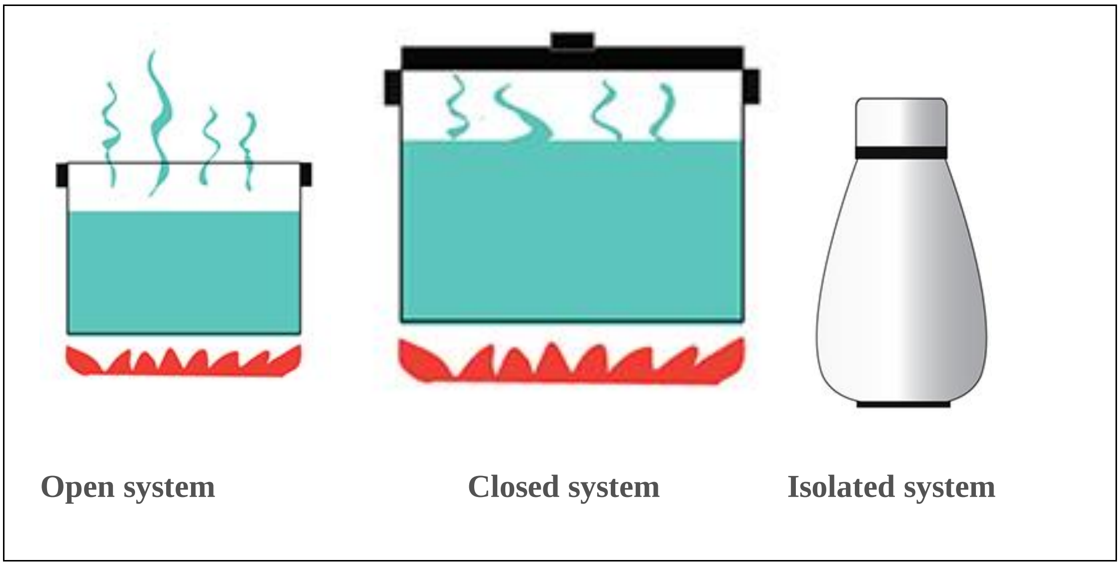


For example, boiling water without a lid - Heat escape into the air. At the same time steam (which is matter) also escapes into the air.

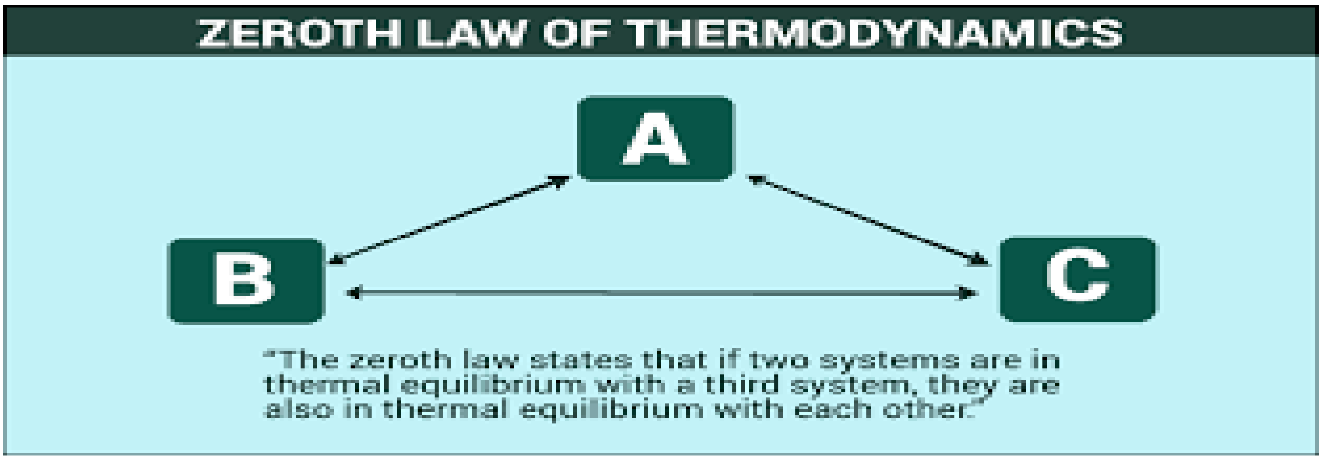
A closed system, on the other hand, does not allow the exchange of matter but allows energy to be transferred. It allows heat to be transferred from the stove to the water. Heat is also transferred to the surroundings. Steam is not allowed to escape. **Example of a closed system** – a pressure cooker.

Isolated Systems

This system is completely sealed. Matter is not allowed to be exchanged with the surroundings Heat cannot transfer to the surroundings. Example – A thermo flask is an isolated system.



The **zeroth law of thermodynamics** states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other.



Concept of Heat and Work:

Heat:

1. Heat appears only at the boundary of the system.

2. Heat appears only during a change in state.

3. Heat is manifested by an effect in the surroundings.

4. Heat is an algebraic quantity. It is positive when heat is absorbed and negative when heat is rejected by the system.

Work:

1. Work appears only at the boundary of the system.

2. Work appears only during a change in state.

3. Work is manifested by an effect in the surroundings.

4. Work is also an algebraic quantity. It is positive when work is done on the system and negative when work is done by the system.

Internal Energy:

To understand the relationship between work and heat, we need to understand a third, linking factor: the change in internal energy. Energy cannot be created nor destroyed, but it can be converted or transferred. Internal energy refers to all the energy within a given system, including the kinetic energy of molecules and the energy stored in all of the chemical bonds between molecules. With the interactions of heat, work and internal energy, there are energy transfers and conversions every time a change is made upon a system. However, no net energy is created or lost during these transfers.

DEFINITION: 1^{ST} LAW OF THERMODYNAMICS:

The First Law of Thermodynamics states that energy can be converted from one form to another with the interaction of heat, work and internal energy, but it cannot be created nor destroyed, under any circumstances. Mathematically, this is represented as

$$\Delta U = Q + W$$

ΔU is the total change in internal energy of a system,
q is the heat exchanged between a system and its surroundings, and
w is the work done by or on the system.

Work done by the system is equal to the negative sign with the multiplication of external pressure on the system and the change in volume and it can be expressed as

$$W = -P\Delta V$$

where P is the external pressure on the system, and ΔV is the change in volume. This is specifically called "pressure-volume" work.

The internal energy of a system would decrease if the system gives off heat or does work. Therefore, internal energy of a system increases when the heat increases (this would be done by adding heat into a system) and

work is done by the system. However, since energy is never created nor destroyed (thus, the first law of thermodynamics), the change in internal energy always equals zero. If energy is lost by the system, then it is absorbed by the surroundings. If energy is absorbed into a system, then that energy was released by the surroundings:

$\Delta U_{system} = -\Delta U_{surroundings}$, where ΔU_{system} is the total internal energy in a system, and $\Delta U_{surroundings}$ is the total energy of the surroundings

Table - 1				
The Process	**Internal Energy Change**	**Heat Transfer of Thermal Energy (q)**	**Work (w=-PΔV)**	**Example**
Q = 0 Adiabatic	+	0	+	Adiabatic system in which heat does not enter or leave into the system
ΔV=0 Constant Volume	+	+	0	A hard, pressure isolated system like a bomb calorimeter
Constant Pressure	+ or -	enthalpy (ΔH)	-PΔV	Most processes occur are constant external pressure
ΔT=0 Isothermal	0	+	-	There is no change in temperature like in a temperature bath

A gas in a system has constant pressure. The surroundings around the system lose 62 J of heat and does 474 J of work onto the system. What is the internal energy of the system?

SOLUTION

To find internal energy, ΔU, we must consider the relationship between the system and the surroundings. Since the First Law of Thermodynamics states that energy is not created nor destroyed, we know that anything lost by the surroundings is gained by the system. The surrounding area loses heat and does work onto the system. Therefore, Q and W are positive in the equation $\Delta U = Q + w$ because the system gains heat and gets work done on itself.

$$\Delta U = 62\ J + 474\ J = 536$$

A system has constant volume (ΔV=0) and the heat around the system increases by 45 J.

- **a. What is the sign for heat (q) for the system?**
- **b. What is ΔU equal to?**
- **c. What is the value of internal energy of the system in Joules?**

SOLUTION

Since the system has constant volume (ΔV=0) the term - PΔV=0 and work are equal to zero. Thus, in the equation ΔU= Q + W, so W = 0 and ΔU = Q. The internal energy is equal to the heat of the system. Since heat around the system increases, so the heat of the system decreases because heat is not created nor destroyed. Therefore, heat is taken away from the system making it negative. The value of Internal Energy will be the negative value of the heat absorbed by the surroundings.

a. negative (Q < 0)
b. ΔU= Q + (-PΔV) = Q+ 0 = Q
c. ΔU_{sys} = - 45 J

Enthalpy and heat capacity at constant pressure

- When heating a system, typically the volume V increases. Thus, often it is simpler to conduct processes at constant P to get the interrelation between the heat q and a state function.

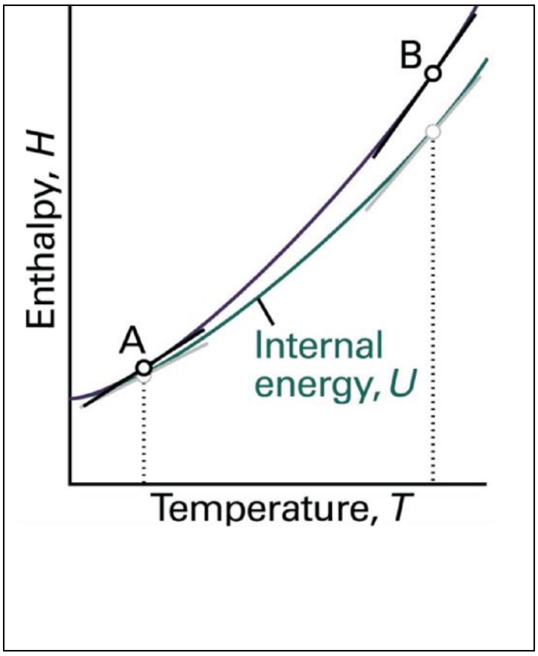
- To analyse e.g. reaction products, we can spontaneously create our system while it is thermally insulated, but in constant mechanical contact with a" volume bath" at pressure P. For example, we could create our system inside a thermally insulated chamber with one movable wall where the external pressure is fixed at P.

- In both cases in addition to the internal energy U of the system, we must also perform work PV in order to make room for the expanding system. The thermodynamic discussion of such systems needs the introduction of enthalpy H:

$$H = E + PV$$

∴ $dH = dE + P\,dV + VdP = dQ + VdP$

∴ $dH_P = dQ_P$



$dH_P = dQ_p$ is the heat for systems under isobaric expansion.

- The enthalpy is important for chemistry, it describes reactions in an open container.
- For solids and liquids: ΔH≈ΔU

Completely analogous to the above equation. we find the exact differential

As illustrated in the above Figure generally $C_P > C_V$ since at constant volume all of the heat added is solely used to raise the temperature. Several experimental approaches exist with similar working principles as the adiabatic bomb calorimeter:

- Differential Scanning Calorimetry (DSC):
  Here a well-defined heating rate $\alpha = \Delta T / t$ is enforced and basically the heating power is monitored.
- Differential thermal analysis (DTA) / Thermo-g

$C_P = (\delta H/\delta T)_P = \delta[(E + PV)/\delta T]_P = (\delta E / \delta T)_P + [\delta (PV)/ \delta T]_P = (\delta E / \delta T)_P + P. (\delta V / \delta T)_P$

Again, $E = f (V, T)$

∴ $dE = (\delta E / \delta V)_T. dV + (\delta E / \delta T)_V. dT = C_V. dT$

∴ $(\delta E / \delta T)_V = C_V$

∴ $(\delta E / \delta T)_P = (\delta E / \delta V)_T. (\delta V / \delta T)_P + (\delta E / \delta T)_V$

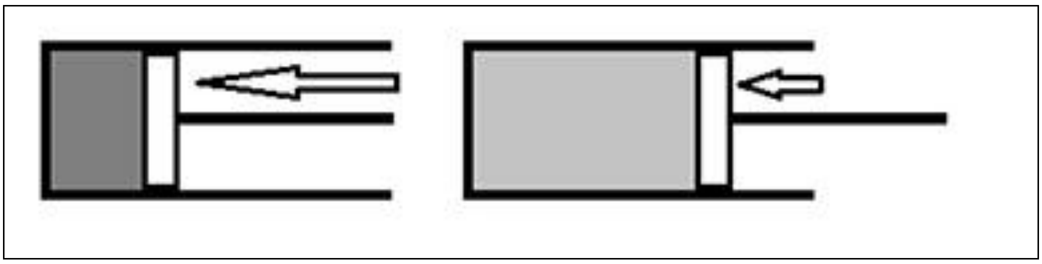
∴ $C_P = (\delta E / \delta V)_T. (\delta V / \delta T)_P + (\delta E / \delta T)_V + P. (\delta V / \delta T)_P$

$= (\delta V / \delta T)_P [P + (\delta E / \delta V)_T] + C_V$

∴ $C_P - C_V = P. (\delta V / \delta T)_P$ as $(\delta E / \delta V)_T = 0$ for the ideal gas

∴ $C_P - C_V = P. n. R/P = n. R$

Or, **$\bar{C}_P - \bar{C}_V = R$ (proved) where $\bar{C}_P$ & $\bar{C}_V$ are molar heat capacities.**



Let us consider the expansion which has no spontaneous direction of change as there is no net force push the gas to seek a larger or smaller volume. The only way this is possible is if the pressure of the expanding gas is the same as the external pressure resisting the expansion at all points along the expansion. With no net force pushing the change in one direction or the other, the change is said to be **reversible** or to occur **reversibly**. The work of a reversible expansion of an ideal gas is fairly easy to calculate.

If the gas expands reversibly, the external pressure (P_{ext}) can be replaced by a single value ($P - dP$) which represents both the pressure of the gas and the external pressure.

$$w = -(P - dP). dV$$

$$w = - \int P. dV - \int dP. dV$$

$$w = -\int P.dV$$

$$= -\int (n\ RT\ /V).\ dV$$

If the temperature is held constant (so that the expansion follows an **isothermal** pathway) the n. RT term can be extracted from the integral.

$$w = -\ n\ RT\ \ln\ (V_1\ /V_2)$$

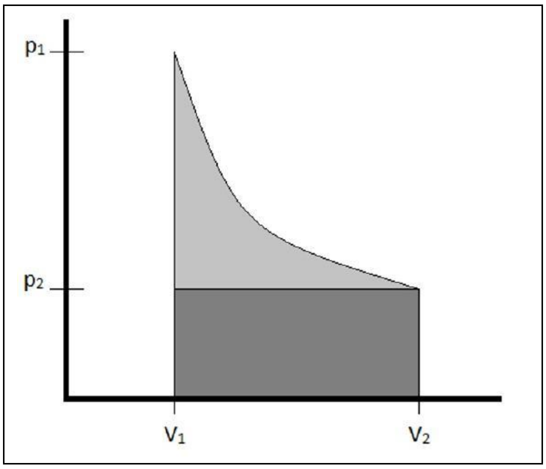
This equation is derived for ideal gases only; a van der Waal gas would result in a different version.

Problem:

What is the work done by 1.00 mol an ideal gas expanding reversibly from a volume of 22.4 L to a volume of 44.8 L at a constant temperature of 273 K?

Solution:

$$W = -\ (1.00\ mol)\ (8.314 J.mol^{-1}\ K^{-1})\ (273\ K)\ \ln\ (44.8L/22.4L) = -1570\ J = -\ 1.57\ kJ$$



The work of expansion can be depicted graphically as the area under the P-V curve depicting the expansion. Comparing examples and for which the initial and final volumes were the same, and the constant external pressure of the irreversible expansion was the same as the final pressure of the reversible expansion, such a graph looks as follows.

The work is depicted as the shaded portion of the graph. It is clear to see that the reversible expansion (the work for which is shaded in both light and dark gray) exceeds that of the irreversible expansion (shaded in dark gray only) due to the changing pressure of the reversible expansion. In general, it will always be the case that the work generated by a reversible pathway connecting initial and final states will be the maximum work possible for the expansion.

It should be noted (although it will be proven in a later chapter) that ΔU for an isothermal reversible process involving only P -V work is 0 for an ideal gas. This is true because the internal energy, U, is a measure of a system's capacity to convert energy into work. In order to do this, the system must somehow store that energy. The only mode in which an ideal gas can store this energy is in the translational kinetic energy of the molecules (otherwise, molecular collisions would not need to be elastic, which as you recall, was a postulate of the kinetic molecular theory) And since the average kinetic energy is a function only of the temperature, it (and therefore U) can only change if there is a change in temperature. Hence, for any isothermal process for an ideal gas, $\Delta U = 0$. And, perhaps just as usefully, for an isothermal process involving an ideal gas, $Q = -W$, as any energy that is expended by doing work must be replaced with heat, lest the system temperature drop.

Constant Volume Pathways

One common pathway which processes can follow is that of constant volume. This will happen if the volume of a sample is constrained by a great enough force that it simply cannot change. It is not uncommon to encounter such conditions with gases (since they are highly compressible anyhow) and also in geological formations, where the tremendous weight of a large mountain may force any processes occurring under it to happen at constant volume.

If reversible changes in which the only work that can be done is that of expansion (so-called P-V work) are considered, the following important result is obtained:

$$dU = dQ + dw = dQ - P.dV$$

$$\text{or, } dU = dQ + dw = dQ - PdV$$

However, dV = 0 since the volume is constant, as such, dU can be expressed only in terms of the heat that flows into or out of the system at constant volume

$$dU = dQv$$

Recall that dQ can be found by

$$dQv = (\partial U/\partial T)_V .dT = C_V. dT = n. \bar{C}_V. dT$$

Therefore, by integrating, we get, $Q_V = n. \bar{C}_V. (T_2 - T_1)$

Consider 1.00 mol of an ideal gas with C_V = (3 / 2) R that undergoes a temperature change from 125 K to 255 K at a constant volume of 10.0 L. Calculate ΔU, Q and W for this change.

Solution:

Since this is a constant volume process, W = 0

For an isochoric process, $Q_V = n. \bar{C}_V. (T_2 – T_1)$ = 1.00 mole .3/2. 8.314 J K^{-1} $mole^{-1}$.(255-125) K

= 1621.23 J

Calculate Q, W, ΔU, ΔH for the isothermal reversible expansion of 1 mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 *K.*

In isothermal process as temperature remains constant both ΔU, ΔH are zero
Applying first law of thermodynamics,

ΔU = W + Q

or, Q = −W = −2.303. n. R. T log (P2 / /P1)

= −2.303×1×8.314×273 log (0.11) =− 5.227 kJ

∴ ΔU = Δ H = 0 as ΔT = 0 for the isothermal process.

References:

1. Degree Physical and General Chemistry; Ahindra Kumar Mondal; Sridhar Publishers.
2. A Text Book of Physical Chemistry; Volume -1; K. L. Chug and S. L. Agnish; Kalyani Publishers.
3. Physical Chemistry; P. C. Rakshit; Sarat Book House.
4. A Text Book of Physical Chemistry; K. K. Sharma and L. K. Sharma; Vikas Publishing House Pvt. Ltd.
5. Patrick Fleming,Assistant Professor (Chemistry and Biochemistry) at California State University East Bay.