Unit – V

Thermodynamics: Zeroth law of Thermodynamics – Absolute Temperature scale – Extensive and Intensive Properties. Internal energy (E), Enthalpy (H), Cp & Cv and their relationship. First law of Thermodynamics – internal energy, enthalpy, heat and work done - calculations work done in isothermal and adiabatic reversible and irreversible processes for ideal gases. Joule – Thompson effect – Joule Thomson Coefficient for ideal and real gases – Inversion Temperature.

Zeroth Law of Thermodynamics

- Consider a fluid system B in a state defined by volume V_B and pressure P_B

- Let it be in equilibrium with another fluid system A in a state defined by volume V_A and pressure P_A

- The values of volume V_A and pressure P_A are determined experimentally

- There may be several values of V_A and P_A at which there may be equilibrium with the system B, at constant temperature θ_1 .

- These values are plotted against each other to get an isotherm.

Zeroth Law of Thermodynamics

- According to Zeroeth law , this isotherm is independent of the nature of the system B because the same values will be obtained by substituting B by any other system in equilibrium with A at the same temperature.

- If the temperature of B still in equilibrium with A , is changed from θ_1 to θ_2 , then another set of values of V_A and P_A at temperature θ_2 will be observed as a new isotherm will be obtained and so on.

- Three isotherms (P_A and V_A graphs) obtained at temperatures θ_1 , θ_2 and θ_3 are shown in Fig.

- several isotherms at various temperatures can be built.

- All systems having the same temperature , will follow the same graph, when brought into thermal contact with the Body A or even with one another.

Zeroth Law of Thermodynamics

❖In this way the unknown temperature of a system at any time can be obtained by comparing its P-V isotherm determined experimentally with those plotted in Fig.

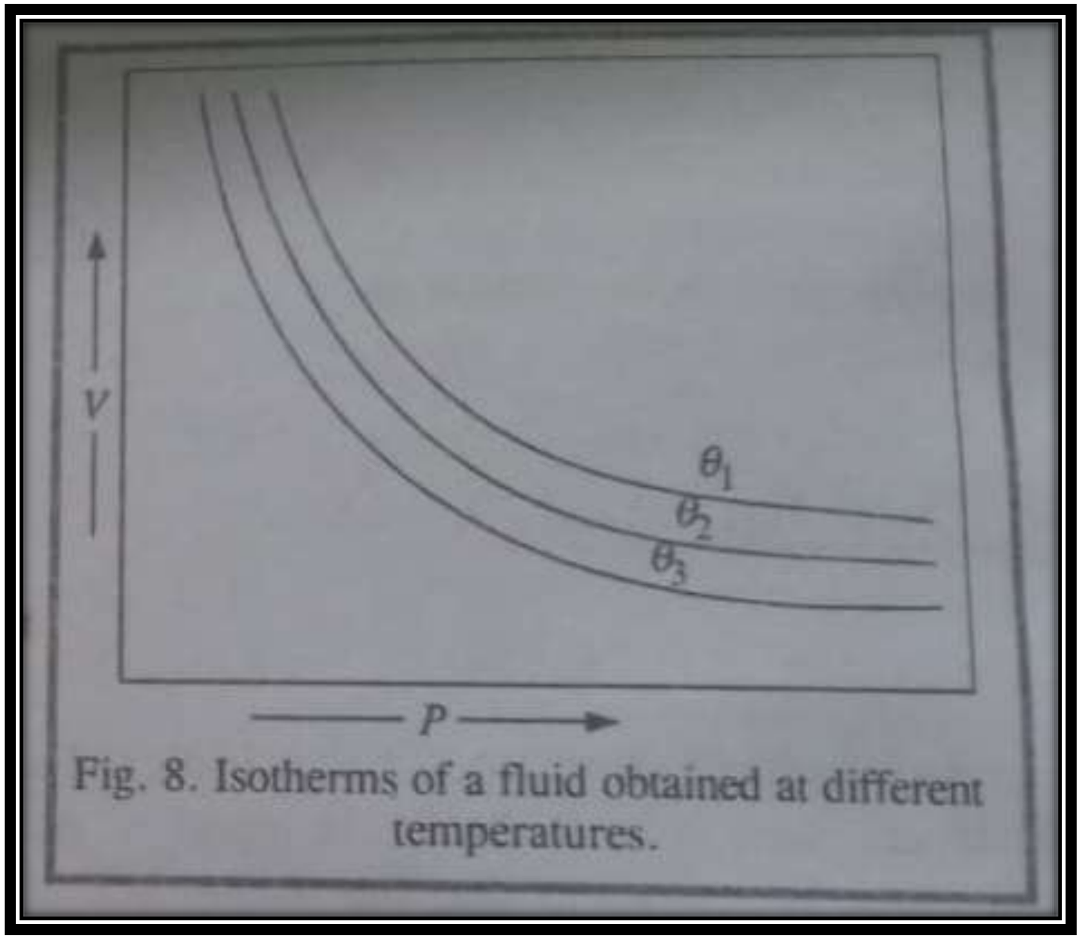


Fig. 8. Isotherms of a fluid obtained at different temperatures.

Ref: Physical Chemistry – Puri Sharma and pathania

Absolute temperature Scale

- Several temperature scales have been known but they are arbitrarily based on freezing and boiling points of water or some other transition temperatures.

- But a true scale is based on the observation that PV-P graphs of all real gases when extrapolated to zero pressure give the same value of PV at a given temperature.

- This value is represented by $(PV)_o$ in general and $(PV)_m$ for one mole of the gas involved.

- The values of $(PV)_m$ vary linearly with the temperature on the centigrade scale.

The variation is represented by

$$(PV_m)_0 = a + bt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

❖Where t is the centigrade temperature measured by a mercury thermometer and a and b are constants.

❖ The values of $(PV_m)_0$ at 0˚ and 100˚C have been found to be 22.4136 and 30.6192 dm^3 atm , respectively.

❖ Substituting these values in eqn 1 we get

❖ $22.4136\ dm^3\ atm = a + 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$

❖ $30.6192\ dm^3\ atm = a + 100b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$

❖ Hence $b = 0.082056\ dm^3\ atm \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$

❖ Substituting the values of a and b in eqn 1, it is possible to calculate the temperature at which $(PV_m)_0$. Thus,

❖ $0 = 22.4136\ dm^3\ atm + (0.082056\ dm^3\ atm)t$

$$t = -273.15\ ˚C$$

The temperature -273.15 deg.C is the natural or true zero. It is defined as the temperature at which the limiting value of $(PV)_m$ at pressures approaching zero, is zero itself.

This zero defines an absolute temperature scale and it based on the behavior of real gases at zero pressure when they behave ideally.

It is known as the ideal temperature scale. However, the size of the degree on the absolute scale is the same on the centigrade scale.

The temperature on the absolute scale is denoted by T.

Thus the boiling temperature of water on this scale is given by T= 273.15+ 100 =373.15

For practical purposes the absolute zero temperature is taken to be -273deg.C.
Thus, T = 273 + t ˚deg.C

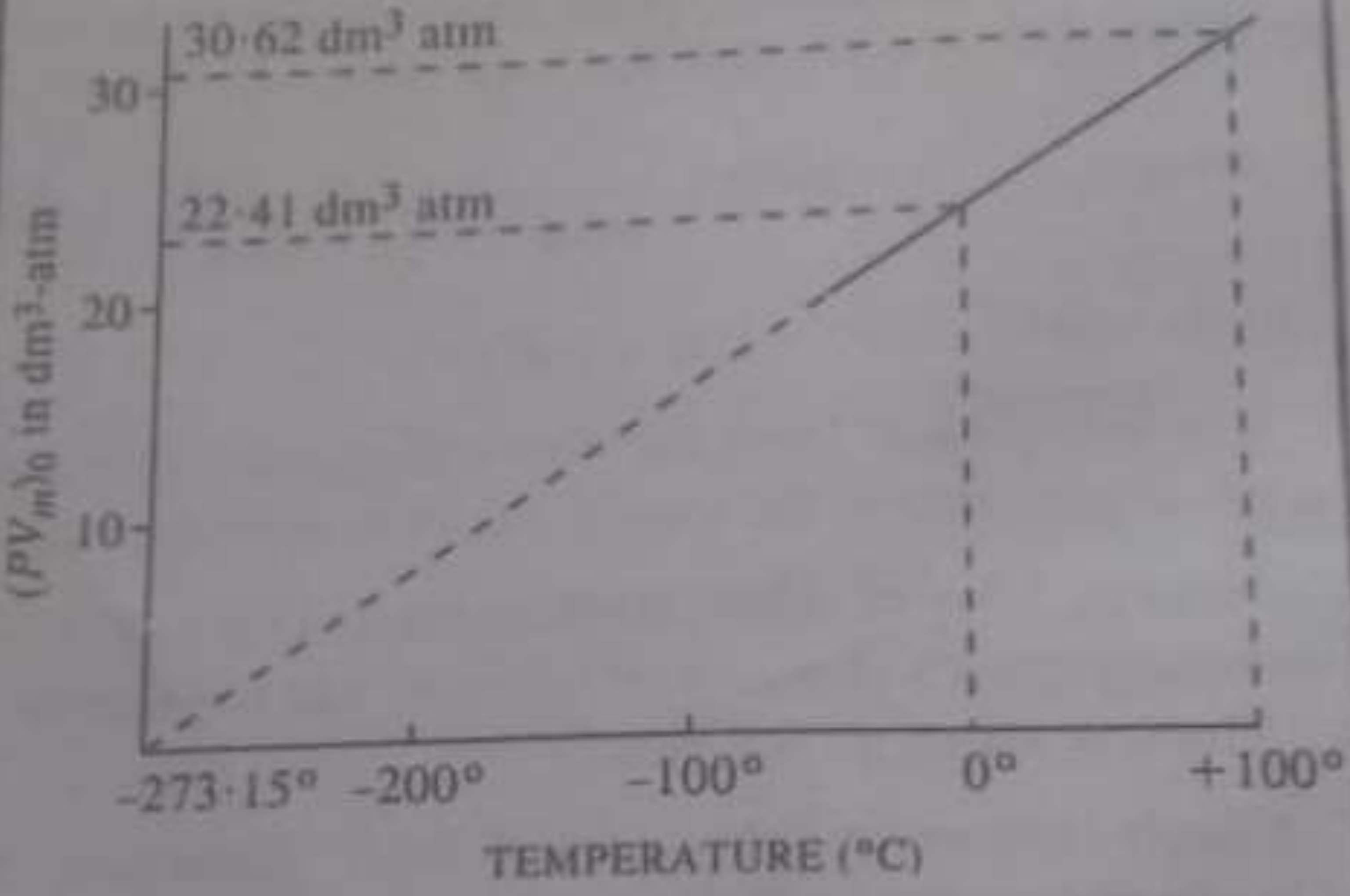
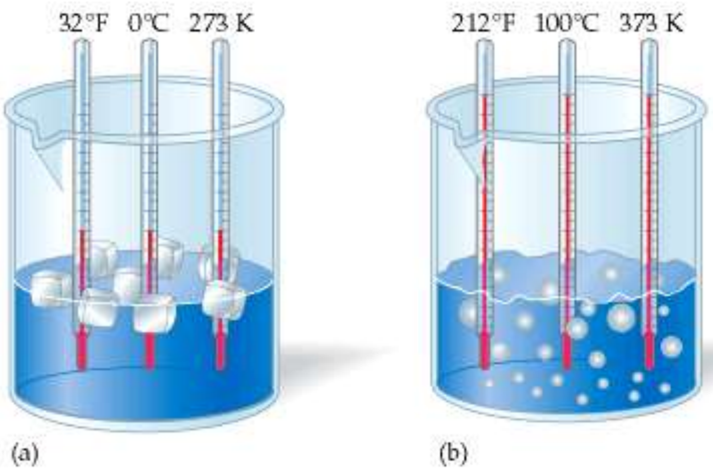
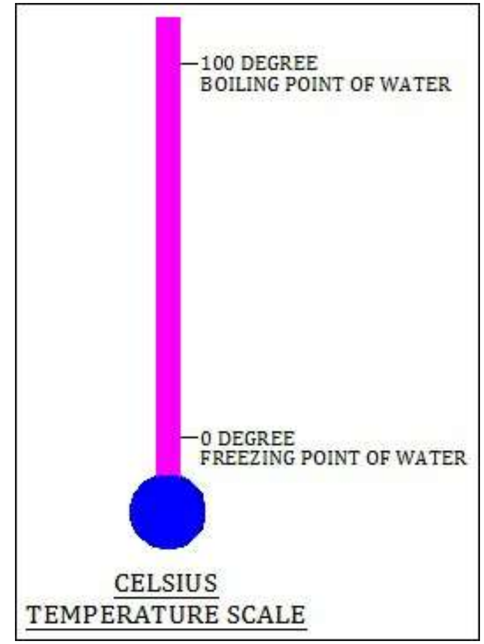


Fig. 9. The $(PV_m)_0$ plot vs. temperature for a real gas.

Ref: Physical Chemistry – Puri Sharma and pathania

Temperature Scale





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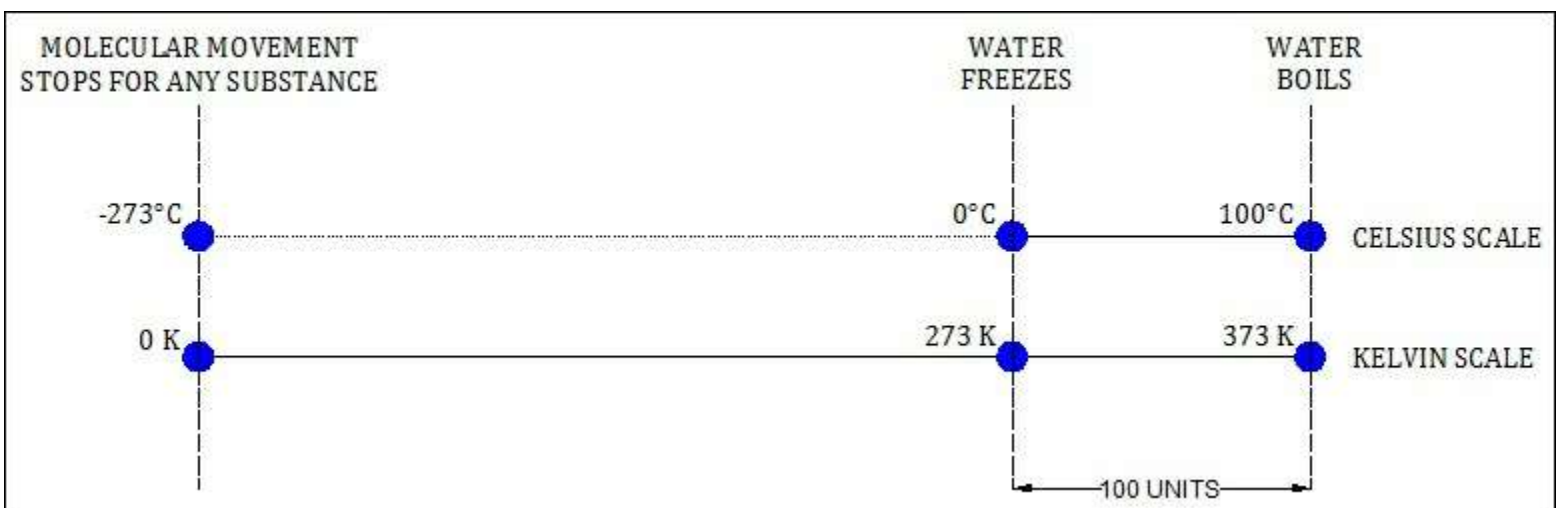


Macroscopic or bulk Properties of a system- Eg. Volume, Pressure, mass etc.,

It can be divided into two classes

i) Intensive Properties

ii) Extensive Properties

i) Intensive Properties

A property which depend only on the nature of the substance and independent on the quantity of the matter present in the system.

Eg. Pressure, Temperature, density, concentration, viscosity, boiling point and freezing point

ii) Extensive Properties

A property which depends on the quantity of the matter present in the system.

Eg.Mass, Internal Energy, enthalpy, entropy, free energy, no.of moles, volume

First Law of Thermodynamics

Statement

- “Energy can neither be created nor destroyed , although it can be transformed from one form to another”

- It is impossible to construct a perpetual motion machine ie., a machine which can produce energy without expenditure of energy.

Internal Energy

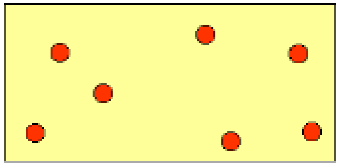
❖ The evolution or absorption of energy in different processes clearly indicates that every substance must be associated with some definite amount of energy.

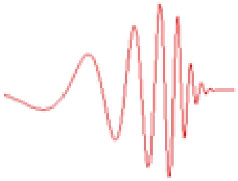
❖ The actual value of which depends upon the nature of the substance (i.e., arrangement of atoms and electrons within the molecules) and the conditions of T,P,V and Composition.

❖ The energy associated with a substance is called its internal energy (E).

❖ It is not possible to find the absolute value of internal energy of a substance because it involves (translational, vibration, rotational, kinetic energies) quantities which cannot be measured.

❖ It is not required to know the absolute value of internal energy possessed by any substance, what is required in different processes is simply the change of internal energy when the reactants change into products or when the system changes from initial state to final state.





❖ This is easily measurable and is represented by ΔE

❖ E_1 is the internal energy of a system in initial state & E_2 is the internal energy of a system in final state

Then $\Delta E = E_2 - E_1$

Similarly in a chemical reaction

E_R is the internal energy of reactants; E_P is the internal energy of products.

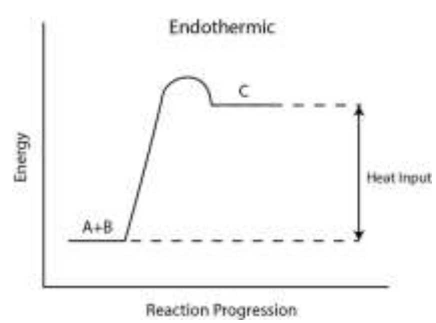
Then $\Delta E = E_P - E_R$

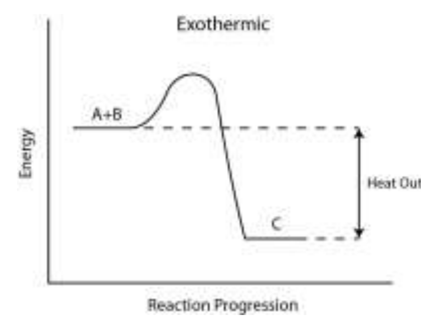
If $E_1 > E_2$ and $E_P < E_R$

❖ Energy is given out $\Delta E = -ve$

❖ If $E_1 < E_2$ and $E_P > E_R$ $\Delta E = +ve$

❖ It is a state function. It depends on the initial and final state. It is independent of the path.





Internal Energy and First Law of Thermodynamics

❖ Suppose , a system is subjected to change of pressure and volume.

❖ Let the initial state be represented by A and the final state by B.

❖ Let E_A and E_B represent the energies associated with systems in state A and B , respectively.

❖ Then the changes in the internal energy,

$$\Delta E = E_B - E_A$$

❖ The system changes from state A to state B by following path I and the change in internal energy is given by ΔE.

❖ Now suppose the same changes of state is brought about by another path say Path II, and the change in energy is given by $\Delta E'$.

- Suppose ΔE > ΔE ‘. Then by coupling of these two processes

A $\longrightarrow$ B (Path I) and

B $\longrightarrow$ A (Path II)

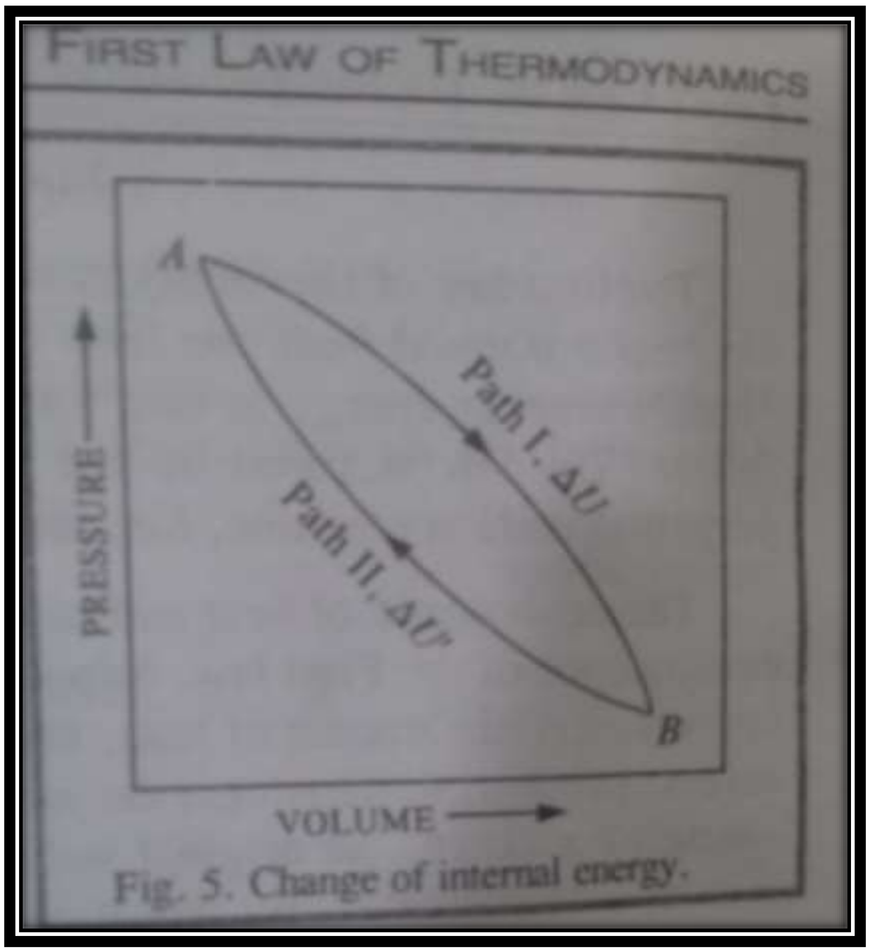


Fig. 5. Change of internal energy.

- The system would return to its initial state and at the same time a surplus of energy equal to

$$\Delta E - \Delta E'.$$

would become available.

- By repeating the same cycle over and over again, energy would be generated continuously and a perpetual motion machine would be possible.

- This is contrary to the First Law of Thermodynamics.

- Hence $\Delta E = \Delta E'$.

- Thus, the internal energy change accompanying a process is a function only of the initial and the final states if the system and is independent of the path or the manner by which the changes is brought about.

Energy Changes in relation to work and heat changes

- Let E_A be the energy of a system in its state A and E_B be the energy of the state B

- Suppose the system while undergoing changes from state A to state B absorbs heat q from the surroundings and also performs some work (mechanical or electrical) equal to w.

❖ The absorption of heat by the system tends to raise the energy of the system.

❖ The performance of work by the system, on the other hand, tends to lower the energy of the system because performance of work requires expenditure of energy.

❖ Hence the change of internal energy ΔE, accompanying the above process will be given by

$$\Delta E = = E_B - E_A = q - w$$

❖ In general, if in a given process, the heat change is q and the work done is w, then the change in internal energy is given by

$$\Delta E = q + w$$

Mathematical Statement of First Law of Thermodynamics

❖ If work is done by the surroundings on the system(as during compression of the gas), w is taken as positive so that

$$\Delta E = q + w$$

❖ If work is done by the system on the surroundings (as during expansion of the gas), w is taken as negative so that

$$\Delta E = q - w$$

State Function

- ❖ It is a property of a thermodynamic system which has a definite value for a particular state of a system.
- ❖ It is independent of the manner in which the state is reached.
- ❖ The change in state function accompanying the change of state of the system depends only on the initial and final states of the system and not on the path followed.
- ❖ Pressure, temperature, volume and energy – State Functions
- ❖ Work and heat – Path Functions

Exact and Inexact Differentials

- In the first Law Equation

$$\Delta E = q + w$$

ΔE is a definite quantity, hence if w is not a state function, q also is not a state function

- Mathematically,

dE is an exact differential and dq and dw are inexact differentials.

$$\int_{U_1}^{U_2} dU = U_2 - U_1$$

$$\int_{q_1}^{q_2} dq \neq q_2 - q_1 \quad \text{and} \quad \int_{w_1}^{w_2} dw \neq w_2 - w_1$$

Work and heat are not definite properties. Internal energy which depends on the initial and final states of the system, w and q are not definite quantities.

The work done in expansion (or contraction) *depends upon the path* long which the process is carried out. Consider, for example, the ork done in passing from state A to state B by four different paths, as lustrated in Fig. 12.3.

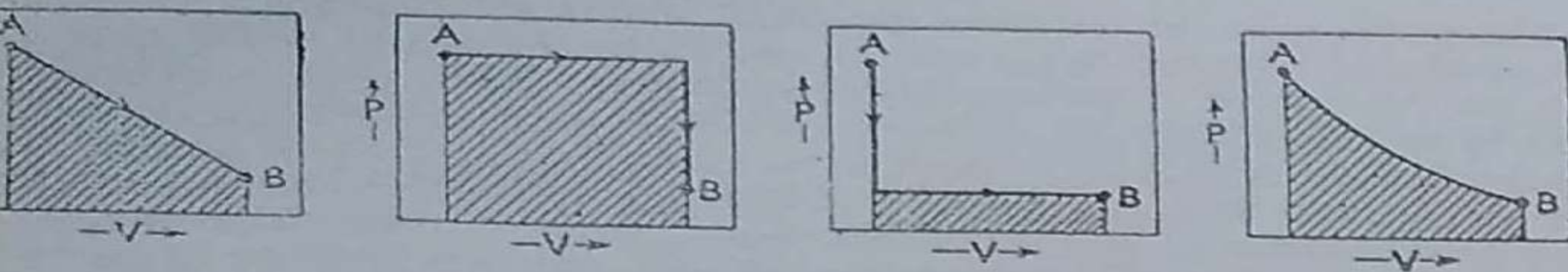


Fig. 12.3. Dependence of work done on the path followed.

As we know, the work done is given by the sum (or integral) of series of PdV terms, where P is external pressure. Accordingly, the alue of w will be given by the *area* under the curve in a P—Vdiagram. his is shown by the shaded regions in Fig. 12.3 for the various paths. is evident that the work done in passing from A to B by *different* aths is *different*. The work, w, therefore, is not a definite property.

Now, in the equation of the First law, *viz*., $\Delta E = q - w$, since E is a definite quantity, therefore, if w is *not* a definite quantity, q so *cannot* be a definite quantity.

If, however, the process is carried out in a *thermodynamically reversi-e manner*, the work obtained is a *definite quantity* since this work is e *maximum* that can be obtained in a given expansion or contraction. such a case, the heat (q) will also be a *definite quantity*.

Ref: Physical Chemistry by Puri, Sharma and Pathania

Referring back to Eq. 8, for an infinitesimally small change, this uation may be put as

$$dE = dq - dw \qquad ...(8)$$

ıere dE is the small increase in energy and dq and dw represent small antities of heat absorbed and external work done by the system, pectively.

Since change in energy depends only on the initial and final states the system and not on the path by which the change is brought out, *dE is a definite quantity*. Mathematically, this fact is expressed stating that in any infinitesimal process, the small change dE is a *nplete* or *exact differential*. However, the same is not true for dq and , as their values vary with the change of experimental conditions, shown above. Hence, dq and *dw are not complete differentials* and in ms of mathematics, Eq. 8 may be written as

$$dE = \delta q - \delta w \qquad ...(9)$$

Ref: Physical Chemistry by Puri, Sharma and Pathania

ENTHALPY OR HEAT CONTENT

❖If a process is carried out at constant pressure, the work of expansion is given by

$$W = P\,\Delta V \text{ .... } (1)$$

❖ ΔV – increase in volume ; P = Pressure (Constant)

❖ According to the First Law of Thermodynamics, we know that

$$\Delta E + w = q \text{ ....} (2)$$

q- heat absorbed by the system
ΔE – change in internal energy of the system.
w- work done by the system

Under conditions of constant pressure, putting

$W = P\,\Delta V$

- The heat absorbed is represented by q_p we get,

$$q_p = \Delta E + P\,\Delta V \text{ ....(3)}$$

- Suppose when the system absorbs q_p calories of heat, its internal energy increases from E_1 to E_2 and the volume increases from V_1 to V_2.

- Then we have

$$\Delta E = E_2 - E_1 \text{ ....(4)}$$

$$\Delta V = V_2 - V_1 \text{ ....(5)}$$

- Substituting in equation (3), we get

$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$

$$q_p = (E_2 + PV_2) - (E_1 + PV_1) \quad \text{.........................(6)}$$

- E, P and V are functions of state. q_p and E+PV must also be a state function.
- The thermodynamic quantity E+PV - heat content or enthalpy (H).
- It is defined mathematically by the equation

$$H = E + PV$$

H_1 is the enthalpy of the system in the initial state and H_2 is the enthalpy of the system in the final state.

- $H_2 = E_2 + PV_2$
- $H_1 = E_1 + PV_1$

Putting these values in equation 6 we get

$$q_p = (E_2+PV_2) - (E_1+PV_1) \text{.........................(6)}$$

$$q_p = H_2 - H_1$$

$$q_p = \Delta H \text{ ....(7)}$$

$\Delta H = H_2 - H_1$

Enthalpy change of the system

Hence the enthalpy change of the system is equal to heat absorbed by the system at constant pressure.

Putting the values of qp from equation 7 in equation 3, we get

$$q_p = \Delta H \text{ ....(7)}$$

$$q_p = \Delta E + P\,\Delta V \text{ ....(3)}$$

We get,

$$\Delta H = \Delta E + P\,\Delta V \text{ ....(8)}$$

Hence the enthalpy change accompanying a process may be defined as "the sum of increase in internal energy of the system and the pressure-volume work done ie., the work of expansion

$P\,\Delta V$ can be replaced by ΔnRT, so that equation 8 can be written as

$$\Delta H = \Delta E + \Delta nRT$$

Physical Significance of Enthalpy

- Every substance or system has some definite energy stored in it – internal energy.
- This energy may be of many kinds.
- The energy stored within the substance or the system that is available for conversion into heat is called enthalpy of the system.
- Absolute value of heat content or enthalpy of the system cannot be measured and is not required.
- In thermodynamic processes, we are concerned only with the changes in enthalpy (ΔH) which can be easily measured experimentally.

Enthalpy of Vaporisation. When a liquid evaporates, it *absorbs* some heat from the surroundings. Thus, evaporation of a liquid is accompanied by *increase* in enthalpy. The increase for the evaporation of one mole of water at 25°C is 43·93 kJ. We may express this result in the form of a thermochemical equation :

$$H_2O\,(l) \longrightarrow H_2O\,(g)\,; \qquad \Delta H = +\,43{\cdot}93 \text{ kJ}$$

When vapours condense to liquid state, they *give out* (*evolve*) heat. Thus, condensation of vapours is accompanied by *decrease* in enthalpy. The value for the condensation of one mole of water vapour at 25°C is also 43·93 kJ. Therefore, we may write

$$H_2O\,(g) \longrightarrow H_2O\,(l)\,; \qquad \Delta H = -\,43{\cdot}93 \text{ kJ}$$

The change in enthalpy (ΔH), *when a liquid changes into vapour state or when vapour changes into liquid state, is known as* enthalpy of vaporisation. This has a positive sign in the former case and a negative sign in the latter case.

Ref: Physical Chemistry by Puri, Sharma and Pathania

Enthalpy of fusion. When a solid melts and changes into liquid state, it *absorbs* heat. On the contrary, when a liquid freezes and changes into solid state, it *gives out* heat. In the first case, enthalpy of the system *increases*. In the latter case, the enthalpy of the system *decreases*. The change in enthalpy for this type of phase-transformation is known as **enthalpy of fusion**.

The enthalpy of fusion for 1 mole of water at 0°C is 6·02 kJ. We may express this result in the following way :

$$H_2O\,(s) \longrightarrow H_2O\,(l)\;; \qquad \Delta H = +\,6{\cdot}02\ \text{kJ}$$

$$H_2O\,(l) \longrightarrow H_2O\,(s)\;; \qquad \Delta H = -\,6{\cdot}02\ \text{kJ}$$

Ref: Physical Chemistry by Puri, Sharma and Pathania

Heat Capacity

❖ The heat capacity of a system is defined as the amount of heat required to rise the temperature of the system through 1˚C.

❖ Thus if q is the amount of heat supplied to the system and as a result the temperature of the system rises from T_1 to T_2, then the heat capacity of a system is given by,

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$

If ∂q is the small amount of heat absorbed by a system which rises the temperature of the system by a small amount dT (T to T+ dT), then the heat capacity of the system will be given by

$$C = \partial q / dT$$

- Since q is not a state function and depends upon the path followed ,

∴ C is also not a state function.

To know the value of C, the conditions such as constant volume or pressure has to be specified which define the path.

Heat Capacity at constant Volume C_v

- According to the First Law of thermodynamics, We know that

- $\partial q = dE + PdV$

$$C = \frac{dE + PdV}{dT}$$

When Volume is kept constant

$dV = 0$ and $C_v = dE/ dT$

- Cv is the heat capacity at constant volume.

Thus, the heat capacity at constant volume may be defined as the rate of change of internal energy with temperature at constant volume.

Heat Capacity at Constant Pressure (C_p)

- When the pressure is constant

$$C_p = (\partial E/ \partial T)_p + P (\partial E/ \partial T)_p$$

$$H= E+PV$$

Differentiating with respect to T at constant P, we get

$$(\partial H/ \partial T)_p = (\partial E/ \partial T)_p + P (\partial V/ \partial T)_p$$

$$C_p = (\partial H/ \partial T)_p$$

C_p Heat Capacity at Constant Pressure

Relation between C_p and C_v

- If the volume of the system is kept constant, when the heat is added to a system, then now work done by the system – Thus the heat absorbed by the system is used up completely to increase the internal energy of the system.

- Again if the pressure of the system is kept constant when the heat is supplied to the system, then some work of expansion is also done by the system it is to be raised through the same value as at constant volume, then some extra heat is required for doing the work of expansion.

Hence $C_p > C_v$

$$C_v = \frac{dE}{dT} \quad \text{and} \quad C_p = \frac{dH}{dT}$$

$$C_p - C_v = \frac{dH}{dT} - \frac{dE}{dT}$$

$H = E + PV$ by definition

$PV = RT$ (for 1 mole of an ideal gas)

$H = E + RT$

Differentiation this equation with respect to T, we get

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

$$\frac{dH}{dT} - \frac{dE}{dT} = R$$

$C_p - C_v = R$ (for 1 mole of ideal gas)

Thus

$C_p > C_v$ by a gas constant R

Expansion of an ideal gas changes in Thermodynamic properties

❖ From the First Law of Thermodynamics it is possible to calculate changes in thermodynamic properties such as q, w, ΔE and Δ H . When an ideal gas undergoes expansion.

❖ The expansion may be isothermal or adiabatic and the process of expansion may be carried out reversibly or irreversibly.

A. Isothermal Expansion

Calculation of ΔE

In an isothermal process, the temperature of the system remains constant throughout the process of expansion. Since for an ideal gas the internal energy E depends only on the temperature, it follows that at constant temperature (isothermal process), the internal energy remains constant.

$$\Delta E = 0$$

Calculation of ΔH

$$H = E + PV \text{ by definition}$$

$$\Delta H = \Delta (E + PV) = \Delta E + \Delta PV$$

$$\Delta H = \Delta E + (\Delta nRT) = \Delta E + \Delta nRT$$

Since for an isothermal process, ΔT as well as ΔE are equal to zero,
Hence,

$$\Delta H = 0$$

Calculation of q and w

According to first law of Thermodynamics

$$\Delta E = q-w$$

Since, for an isothermal process, $\Delta E = 0$, hence

$$q = w$$

❖ This shows that in an isothermal expansion, the work is done at the expense of the heat absorbed.

❖ The magnitude of w (or q) depends upon the manner in which the process of expansion is carried out, i.e., whether it is carried out reversibly or irreversibly.

Work done in Reversible Isothermal Expansion of a Gas

❖ Consider a gas enclosed in a cylinder fitted with a weightless and frictionless piston.

Source: Internet

❖ The cylinder is not insulated. It is supposed to be in thermal equilibrium with the surroundings so that the temperature of the gas remains constant all along.

- The external pressure P. on the piston is equal to the pressure of the gas within the cylinder .

- If the external pressure is lowered by an infinitesimal amount dP i.e., it falls from P to P-dP, the gas will expand by an infinitesimal volume dV i.e., the volume changes from V to V+dV.

- As a result of expansion, the pressure of the gas within the cylinder falls to P-dP i.e., it becomes again equal to the external pressure. Then the piston comes to rest.

- If the external pressure is lowered again second time by the same infinitesimal amount dP, the gas will undergo the second infinitesimal expansion dV before the pressure again equals to the external pressure.

- The piston again comes to rest. The process is continued such that the external pressure is lowered by successive small amounts and as a result, the gas undergoes a series of small successive increments of volume dV at a time.

❖ The system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced as a result of infinitesimally small expansion of the gas at each step is offset by the heat absorbed from the surroundings and the temperature remains constant throughout the operation.

❖ The work done dw by the gas in each step of expansion is given by the product of the external pressure and the increase in volume. Thus

❖ $dw = (P-dP)\, dV = PdV$

❖ ignoring the product dPdV, as both the quantities are infinitesimal.

❖ The total work done w done by the gas in expansion, say, from original volume V_1 to final volume V_2 , will be the sum of the series of the terms PdV in which the value of P keeps on decreasing while volume of the gas keeps on increasing gradually.

❖ The result may be expressed mathematically as

$$w = \int_{V1}^{V_2} PdV$$

Where V_1 is the volume in the initial state and V_2 is the volume in the final state.

- The above integral can be evaluated by substituting

  $P = RT/ V$

For one moles of an ideal gas.

$$w = RT \int_{V1}^{V_2} dV/V = RT \ln V_2/V_1$$

Since in an ideal gas $P_1V_1= P_2V_2$

at constant temperature, above equation may also be written as

$$w= RT \ln (P_1/P_2)$$

For n moles, the above expressions may be written as

$$w =nRT\ln(V_2/V_1) = nRT \ln (P_1/P_2)$$

Work done in Reversible Isothermal Compression of a Gas

- ❖ Now suppose the gas undergoes isothermal reversible compression from volume V_2 to volume V_1 .
- ❖ The external pressure is will be made infinitesimally higher than P, the pressure of the gas inside the cylinder.
- ❖ Let the external pressure be P+dP. There will be an infinitesimal contraction in volume, dV, of the gas.
- ❖Then the work done by the surroundings in pushing the piston downward is given by

$$dw = (P+dP)dV = PdV$$

- ❖ ignoring the quantity dPdV,

❖ If compression is carried out reversibly in a series of steps from the initial volume V_2 to the final volume V_1, the work done W by the surroundings on the gas will be given by

$$w = \int_{V_2}^{V_1} P\,dV$$

❖ Assuming the gas to be ideal, P may be substituted by RT/ V in the above equation.

$$w = RT \int_{V_2}^{V_1} dV / V$$

$$w = RT \ln (V_1/V_2) = RT \ln (P_2/ P_1)$$

- For n moles of the gas, the above expression may be written as

$$w = nRT \ln (V_1/V_2) = nRT \ln (P_2/ P_1)$$

In the expansion of a gas – work done by the system on the surroundings
W= + ve

In the compression of a gas – work done by the surroundings on the system
W= - ve

Maximum work

- Work done by a gas on expansion= $P^{Ext} \Delta V$

- Where ΔV is the increase in volume.

- If expansion takes place reversibly , the external pressure P^{Ext} is only infinitesimally smaller than the pressure P of the gas.

- If however the external pressure is much smaller than the gas pressure, the expansion will take place rapidly i.e., irreversibly and the work done for the same amount of expansion will be much smaller since P^{Ext} is smaller.

- In extreme cases – the external pressure is zero

ie., gas expands in vacuum – the work done will be zero – No work is done by the system.

- The magnitude of work done by a system on expansion depends upon the magnitude of the opposing pressure.
- The closer is the opposing pressure to the pressure of the gaseous system in the cylinder, the greater is the work performed by the system on expansion.
- Maximum work coincides with thermodynamic reversibility.

Work done in Irreversible Expansion

i) Expansion against zero pressure (Vacuum) – free expansion
ii) Expansion against a particular constant external pressure

$P^{ext} < P$ – intermediate pressure.

In free expansion – external pressure is zero.

$$w = \int dw = \int P^{ext} dV = 0$$

Intermediate Expansion

Suppose the volume of the gas increases from V_1 to V_2 against a constant external pressure, P^{ext}.

.

- The work done is given by

$$w = \int_{v_2}^{v_1} P^{ext}\, dV = P^{ext} (V_2 - V_1)$$

P^{ext} is less than P, the work done during intermediate Expansion is less than the work done during reversible Expansion in which $P^{ext} = P$

Adiabatic Expansion

- No heat is allowed to enter or leave the system.

$$q = 0$$

From I law of Thermodynamics,

$$\Delta E = q - w$$

$$q = 0; \quad \Delta E = 0 - w$$

$$w = -\Delta E$$

Expansion

- Work is done by the system on the surroundings w= + ve
- Accordingly ΔE is negative, the temperature falls.
- The work done in this case is done at the expense of the internal energy of the gas.
- In compression w will be negative and hence ΔE = + ve
- Increase in internal energy and increase in temp.
- The work done by the surrounding on the system and work is stored in the system in increasing the internal energy .

- Calculation of ΔE

$$C_v = (\partial E/ \partial T)_v$$

$$dE = C_v\, dT$$

For a finite change

$$\Delta E = C_v\, \Delta T$$

Calculation of ΔH

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta (PV)$$

$$= \Delta E + R\Delta T$$

Substituting the value of ΔE, we get

$$\Delta H = C_v\, \Delta T + R\, \Delta T$$

$\Delta H = C_v \Delta T + R \Delta T$

$\Delta H = (C_v + R) \Delta T$

$\Delta H = (C_p) \Delta T$

Calculation of w

$q = 0; \ \Delta E = 0 - w$ $\quad w = -\Delta E = -C_v \Delta T$

It is known from the above equation that ΔE is dependent on ΔT.

The value of ΔT depends on the nature of the process – reversible or irreversible

The magnitude of thermodynamic properties also vary with the nature of the process.

Reversible Adiabatic Expansion

The final temperature in a reversible adiabatic expansion can be calculated from the expressions which relate the initial and final temperatures to the respective volume and pressure.

Relation between Temperature and Volume

Let P be the external pressure against which expansion takes place and ΔV is the increase in volume.

Then the external work done = $- P\Delta V$

Hence according to the first law

$$\Delta E = - P\Delta V$$

If ΔT is the fall in temperature , then

$$\Delta E = C_v \, dT$$

$$C_v \, dT = - PdV$$

For infinitesimally small quantities, as in reversible expansion

$$C_v\,dT = -\,PdV \qquad = -\,\frac{RT\,dV}{V}$$

$$C_v\,\frac{dT}{T} = -\,R\,\frac{dV}{V}$$

$$C_v\,d\ln T = -\,R\,d\ln V$$

Integrating the above equation between temperature T_1 and T_2

When the corresponding volumes V_1 and V_2, we have

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

$$\ln \frac{T_2}{T_1} = \frac{R}{C_v} \ln \frac{V_1}{V_2}$$

We know that $C_p - C_v = R$

Putting $\frac{Cp}{Cv} = \gamma$

$$\ln \frac{T_2}{T_1} = (\gamma - 1) R \ln \frac{V_1}{V_2}$$

$$\ln \frac{T_2}{T_1} = R \ln \left[\frac{V_1}{V_2} \right]^{(\gamma - 1)}$$

$$\frac{T_2}{T_1} = \left[\frac{V_1}{V_2} \right]^{(\gamma - 1)}$$

Relationship between Temperature and Pressure

For two states of one mole of an ideal gas

$$P_1 V_1 = RT_1$$

$$P_2 V_2 = RT_2$$

$$\therefore \frac{T_2}{T_1} = \frac{P_2}{P_1} \cdot \frac{V_2}{V_1} \quad \text{and} \quad \frac{V_1}{V_2} = \frac{P_2}{P_1} \cdot \frac{T_1}{T_2}$$

We know that

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad \text{——} \quad (1)$$

Substitute in eqn (1)

$$\therefore \frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\therefore P_2 V_2 (V_2)^{\gamma-1} = P_1 V_1 (V_1)^{\gamma-1}$$

(or) $$P_2 V_2^{\gamma} = P_1 V_1^{\gamma}$$

In general the relation between Pressure and volume is

$$PV^{\gamma} = \text{Constant}.$$

$$\frac{T_2}{T_1} = \left(\frac{P_2 \; T_1}{P_1 \; T_2}\right)^{\gamma-1}$$

$$\therefore \frac{T_2 \left(T_2\right)^{\gamma-1}}{T_1 \left(T_1\right)^{\gamma-1}} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\frac{T_2^{\gamma}}{T_1^{\gamma}} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

Irreversible Adiabatic Expansion

Free Expansion

The external pressure is zero, the work done w is also zero.

$$\Delta H = \Delta E + n\,R\,\Delta T = 0$$

Since for an ideal gas, E is a function of temperature.

$$\Delta E = 0 \;;\; \Delta T = 0$$

$$\Delta H = \Delta E + n\,R\,\Delta T = 0$$

$$\Delta E = 0 \;;\; \Delta T = 0 \qquad\qquad \Delta H = 0$$

Intermediate Expansion

Suppose volume of the gas increases from V_1 to V_2 against a constant pressure P^{ext} of the gas

$$- W = P^{ext} (V_2 - V_1) \text{ ------------------ (1)}$$

For First Law ($\Delta E = q + w$) in adiabatic expansion

$$W = \Delta E = C_v (T_2 - T_1) \text{ --------------- (2)}$$

$$- P^{ext} (V_2 - V_1) = C_v (T_2 - T_1)$$

$$C_v (T_2 - T_1) = P^{ext} (V_1 - V_2) = P^{ext} \left(\frac{RT_1}{P_1} - \frac{RT_2}{P_2} \right)$$

$$R\,P^{ext} \cdot \frac{(T_1 P_2 - T_2 P_1)}{P_1 P_2}$$

By calculating the values of C_v, T_1, P_1 P_2, we can calculate the temperature.

Joule Thomson Effect

- If a stream of gas at high pressure is allowed to expand by passing through a porous plug into vacuum or into a region of low pressure under adiabatic conditions, it gets cooled appreciably.

- Hydrogen and Helium are exceptions as they get warmed up in these conditions.

- The temperature below which a gas becomes cooler on expansion is known as the inversion temperature. For example, the inversion temperature of hydrogen is –48°C while that of helium is –242°C.

Joule Thomson Effect

- The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as Joule Thomson Effect.
- The cooling effect is due to decrease in the kinetic energy of the gaseous molecules since a part of this energy is used up in overcoming the van der Waals force of attraction existing between the molecules during expansion.

- It has been found that the Joule-Thomson effect is very small when a gas approaches ideal behavior.
- It has been concluded, Joule-Thomson effect is zero for an ideal gas.
- When an ideal gas expands in vacuum ,there is neither absorption nor evolution of heat (q=0).
- In an ideal gas van der Waals forces are negligible and there is no expenditure of energy in overcoming these forces of expansion.

- If an ideal gas expands in vacuum, it does no work because the pressure against which it expands is zero. w= 0. From First Law ΔE =0 (no change in internal energy).

- $$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

- An ideal gas is thermodynamically defined by two equations

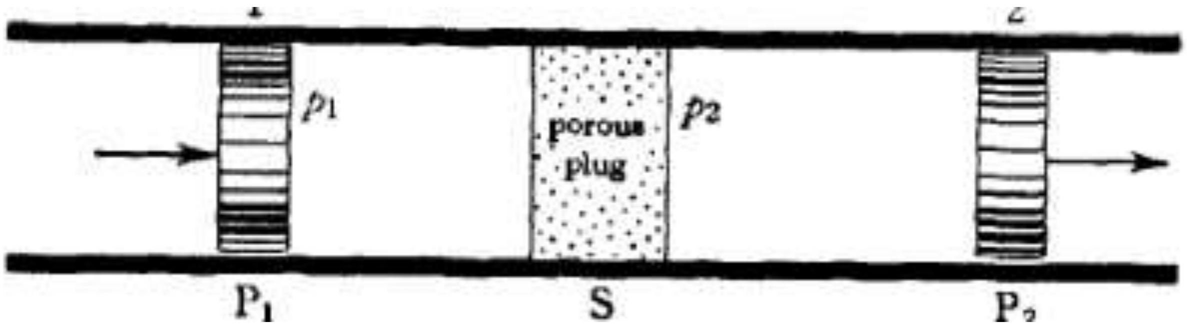
  PV = constant at constant temperature

- $$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

This is the internal pressure and is equal to zero because there are no intermolecular forces in a perfect gas.

Joule Thomson Coefficient

- It is an experimental technique for deriving the mathematical relationship between the fall of pressure of a gas on expansion and the resulting lowering of temperature.



The Porous Plug Experiment

- A tube made of non-conducting material is fitted with a porous plug in the middle and two pistons A and B on the sides.

- The tube is thoroughly insulated to ensure adiabatic conditions.
- A volume V_1 of the gas enclosed between the piston A and the porous plug G at a pressure P_1 is forced slowly through the porous plug by moving the piston A inwards and is allowed to expand to a volume V_2 at a lower pressure P_2 by moving the piston B outward,

- Work done on the system at the piston A = $+P_1V_1$

- Work done by the system at the piston B = $-P_2V_2$

- Net work done by the system at the piston A = $-P_2V_2 + P_1V_1$

- Since the expansion of the gas is done adiabatically, the system is not in a position to absorb heat from the surroundings. Therefore the system, performs work at the expense of the internal energy.

- The internal energy of the system changes from E_1 to E_2.

$$-P_2V_2 + P_1V_1 = E_2 - E_1$$

$$E_1 + P_1V_1 = E_2 + P_2V_2$$

$H_2 = H_1$ $\Delta H = 0$

Joule- Thomson expansion of a real gas occurs not with internal energy but with constant enthalpy. It is an isenthalpic process.

Since H is a state function dH is a complete differential, H is taken as function of P and T

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_p \, dT$$

For an adiabatic expansion, $\Delta H = 0$, hence

$$\left(\frac{\partial H}{\partial P}\right)_T dP + C_p \, dT = 0$$

$$C_p \, dT = -\left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\frac{dT}{dP} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_p} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_p}$$

$$\left(\frac{\partial T}{\partial P}\right)_H$$ - Joule-Thomson Coefficient ($\mu_{J.T}$)

Assuming $\mu_{J.T}$ to be constant over a small range

On rewriting eqn (1)

$$\frac{dT}{dP} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_p} \qquad \text{.........................} \quad (1)$$

$$\Delta T = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_p} \Delta P$$

ΔT is the fall in temperature produced by the fall in pressure ΔP.

Joule –Thomson Coefficient of an Ideal gas

- Since H = E + PV

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T} = -\frac{1}{C_p}\left[\frac{\partial (E + PV)}{\partial P}\right]_T$$

$$= -\frac{1}{C_p}\left\{\left(\frac{\partial E}{\partial P}\right)_T + \left(\frac{(\partial PV)}{\partial P}\right)_T\right\}$$

$$\mu_{J.T} = -\frac{1}{C_p}\left[\left\{\left(\frac{\partial E}{\partial V}\right) \times \frac{\partial V}{\partial P}\right\}_T + \left(\frac{(\partial PV)}{\partial P}\right)_T\right] \text{-------------(a)}$$

Since for an ideal gas

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

Hence equation (a) reduces to

$$\left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = 0$$

Since for an ideal gas, PV is a constant at constant temperature ,

$$= \left(\frac{(\partial PV)}{\partial P}\right)_T = 0$$

Hence equation (a) reduces to zero and $\mu_{J.T} = 0$

Joule –Thomson Coefficient for a real gas

- For a real gas $\left(\frac{\partial E}{\partial V}\right)_T$ is positive.
- Suppose a real gas expands in vacuum thus doing no external work.
- However some work will definitely be done in separating the gas molecules against the force of cohesion (van der Waals force) which exist between the molecules of a real gas.
- The work is stored in the gas in the form of potential energy.
- The potential energy of the gas increases.

- If no heat is gained from outside, the kinetic energy of the gas decreases by an equivalent amount and there would be a fall of temperature of the gas.

- Temperature is kept constant, by absorption of heat from outside.

- The kinetic energy remains the same.

- Thus, during isothermal expansion of a real gas there is net increase in the energy of the gas (Potential energy).

- Hence,

$$\left(\frac{\partial E}{\partial V}\right)_T \text{ is positive.}$$

- But, the factor $\left(\frac{\partial V}{\partial P}\right)_T$ in equation (a) is negative

the volume of a gas invariably decreases as the pressure increases at constant temperature.

Hence the factor is $\left(\frac{\partial E}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial P}\right)_T$ negative.

For reference only

$$\mu_{J.T} = -\frac{1}{C_p}\left\{\left(\frac{\partial E}{\partial V}\right) \times \frac{\partial V}{\partial P}\right\}_T + \left(\frac{(\partial PV)}{\partial P}\right)_T \text{-------------(a)}$$

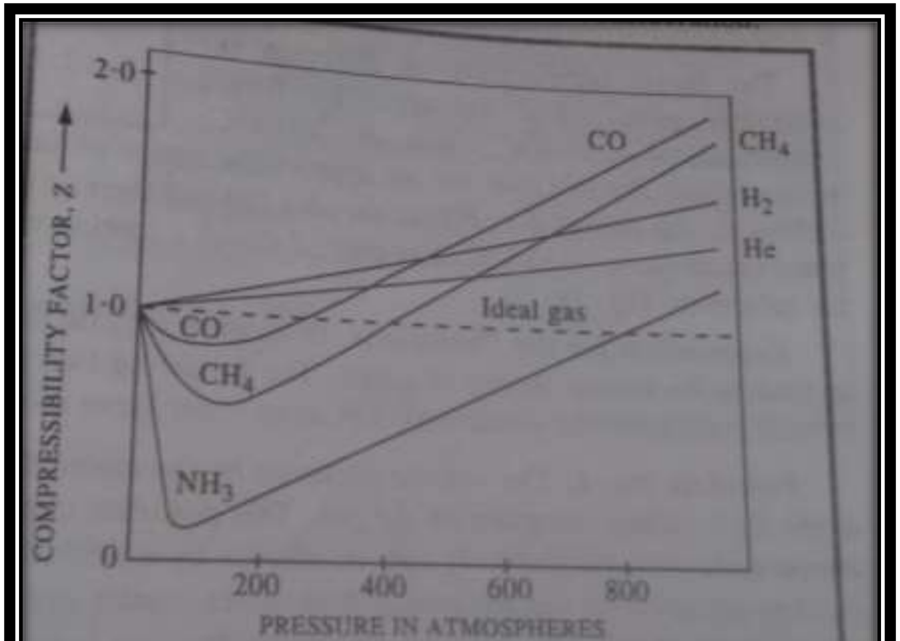


Fig. 1. Deviations of real gases from ideal behaviour.

Ref: Puri, Sharma & Pathania

❖Some of the real gases at ordinary temperature show the above behavior.

❖ At extremely low pressures all the gases are known to have the values of Z (compression factor) close to unity – ideal behavior.

At high pressures $Z > 1$ indicating the gases are less compressible than ideal gas. This is because at high pressures the molecular forces are repulsive.

❖ Thus at ordinary temperatures and low and moderate pressures , both the terms in bracket in eqn (a) are negative.

- Since the heat capacity is always positive, it follows $\mu_{J.T}$ is positive for real gases at ordinary temperature and at low and moderate pressures.

- Thus, if ΔP is negative there is fall in pressure, then ΔT is also negative.

From Figure

- When the pressure is very high, the value of PV for all gases increases as the pressure increases…

$$\left(\frac{\partial (PV)}{\partial P}\right)_T$$

becomes positive.

Hence the factor is $\left(\frac{\partial E}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial P}\right)_T$ negative, almost remains constant.

- Two factors within the brackets in eqn (a) one remains negative and practically constant, but the other factor becomes positive and its magnitude increases with increase in pressure.

- Hence as the pressure increases , the magnitude of Joule-Thomson coefficient goes on decreasing and becomes zero when the two factors become equal in magnitude.

- With continued increase in pressure, the magnitude of the positive term exceeds that of the negative term.

- Joule- Thomson coefficient in that case becomes negative.

- If ΔP is negative; ΔT is positive.

- Under such conditions, the throttled expansion of a real gas is accompanied by increase in temperature. For reference only

$$\mu_{J.T} = -\frac{1}{C_p}\left\{\left[\left(\frac{\partial E}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial P}\right)_T\right] + \left[\frac{\partial (PV)}{\partial P}\right]_T\right\} \quad \text{-------------(a)}$$

Calculation of Joule-Thomson Coefficient and the Inversion Temperature

It can be done with the help of van der Waal's equation. Since both a and b are small, the term ab / V^2 in the van der Waals's equation can be neglected provided the pressure is not high.

$$PV = RT - \frac{a}{V} + bP$$

$$PV = nRT \quad ; \quad n=1 \qquad\qquad V = \frac{RT}{P}$$

$$PV = RT - \frac{aP}{RT} + bP$$

Divide through out by P

$$\frac{PV}{P} = \frac{RT}{P} - \frac{aP}{PRT} + \frac{bP}{P}$$

$$V = \frac{RT}{P} - \frac{a}{RT} + b$$

Differentiate with respect to temperature at constant pressure, we get

$$\left[\frac{\partial V}{\partial T}\right]_P = \frac{R}{P} - \frac{a}{R}\left[\frac{1}{T}\right]$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2}$$

We know that

$$V = \frac{RT}{P} - \frac{a}{RT} + b$$

Multiply the equation by P

$$PV = \frac{PRT}{P} - \frac{aP}{RT} + bP$$

$$PV - bP + \frac{aP}{RT} = RT$$

$$PV - bP + \frac{aP}{RT} = RT$$

Divide throughout by PT

$$\frac{P(V - b)}{PT} + \frac{aP}{RTPT} = \frac{RT}{PT}$$

$$\frac{(V - b)}{T} + \frac{a}{RT^2} = \frac{R}{P}$$

Substituting the value of R/P in the equation

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2}$$

$$\frac{(V - b)}{T} + \frac{a}{RT^2} = \frac{R}{P}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{(V-b)}{T} + \frac{a}{RT^2} + \frac{a}{RT^2}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{(V-b)}{T} + \frac{2a}{RT^2}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T}\left[(V-b) + \frac{2a}{RT}\right]$$

$$T\left(\frac{\partial V}{\partial T}\right)_P = (V-b) + \frac{2a}{RT}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b$$

From thermodynamics we have

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \frac{\partial H}{\partial P}$$

Substitute for V in the above equation

$$T\left(\frac{\partial V}{\partial T}\right) - T\left(\frac{\partial V}{\partial T}\right)_P + \frac{\partial H}{\partial P} = \frac{2a}{RT} - b$$

$$-\left(\frac{\partial H}{\partial P}\right)_T = \frac{2a}{RT} - b$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{-\left(\frac{\partial H}{\partial P}\right)_T}{C_p}$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

From the above expression we conclude that Joule Thomson coefficient will be positive when 2a/RT is greater than b. It will become zero when 2a/RT is equal to b and negative if 2a/RT is less than b. Since a, b and R are constants, therefore magnitude and sign of Joule Thomson coefficient will be dependent only on the temperature at which the expansion of the gas occurred.

The temperature at which the sign of the Joule-Thomson coefficient changes is known as the inversion temperature. At this temperature. $\mu_{J.T.}$ is zero. Thus equation (21) will be zero when term inside the parenthesis will be zero so we get,

$$2a / RT_i = b \text{ or } T_i = 2a / Rb \qquad \text{...(22)}$$

where Ti stands for the inversion temperature. Thus, the inversion temperature is dependent on the van der Waals constants a and b of the gas.

$$\mu_{J.T} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$