

Relation between Cp & Cv for an ideal gas is..

Chemical Thermodynamics

- ❖ **Basic Definitions and First Law of Thermodynamics:** The subject of thermo dynamics deals with the inter section of one body with another in terms of the quantities of heat and work.
- ❖ **Basic Definitions:**
 - In thermodynamics, a few terms with the specific definitions are involved.
 - **System:** The system is any regions of space being investigated. Three types of systems may be distinguished.
 - **Closed system:** Matter can neither be added nor removed from it.
 - **Open system:** Matter can be added or removed.
 - **Isolated system:** Neither energy nor matter can be transferred to or from it.
 - **Surroundings:** The surroundings are considered to be all other portion of universe which can interact with the system.
 - **Boundary:** Anything which separates the system an surroundings is called boundary (or envelope or wall). The boundary may be imaginary or real; it may be rigid or nonrigid; it may be a conductor of heat (diathermic wall) or a nonconductor of heat (adiabatic wall).
 - **State Variables:** The state of system is defined by ascribing values of some variables such as pressure, volume, temperature, density, etc. These variables are known as state variables. Two types of variables may be distinguished based on the size of system.
 - **Intensive Variables:** The values of such variables do not change on dividing the system into two or more parts. Examples are temperature, pressure, concentration, density, surface tension, vapour pressure, viscosity, molar volume and specific heat capacity.
 - **Extensive Variable:** The values of such variable do change on dividing the system into two or more parts. Examples are volume, energy, heat capacity, mass, enthalpy, entropy and free energy.
 - **Process :** A process is the

path along which a change of state of a system take place. The following ways of carrying a process may be considered.

Isothermal Process:

- This involves constant temperature of the system.

Isobaric process :

- This involves constant pressure of the system.
- **Isochoric process:** This involves constant volume of the system.
- **Adiabatic process:** This involves no exchange of heat from or to the system.
- **Cyclic process:** This involves a series of exchange and ultimately the system comes back to the initial state.
- **Reversible Process :** This involves a system to be virtually in a state of equilibrium during the process . In other words, the system departs only infinitesimally from the equilibrium state. Such a process is difficult to carry out in natural practice, however these can be carried out theoretically.
- **Irreversible process:** This process does not require the system to be virtually in a state of equilibrium. All real processes are irreversible processes.
- **State Functions :** If the change in property of a system does not depend upon the path adopted ingoing from one state to another, the property is said to be state function.

❖ **IUPAC Recommendations Regarding the Transfer of Heat and Work:**

- Energy of a system can be changed in two modes. These are (i) transfer of heat and (ii) in the form of work. The mode in which inertial energy of a system is increased is assigned a positive sign. Thus heat added to the system and work done on the system increase inertial energy of a system, these are assigned positive sign. The converse of these ways namely (i) heat withdrawn from a system, and (ii) work done by the system are assigned negative sign.

❖ **First Law of Thermodynamics:**

- The internal energy (symbol : U) of a system can be changed in two modes, (i) transfer of heat (symbol : q)



and (ii) in the form of work (symbol : w). Thus for an infinitesimally process , we write $dU = dq + dw$ (1) For a infinite process we write $\Delta U = q + w$ (2)

Note: For a finite process, change in internal energy is written as ΔU where as heat and work are simple written as q and w . This follows from the fact that U is a state function whereas q and w are path dependent.

❖ **Law of Conservation of Energy:**

- For an isolated system, both q and w are zero. Hence from Eq (2) , it follows that
- $\Delta U = 0$, i.e., U is a constant. (3)
- In words, no matter what changes of state may occur in a isolated system, the value of energy function is always a constant.

❖ **Expression of Mechanical Work :**

- The volume change of a gaseous system against an external pressure is known as mechanical work.

Fig. 1

• Consider a gaseous system as shown in fig. If the piston as pushed through a distance dl. Then the work involved is :
 Work = Force x Distance
 = (pressure x area) distance
 i.e., $dw = (p_{ext} \times d)$
 $= p_{ext}(Adl) = p_{ext}dv$ (4)

- Where dv is the change in volume of the gas. In accordance to IUPAC recommendation the expression of w is $w = p_{ext}dv$

Note: For expansion of the gas, dv is positive and dw is negative and work is done by the system. For compression of the gas, dv is negative and dw is positive and work is done on the system.

Effect of Adding Heat at Constant Volume:

- The first law of thermo dynamics is $dU = dq + dw$
- If only mechanical work is involved then, $dU = dq - p_{ext}dv$ (5)
- If heat is added at constant volume, then $dU = dqv$ or $\Delta U = qv$ (6)
- That is heat added removed at constant volume changes internal energy of the system. Though q is not state function but qv is state function.

❖ **Enthalpy Function:**

- For $p_{ext} = p$, pressure of the system. Eq becomes $dU = dq - pdv$
 Adding and subtracting Vdp on the right side, we get
 $dU = dq - pdv + (Vdp - Vdp)$
 $= dq - (pdv + Vdp) + Vdp$
 $= dq - d(pV) + Vdp$ or
 $d(U + pV) = dq + Vdp$ or
 $dH = dq + Vdp$ (7)

where $H = U + pV$ and is known as enthalpy function.

❖ **Heat Added at Constant Pressure:** If heat is added at constant eq (7) becomes $dH = dq$ or $\Delta H = qp$ (8) that is, heat added or removed at constant pressure changes enthalpy of the system. Though q is not a state function but qp is a state function.

Change in Energy

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and Enthalpy with change in Temperature:

By definition, heat capacity of a system is the heat required to change the temperature of the system by 10C (i.e., 1K) if dT is the increase in temperature by adding heat dq , then the heat capacity is $c = \frac{dq}{dT}$ (9)

For gaseous system, two types of heat capacities may be considered. These are Heat capacity at constant volume
 $Cv = (dq / dT) V$
 Heat capacity at constant pressure
 $Cp = (dq / dT) p$
 With these Eqs (6) and (8) becomes
 $dU = dq = Cv dT$ (10 a)
 $dH = dq = Cp dT$ (10 b)

❖ **Relation between ΔH and ΔU :**
 We have $H = U + pV$
 Hence, $\Delta H = \Delta U + \Delta(pV)$
 For condensed phase (solid or liquid), $\Delta(pV) = 0$
 Hence, $\Delta H = \Delta U$ (11)

For an ideal gas
 $\Delta(pV) = \Delta(nRT) = nR(\Delta T)$
 Hence, $\Delta H = \Delta U + nR\Delta T$ (12)

❖ **Relation between Cp and Cv for an ideal gas :**
 We have $H = U + pV$
 Hence, $dH = dU + d(pV)$
 or $dH = dU + nRdT$
 using eq (10 a) and (10 b), we get
 $Cp dT = Cv dT + nRdT$ or
 $Cv = Cp - nR$
 For one mole of an ideal gas
 $C_{pm} - C_{vm} = R$ (13)

Work of expansion or compression of an ideal gas: The expression of work involved in the expansion or compression of a system is
 $dw = - p_{ext}dv$ (14)

- The negative sign is due to IUPAC sign convention of the work.
- Let an ideal gas undergo expansion from $V1$ to $V2$ (or compression from $V2$ to $V1$). Since the work involved is path dependent, we consider the following ways of changing the said volume.