- **INTRODUCTION:**

This is an important branch of physical chemistry. The chapter deals with quantitative relationships between heat and other forms of energy.

Thermodynamics consist of three laws: first law is the conservation of energy while second law deals with the condition of feasibility of a process. Third law provides method of evaluation of various thermo-dynamical properties. Later zeroth law introduces the concept of temperature. The laws are derived from the direct human experience and so it has no exception. This is why it is called exact science.

The laws of thermodynamics (TD) apply to the system at equilibrium and so time variable is totally absent in this chapter. Thermodynamics concerns with the macroscopic properties viz. pressure (P), temperature (T), volume (V) and mole number (n) of the system. Thermodynamics does not consider the constituent particles of the system as such.

Thermodynamics has a predicting value. It can predict whether a process is feasible or not under a set of experimental conditions.

Some important terms used in thermodynamics:

1) System and Surroundings: System is a part of the universe selected for thermodynamic-study and separated by definite boundary – real or imaginary. The rest part of the Universe is called Surroundings.
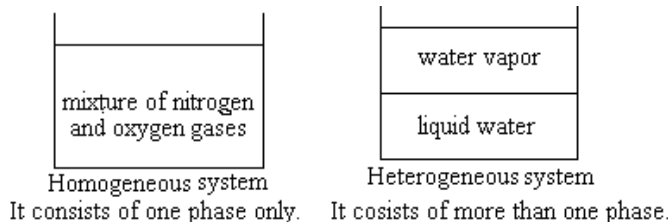
That is,

The laws of thermo-dynamics

Valid for equilibrium

Predicting value

Homogeneous and heterogeneous system
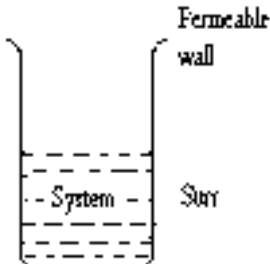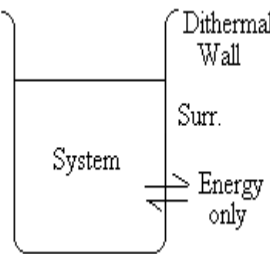
System + Surroundings = Universe
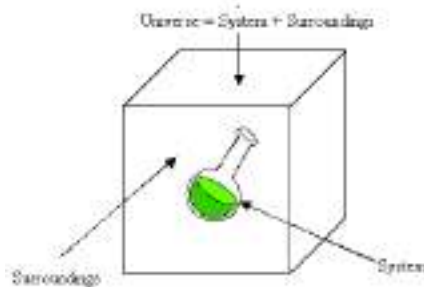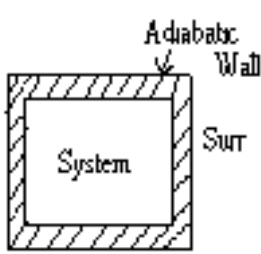
System may be homogeneous (uniform in all parts) or heterogeneous (not uniform in all parts). Examples of homogeneous system are, mixture of gases, mixture of miscible liquids, pure solid etc. Heterogeneous system is liquid with vapor, mixture of immiscible liquids, mixture of solids etc.

Universe = System + Surroundings

Surroundings

System

mixture of nitrogen and oxygen gases

Homogeneous system
It consists of one phase only.

water vapor
liquid water

Heterogeneous system
It cosists of more than one phase.

On the basis of types of boundary walls, systems can be again classified into three types-

(a) Open System	(b) Closed System	(c) Isolated System
Energy and mass are exchanged between system and surroundings. Example: water in a beaker, Zn is reacting with dilute H_2SO_4 in a beaker. Mass and energy both are not conserved in the system.	Mass is not allowed to transfer between system and surroundings so mass of the system is conversed (fixed). Energy is exchanged. Example: liquid in equilibrium with vapor in a sealed tube.	Mass and energy both are not allowed to exchange between the system and surroundings. Both energy and mass of the system remains fixed. Example: boiling water in a thermo flask

Three types of systems (margin label)

Interaction of the open system with the surroundings is maximum while that of the isolated system is nil. Any impact on the isolated system by the surroundings is taken zero.

2) **Properties of a system :**

The measurable properties of a system are of two types.

Extensive and intensive properties. (margin label)

a) Extensive: Dependent on the amount of material present in the system.
For example, volume, mass, heat capacity, mole number (n) and the thermodynamical properties like internal energy (U) , enthalpy (H), entropy (S) , work function (A) and free energy (G).

b) Intensive: Independent of amount of material present in the system.
For example, temperature(T), pressure(P), density(d), refractive index, viscosity, surface tension, concentration and molar properties.

3) **State of System:**

The state of a system is described by the state variables like P, T, V and n.
But for closed system, n is fixed and since these state variables are connected by an equation, hence, out of P, T and V only any two can describe the state of the system.
Thus for closed or isolated system, state is designated by either (T, V) or (T, P) or (P, V) while n is fixed.
Any change in the values of the variables will change the state of the system and it will attain a new state. If it is desired to bring the system back to its initial state, the variables will have to obtain their original value.

4) **Path:**

It is the sequence of intermediate steps or stages arranged in order for the system to follow from initial state to final state.

5) Thermodynamical Equilibrium:

When all the observable properties like T, P, chemical composition remain time-invariant, the system is under thermodynamic equilibrium
(It satisfies simultaneously thermal, mechanical and chemical equilibria).
Difference with steady state:

Thermodynamic equilibrium and steady-state

(a) An isolated system is in equilibrium when its macroscopic properties remain constant with time.

(b) An non-isolated system is in equilibrium when the following two conditions hold

(i) The system's macroscopic properties remain constant with time and

(ii) Removal of the system from contact with its surroundings causes no effect in the properties of the system.

If the condition (i) holds but condition (ii) does not hold, the system is in steady state.
[Ph. Ch. – Levine (P5)]

6) Process: It is the method of operation by which the system changes its state.

It is of following types:

(a) Cyclic process: After a series of changes the system comes back to its initial state. All the variables take its initial value.

(b) Isothermal process: Temperature (T) remains constant during the process. Heat-exchange continues. Walls of the system must be perfectly conducting thermally.

Different types of processes

(c) Adiabatic process: Heat exchange is not allowed with the surroundings during the process. Temperature varies. It occurs for the isolated system only.

(d) Isobaric process: Pressure (P) remains constant thus volume will vary. For example, heating of water in a beaker, open to 1 atm pressure.

(e) Isochoric process: Volume (V) remains constant, so pressure (P) changes.

(f) Polytropic process: Heat capacity remains fixed.

(g) Reversible process: During the change of state, driving force and opposing force differ by infinitesimal amount and final state of the system can be reversed without the aid of external agency.

Let n mole of a gas is enclosed in a cylinder fitted with weightless, frictionless movable piston. The gas is expanded from the initial state (P_1, V_1) to (P_2, V_2) by reversible process. The driving pressure (force per unit area) P_1, infinitesimally greater than opposing pressure P_1-dP, where, $dP \to 0$.
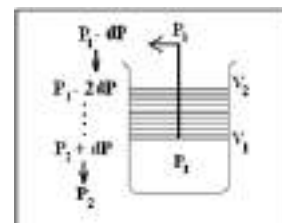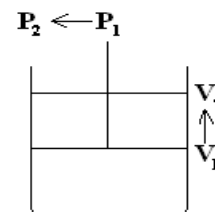
Reversible expansion of a gas process

The volume is increased by dV. At each step, the system attains equilibrium. For the expansion of the gas, infinite time is required to effect the change so it is not a real process, but a concept.

Only reversible phase change (viz. melting of ice at 0^oC and 1 atm. pressure) is a real reversible process. The rev. process involves very large number of equil^m. states, so reversible process is also called equil^m. process.

(h) Irreversible process: When the above conditions are not maintained, the process becomes irreversible. This process is rapid and spontaneous. It occurs against constant opposing pressure. The initial state of the system can not be reversed without the aid of external agency by this process.

Irreversible process

In the example of expansion of a gas, the process occurs against constant external pressure. This is a real process.

7) Perfectly differential quantity (X):

For a quantity to be perfectly differential, following conditions are to be satisfied.
Let the property be X, then
(i)   X must be a state function and single valued.
(ii) dX will be independent of path of transformation between two specified states.
(iii) $\oint dX = 0.$ i.e. change of X of the system in the cyclic process is zero.

(iv) If X = f(T, P), then $\dfrac{\partial^2 X}{\partial T \partial P} = \dfrac{\partial^2 X}{\partial P \partial T}$ i.e. it obeys Euler's reciprocal relation.

8) Work (w):

Different types of work

When an object is displaced through a distance dx against a force F, the work done,
w = F$_{opposing}$. dx
(i)   Mechanical work = = P$_{opp.}\times$ dV
(ii) Gravitational work = mgh
(iii) Electrical work = Q $\times$ dE, when dE is the potential difference through which
      Q amount of charge is flowing.

9) Heat (q):

Heat is a form of energy. It can be produced from work or partly converted into work. Heat flows from higher temperature to lower temperature until T becomes equal (thermal equilibrium).
Heat is a special form of energy, since all other forms of energy are easily converted into heat energy but latter has no tendency to be transformed into other forms of energy. This is why vast amount of heat energy is stored in the universe.

10) Internal energy (U):

Origin of internal energy

A system by virtue of its existence must possess a store of energy. This is evidenced by the evolution of heat energy when liquid freezes, by production of electrical energy in Daniel cell using the chemical reaction between Zn and H_2SO_4. Carbon (C) when burnt produces huge amount of heat energy.
This stored-up energy is called the internal energy of the system. This thermodynamic property is denoted by U. It is a perfectly differential quantity and an extensive in nature. U is normally a function of T and V i.e. U = f (T, V). The energy possessed by a system due to translational, vibrational and rotational motion of the molecule, constitutes the magnitude of internal energy. The motions of electrons and nuclei also contribute to U.
This energy is associated with the system by virtue of its molecular constitution i.e. inter-particle attractive and repulsive potential (called internal potential energy) and by virtue of its motion of constituent particles (internal kinetic energy).
Energy acquired by a system in a force field like electrical, gravitational, magnetic or surface etc. are termed as external energy, and not considered as part of internal energy.

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Related questions with hints to answer:

1. Justify/Criticize the following statement:
  (a) A finite change through a reversible process would require an infinite time. [BU'92]
     HINT. Partially correct. True for reversible expansion of a gas but not true for
   reversible phase change of a substance.

2. A cyclic process ABCA shown in the following V-T diagram is performed with a constant mass of an ideal gas. Show the same process on P-V diagram. Give your arguments.[BU'95]
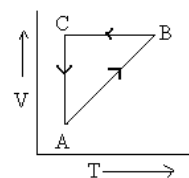
HINT: Arguments: In V-T diagram, A → B, P is constant, so
V α T, linear plot. B→C, V is constant, T decreases so P will decrease.

C → A, T is constant, V decreases so P will increase.

Thus in P – V diagram, A→B, P constant, but V increases, B → C, V is constant But P decreases, C → A, T is constant so the plot is rectangular
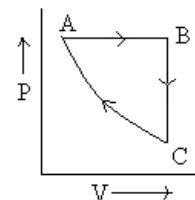
hyperbola (Boyle's law).

3 Explain with reason ─ an infinitely slow process is not necessarily a reversible process.
[BU'90]

Ans: For a process to be reversible, the following conditions are maintained.
(a) Driving force and opposing force must differ by infinitesimal amount and
(b) the process could be reversed without help of external agency.
The process may be slow and this is not the criteria of reversibility of a process.

4(i) Identify with reasons, the following process as thermodynamically reversible or irreversible.
[CU'91]
(ii) Freezing of water at 0^oC and 1 atm pressure. Ans. Reversible process.

(iii) Freezing of super cooled water at $–10^0$C and 1 atm pressure. Ans. Irreversible process.

(iv) 1 mole of N_2 at constant T is held by a piston under 20 atm pressure and the pressure is suddenly released to 10 atm. Ans. Irreversible Process → sudden change.

5(i) Classify the following as extensive and intensive properties:
Pressure, volume, Free energy, Chemical potential, Temperature and Density
Ans. Extensive→ volume, free energy
Intensive→ pressure, chemical potential, temperature, density.

Statement of the Law.

It is the law of conservation of energy. It states that "The energy can neither be created nor be destroyed but it can be transformed from one form to another."

1ˢᵗ law & perpetual motion machine

In other words, whenever one form of energy disappears, an exactly equivalent amount of another form must reappear. This statement rejects the possibility of constructing perpetual motion machine of the first kind. Formerly it was supposed that it is possible to construct a machine which would produce work for indefinite period of time without supplying any form of energy.

Mathematical formulation of the law

Let q amount of heat is supplied to a system containing one mole of gas in a cylinder fitted with weightless, frictionless movable piston. The gas expands from volume V_1 to V_2 while temperature changes from T_1 to T_2 at constant pressure. It is found that q 〉 w, so it supposed that (q- w) amount of heat goes to increase the internal energy of the system.

Thus, q – w = dU. Or, q = dU + w ------ (1)

This is the mathematical form of the 1ˢᵗ law.

Different forms of the law

When w is restricted to the mechanical work only, w = +PdV
[Workdone by the system is (+)ve while work done on the system is (–)ve].

Putting this, we get the 1ˢᵗ law as, q = dU + PdV --------- (2)

Again, U = f (T, V), so, on partial differentiation, $dU = \left(\dfrac{\partial U}{\partial T}\right)_V dT + \left(\dfrac{\partial U}{\partial V}\right)_T dV$

Putting we get generalized mathematical form of the law,

$$q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV \quad \text{--------- (3)}$$

If the process is conducted at constant V, then $q_V = \left(\dfrac{\partial U}{\partial T}\right)_V dT$

Thermodynamical definition of C_V

or, $\left(\dfrac{q}{\partial T}\right)_V = \left(\dfrac{\partial U}{\partial T}\right) = C_V$ constant volume molar heat capacity. So, $\left(\dfrac{\partial U}{\partial T}\right) = C_V$.

Therefore, $q = C_V dT + \left[P + \left(\dfrac{\partial U}{\partial V}\right)_T\right]dV$ ---------- (4)

For ideal gas, $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$, since there is no molecular interaction in ideal gas, so internal energy does not depend on expansion or contraction of the gas.

Thus, for ideal gas, U = f (T) only and independent of volume.

The 1ˢᵗ law for ideal gas becomes, $q = C_V dT + PdV$ ---------- (5)

For n moles of ideal gas, $q = nC_V dT + PdV$ ---------- (6)

For real gas which obeys Vander Waals equation, $\left(\dfrac{\partial U}{\partial V}\right)_T = \dfrac{a}{V^2}$. So the 1ˢᵗ law becomes

$$q = C_V dT + \left[P + \frac{a}{V^2} \right] dV \quad \text{------------ 1 mole vander Waals gas --------(7)}$$

$$q = nC_V dT + \left[P + \frac{an^2}{V^2} \right] dV \quad \text{----------- n moles vander Waals gas ------(8)}$$

Expression of ΔU for ideal & real gases

For n moles ideal gas, $dU = nC_V dT$ and for vander Waals gas, $dU = nC_V dT + \frac{an^2}{V^2} dV$

These relations can be used to calculate the change in internal energy of a process provided no phase change or chemical transformations occur. For these two latter cases, relations are not valid.

Some special cases of the law

(1) Cyclic process: The internal energy change in this process is $dU = 0$ so, $q = w$
 i.e. heat is completely converted into work in the cyclic process.

(2) Isothermal process: For ideal gas, $dU = C_V dT = 0$ since T is constant. $dT = 0$.
 1st law is $q = w$, i.e. heat is completely converted into work.

(3) Adiabatic process: $q = 0$. So, $0 = dU + w$ or, $w = -dU$.
 The work done by the system is at the cost of its own internal
 energy. When the system does work, its internal energy
 decreases.

Fall in T in adiabatic expansion

 For ideal gas, $dU = C_V dT = C_V (T_2 - T_1)$ and $w = PdV = P(V_2 - V_1)$.
 Putting, $P(V_2 - V_1) = -C_V(T_2 - T_1)$
 Or, $P(V_2 - V_1) = C_V(T_1 - T_2)$ ....ideal gas, mech. work, adiab. proc.
 Thus for adiabatic expansion, $V_2 \rangle V_1$, so, $T_1 \rangle T_2$
 i.e. adiabatic expansion of an ideal gas causes fall in temperature.
 Similarly, adiabatic compression of an ideal gas causes rise in temperature

(4) Isochoric process: V = constant, so $dV = 0$, $q = dU$ if work is only mechanical.
 i.e. no work is done and total heat supplied goes to increase

 the internal energy .

Relation between P, V and T for ideal gas in reversible adiabatic process:

(i) 1st law for adiabatic process and ideal gas, $0 = C_V dT + PdV$ or, $C_V dT = -PdV$.

But for 1 mole ideal gas $P = \frac{RT}{V}$. So $C_V \frac{dT}{T} = -R \frac{dV}{V}$.

Integrating (since the process is reversible), within limits and assuming C_V independent of T,

we have, $C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$ or, $C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$

or, $\ln \frac{T_1}{T_2} = \frac{R}{C_V} \ln \frac{V_2}{V_1}$ or, $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\frac{R}{C_V}}$

since, $R = C_P - C_V$ for ideal gas, or R/C_V $(C_P - C_V)/C_V = \gamma - 1$, as , $\gamma = C_P/C_V$.

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

Relation between T & V

or, $$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad \text{------- ideal gas, rev. adiab. proc.}$$

(ii) Using 1st law for adiabatic process, $0 = C_V dT + PdV$. But for ideal gas $PV = RT$

or, $PdV + VdP = RdT$. Replacing dT from the 1st law equation,

$$0 = \frac{C_V}{R}\left(PdV + VdP\right) + PdV \qquad or, \qquad \frac{C_V + R}{R}PdV = -\frac{C_V}{R}VdP .$$

But, $\qquad \dfrac{C_V + R}{R} = \dfrac{C_P}{R}$. $\qquad$ Rearranging, $\qquad C_P\dfrac{dV}{V} = -C_V\dfrac{dP}{P}$.

Integrating within limits, $\quad \displaystyle\int_{P_1}^{P_2}\frac{dP}{P} = -\frac{C_P}{C_V}\int_{V_1}^{V_2}\frac{dV}{V} \quad or,\ \ln\frac{P_2}{P_1} = -\gamma\ln\frac{V_2}{V_1}$

Relation between P & V

or, $\qquad\qquad P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \qquad$ ….. ideal gas rev. adiab. proc.

(iii) Replacing dV using ideal gas equation in the 1st law, we get

$$0 = C_V\,dT + R\,dT - V\,dP = \left(R + C_V\right)dT - V\,dP \qquad or, \qquad VdP = C_P dT$$

Replacing $\qquad\qquad V = \dfrac{RT}{P}, \qquad$ we get, $\qquad RT\dfrac{dP}{P} = C_P dT$.

So integrating, $\quad \dfrac{R}{C_P}\displaystyle\int_{P_1}^{P_2}\frac{dP}{P} = \int_{T_1}^{T_2}\frac{dT}{T} , \quad or,\ \ln\frac{T_2}{T_1} = \ln\left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}} or, \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}} .$

But, $\dfrac{R}{C_P} = \dfrac{C_P - C_V}{C_P} = 1 - \dfrac{1}{\gamma} = \dfrac{\gamma - 1}{\gamma}$.

So, $\qquad\qquad \dfrac{T_2}{T_1} = \left(\dfrac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \qquad or, \qquad \dfrac{T_2}{T_1} = \left(\dfrac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}}$

Relation between T & P

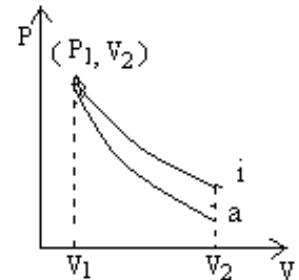or, $\qquad\qquad T_1^{\gamma}P_1^{1-\gamma} = T_2^{\gamma}P_2^{1-\gamma} \qquad$ … ideal gas rev. adiab. proc.

Show that adiabatic curve is steeper than isothermal in the P – V diagram.

We have to show adiabatic slope $\rangle$ isothermal slope

or, $\qquad\qquad \left(\dfrac{dP}{dV}\right)_a \rangle \left(\dfrac{dP}{dV}\right)_i$

For isothermal change, $\ PV = $ const. or, $PdV + VdP = 0$

or, $\left(\dfrac{dP}{dV}\right)_i = -\dfrac{P}{V}$ -------- rev. isotherm. proc., ideal gas.

For adiabatic change of ideal gas, $\ PV^{\gamma} = $ const. $\qquad$ or, $\qquad \ln P + \gamma \ln V = $ const.

or, $\qquad\qquad \dfrac{1}{P}dP + \dfrac{\gamma}{V}dV = 0 \qquad$ or, $\qquad\qquad \left(\dfrac{dP}{dV}\right)_a = -\gamma\left(\dfrac{P}{V}\right)$.

But, $\qquad \gamma \rangle 1 \qquad$ so, $\qquad \dfrac{\left(dP/dV\right)_a}{\left(dP/dV\right)_i} = \gamma \rangle 1$

Thus adiabatic curve is steeper than isothermal in the P-V diagram.
The comparison of reversible isothermal expansion and reversible adiabatic expansion of a gas can be understood in the following way.
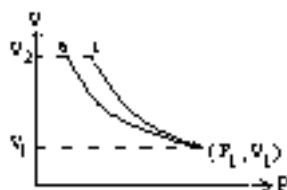Let the gas expands from the initial volume V_1 and pressure P_1 to the final volume V_2 in the above two processes.

Final pressure in a adiab. proc. is less than that in isotherm proc.

For isothermal expansion, $T_1 = T_2$ but for adiabatic expansion $T_1 \rangle T_2$, since temperature falls in adiabatic expansion. Hence, the final pressure (P_2') in adiabatic process must be less than the final pressure (P_2) for the isothermal expansion.

So, adiabatic curve is steeper than isothermal in the P – V diagram.
However, when V is plotted against P, isothermal curve is steeper than adiabatic curve

For this reversible expansion of ideal gas, final pressure in the adiabatic process is less than that in the isothermal process. Since the initial state of the gas is same in both the processes, isothermal curve is more steep than the adiabatic curve.

Related questions with hints to aswer:

BU'96

A gas is suspected to be Neon or Nitrogen. When a given sample of the gas at 25^0C is expanded adiabatically from 5L to 6L, the temperature came down to 4^0C. What was the gas?

Solution

Using the relation $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ or, $\left(\dfrac{V_2}{V_1}\right)^{\gamma-1} = \dfrac{T_1}{T_2}$ or, $\left(\dfrac{6}{5}\right)^{\gamma-1} = \dfrac{298}{277}$

solving, $\gamma = 1.4$.   So the gas was diatomic, hence it was nitrogen.

CU'91

Identify with reasons, the following processes as thermodynamically reversible or irreversible:
(l) Freezing of water at 0^oC and 1 atm pressure.
(m) Freezing of super cooled water at $– 10^o$C and 1 atm.
 (n) One mole of nitrogen at constant T is held by a piston under 20 atm pressure and the pressure is suddenly released to 10 atm.

Answer

(l) It is reversible phase change.
 (m) A small jerk to the system makes the process to occur rapidly so it is an irreversible phase change.
 (n) Irreversible process as it occurs suddenly.

CU'91

State whether the thermodynamic relation PV^{γ} = constant, is valid for a reversible process, an irreversible process or both. Give reasons.

Answer

It is valid only for reversible process. Integration is done to get the relation, as P and V change continuously so the process is reversible.

CU'93

Establish the relation PV^{γ} = constant for an adiabatic process.
Ans. See in the Text, page 8.

CU'94,

(i) From the conventional treatment of the 1st law of thermodynamics (conservation of energy principle), arrive at an alternative statement " in an isolated system, work done is independent of the path. (m = 2).
 (ii) If in a P – V change, work done can be obtained by integration, what should be the essential condition for the process? (m = 2)

Answer

(i) 1st law states, q = dU + w . For isolated system, q = 0, so w = $–$ dU , but U is a state function so dU does not depend on path. Hence w is also independent of path.
 (ii) The P-V change should be the reversible as P and V change continuously.

CU'98, (ii): Is it possible to draw the path for state I to state II if the change is brought about irreversibly? Explain. (m = 2).

Answer It is not possible to draw the path as the intermediate state points are not known for the change. Only the coordinates of the state I and state II are known.

BU'92, Justify / criticize: "A finite change through a reversible process would require an infinite time."

(4)

Answer The statement is not always true. For reversible expansion of a gas, opposing pressure is infinitesimally smaller than driving pressure i.e. $dP \rightarrow 0$, so infinite time is required for completion of the process.

But in the reversible phase change, viz. melting of ice at $0^{\circ}C$ and 1 atm pressure, finite time is required to complete the process.

Problem: For silver C_P (J K^{-1} mol^{-1}) = 23.43 + 0.00628 T. Calculate ΔH if 3 moles of silver are raised from $25^{\circ}C$ to the melting point $961^{\circ}C$ under 1 atm. (Ph.Ch.— Castellan, Ex.7.2)

Solution: At constant pressure, $dH = n\,C_P\,dT$ .Integrating within limits & using data given,

we get, $\int_{H_1}^{H_2} dH = n\int_{T_1}^{T_2} C_P dT$ $or, H_2 - H_1 = n\int_{T_1}^{T_2} \left(23.43 + 0.00628T\right)dT$ = 79,290 J.

$$\Delta H = n\left[23.43(T_2 - T_1) + \frac{0.00628}{2}\left(T_2^2 - T_1^2\right)\right]$$

$$= 3\left[23.43(1234 - 298) + \frac{0.00628}{2}\left(1234^2 - 298^2\right)\right] = 79,300\,J.$$

Joule's Expansion (Free Expansion):

In 1843, Joule tried to determine $\left(\frac{\partial U}{\partial V}\right)_T$ of a gas by measuring the temperature change after free expansion of the gas into vacuum. This experiment is repeated by Keyes and Sears in 1924 with an improved set-up. Bulb A is filled up with gas at pressure P while bulb B is evacuated. The walls of the bulbs are adiabatic. The valve is operated and the gas expands against vacuum. When equilibrium is reached, the temperature is noted by the thermometer (T).

Improved
Set-up
by Keyes
& Sears
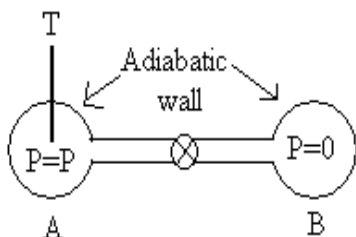
Since the walls of the bulbs are adiabatic, so $q = 0$.

The gas expands against vacuum, so, $w = P_{ext}\, dV = 0$.

Therefore $q = dU + w$ or, $0 = dU + 0$ or, $dU = 0$.

This is a constant internal energy process, U = constant. The experiment measures temperature change with change in volume at constant U,

$\left(\frac{\partial T}{\partial V}\right)_U$ or more precisely $\Delta T/\Delta V$ at constant U.

This quantity is called Joule's co-efficient (μ_J) and $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$.

Relation between μ_J and $\left(\frac{\partial T}{\partial V}\right)_U$: We know that $U = f(T,V)$

so, $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$ But for this Joule's free expansion, $dU = 0$.

So, $0 = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$ Or, $0 = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$

$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$ or, $\mu_J = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$

Relation
between μ_J
&
$\left(\frac{\partial U}{\partial V}\right)_T$

or, $\left(\frac{\partial U}{\partial V}\right)_T = -C_V \times \mu_J.$

Joule measured $\mu_J = 0$ hence, $\left(\frac{\partial U}{\partial V}\right)_T = 0.$

But his experimental set-up is so poor that his result is meaningless. Keyes-Sears showed that $\left(\frac{\partial U}{\partial V}\right)_T$ is small but definitely non-zero.

Now it is taken, $\left(\frac{\partial U}{\partial V}\right)_T = 0.$ for ideal gas and $\neq 0$ for non-ideal gas.

Heat-change (*q*) and work-done (*w*) are not perfectly differential quantity

The heat change (*q*) and work done (*w*) of a system between fixed initial and final states depend on nature of the process. Various examples can be cited in support of the fact. But we shall prove it by use of Euler's theorem. Let the heat change is perfectly differential and denoted by *dq* instead of q. Hence, from the 1st law, we have

$$dq = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV \quad \text{or,} \quad \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

Use of Euler's theorem

Differentiating with respect to *V* at constant *T*, $\quad \frac{\partial^2 q}{\partial V \partial T} = \frac{\partial^2 U}{\partial V \partial T}$ ----------(A)

Again, $\qquad\qquad\qquad \left(\frac{\partial q}{\partial V}\right)_T = P + \left(\frac{\partial U}{\partial V}\right)_T.$

Differentiating with respect to *T* at constant *V*, $\quad \frac{\partial^2 q}{\partial T \partial V} = \left(\frac{\partial P}{\partial T}\right)_V + \frac{\partial^2 U}{\partial T \partial V}$ ------ (B)

But RHS of (A) & (B) are not equal since $\left(\frac{\partial P}{\partial T}\right)_V \neq 0$, hence, $\frac{\partial^2 q}{\partial V \partial T} \neq \frac{\partial^2 q}{\partial T \partial V}$

Euler's theorem is not satisfied, so *dq* is not perfectly differential and hence we represent it as *q̣*. đq is often written instead of q to denote that heat change is not exactly differential quantity. By the same argument, we can prove that *w* is not perfectly differential. Let it be represented as dw and

$$dw = PdV \text{ but } V = f(T,P) \text{ or, } dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

so, $\qquad\qquad\qquad dw = P\left(\frac{\partial V}{\partial T}\right)_P dT + P\left(\frac{\partial V}{\partial P}\right)_T dP.$

By the use of Euler's theorem, it could be shown that $\frac{\partial^2 w}{\partial T \partial P} \neq \frac{\partial^2 w}{\partial P \partial T}$.

Hence *dw* is not perfectly differential and we write work done by w only.

Enthalpy (H): It is defined as,

$$H = U + PV.$$

Definition

Since, U, P & V are all state functions, so H is also a state function and perfectly differential quantity.
Again, U = internal energy and PV = energy term, so *H* is also an energy term.
As, PV is external energy of the system, so, H is called total heat content of a system.

Physical significance

On differential, $\qquad\qquad\qquad dH = dU + PdV + VdP$
or, $\qquad\qquad\qquad\qquad\qquad\qquad dH = q + VdP.$
For a change of state of a system at constant *P*, $\quad dH_P = q_P.$
This signifies that heat supplied to a system at constant pressure increases the enthalpy of the system.

We may summarize the different relations with the change of enthalpy and internal energy of the system:

Comparison between H and U

(1) In chemical reaction, $\Delta H = Q_P$ and $\Delta U = Q_V$ i.e. heat change at constant pressure is identical with ΔH and that at constant volume by ΔU.

(2) Dividing by dT at constant P, $\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{q}{\partial T}\right)_P = C_P$ when one mole gas is considered,

thus, $C_P = \left(\dfrac{\partial H}{\partial T}\right)_P$, called constant pressure molar heat capacity

and $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$, called constant volume molar heat capacity.

(3) Again, $dH = C_P\,dT$ at constant P and $dU = C_V\,dT$ at constant V.
However these two expressions can not be applied to the rev. phase change of a substance and chemical transformations.

(4) It is usual to write, $\qquad\qquad$ U = f (T,V) and H = f (T,P).
But for ideal gas, $\qquad\qquad$ U = f (T) only and H = f (T) only.

Expression of $C_P - C_V$:

Thermodynamic definition gives $C_P - C_V = \left(\dfrac{\partial H}{\partial T}\right)_P - \left(\dfrac{\partial U}{\partial T}\right)_V$.

Expression of $C_P - C_V$

but, $\qquad$ H = U + PV $\qquad$ so, $\qquad$ $C_P - C_V = \left[\dfrac{\partial(U + PV)}{\partial T}\right]_P - \left(\dfrac{\partial U}{\partial T}\right)_V$

or, $\qquad$ $C_P - C_V = \left(\dfrac{\partial U}{\partial T}\right)_P + P\left(\dfrac{\partial V}{\partial T}\right)_P - \left(\dfrac{\partial U}{\partial T}\right)_V$.

Again, $\qquad$ U = f (T,V) $\qquad$ so, $\qquad$ $dU = \left(\dfrac{\partial U}{\partial T}\right)_V dT + \left(\dfrac{\partial U}{\partial V}\right)_T dV$

or, $\qquad$ $\left(\dfrac{\partial U}{\partial T}\right)_P = \left(\dfrac{\partial U}{\partial T}\right)_V + \left(\dfrac{\partial U}{\partial V}\right)_T\left(\dfrac{\partial V}{\partial T}\right)_P$.

Using this relation in the expression of $C_P - C_V$,

$$C_P - C_V = \left[P + \left(\dfrac{\partial U}{\partial V}\right)_T\right]\left(\dfrac{\partial V}{\partial T}\right)_P .$$

This expression is not so useful as $(\partial U/\partial V)_T$ is not directly measurable quantity.

However, thermodynamic equation of state is given by $P + \left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial P}{\partial T}\right)_V$

Generalized form of $C_P - C_V$

Thus, generalized expression of $C_P - C_V$ is obtained by the use of the equation.

$$C_P - C_V = T\left(\dfrac{\partial P}{\partial T}\right)_V\left(\dfrac{\partial V}{\partial T}\right)_P .$$

This form is applicable to ideal or real gases and also to other states of aggregation of the substances.

(i) $C_P - C_V$ for ideal gases: Ideal gas obeys the relation $PV = RT$

so, $\left(\dfrac{\partial P}{\partial T}\right)_V = \dfrac{R}{V}$ and $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P}$.

Thus, $\qquad\qquad$ $C_P - C_V = \dfrac{R^2 T}{PV} = \dfrac{R^2 T}{RT} = R$

So, $\qquad\qquad$ $C_P - C_V = R$ ---------------- ideal gas.

(ii) $C_P - C_V$ for the gas obeying $P(V - b) = RT$ equation:

$P = \dfrac{RT}{V - b}$ $\quad$ or, $\left(\dfrac{\partial P}{\partial T}\right)_V = \dfrac{R}{V - b}$ $\qquad$ and $\quad V = \dfrac{RT}{P} + b$ or, $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P}$.

Thus, $\qquad$ $C_P - C_V = T \times \dfrac{R}{V - b} \times \dfrac{R}{P} = \dfrac{R^2 T}{P(V - b)} = \dfrac{R^2 T}{RT} = R$.

The relation is thus, $\qquad\qquad$ $C_P - C_V = R$.

(iii) $C_P - C_V$ for water at 4^0C:

The liquid water attains minimum molar volume at 4^0C. So V = minimum at 4^oC.

Thus, $\left(\frac{\partial V}{\partial T}\right)_P = 0$ so, $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = 0$.

So for water at 4^0C, $C_P - C_V = 0$ and $C_P = C_V$.

(iv) $C_P - C_V$ for vander Waals gas: The equation for 1 mole gas,

$\left(P + \frac{a}{V^2}\right)(V - b) = RT$, where, a and b are characteristic constants of the gas.

For this expression, some approximations are to be taken as it involves $\left(\frac{\partial V}{\partial T}\right)_P$.

Now, $P = \frac{RT}{V - b} - \frac{a}{V^2}$ or, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$.

Again, multiplying fully, vander Waals equation becomes $PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$,

neglecting the small term ab/V^2, we get

$PV - Pb + \frac{a}{V} = RT$ or, $P\left(\frac{\partial V}{\partial T}\right)_P - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P = R$.

Or, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - a/V^2}$

$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T \times \frac{R}{V - b} \times \frac{R}{P - a/V^2} = \frac{R^2 T}{(V - b)\left(P + \frac{a}{V^2} - \frac{2a}{V^2}\right)}$

$= \frac{R^2 T}{(V - b)\left(\frac{RT}{V - b} - \frac{2a}{V^2}\right)} = \frac{R^2 T}{(V - b) \times \left(\frac{RT}{V - b}\right)\left[1 - \frac{2a(V - b)}{RTV^2}\right]} = \frac{R}{1 - \frac{2a(V - b)}{RTV^2}}$.

But $V \gg b$, so $C_P - C_V = \frac{R}{1 - \frac{2a}{RTV}} = R\left(1 - \frac{2a}{RTV}\right)^{-1}$

and $\frac{2a}{RTV}$ is small correction term originating from non-ideality of a gas.

So, $C_P - C_V = R\left(1 + \frac{2a}{RTV}\right) = R + \frac{2a}{TV}$,

V is replaced by using ideal gas equation as an approximation.

Thus, $C_P - C_V = R + \frac{2aP}{RT^2}$.

This shows that $(C_P - C_V) \rangle$ R for vander Waals gas.

(v) $C_P - C_V$ in terms of α and β: We have $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$,

But, α = thermal expansion co-efficient or thermal expansivity $= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

and β = co-efficient of compressibility or isothermal compressibility $= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\frac{\alpha}{\beta} = -\frac{\left(\partial V/\partial T\right)_P}{\left(\partial V/\partial P\right)_T} = -\left(\partial V/\partial T\right)_P\left(\partial P/\partial V\right)_T$$

But, V = f(T,P), so by partial differentiation, it is possible to show that

$$\left(\partial V/\partial T\right)_P\left(\partial T/\partial P\right)_V\left(\partial P/\partial V\right)_T = -1 \text{ or } \left(\partial V/\partial T\right)_P\left(\partial P/\partial V\right)_T = -1/\left(\partial T/\partial P\right)_V.$$

Thus, $$\frac{\alpha}{\beta} = \frac{1}{\left(\partial T/\partial P\right)_V} = \left(\partial P/\partial T\right)_V \text{ and,} \left(\partial V/\partial T\right)_P = \alpha V.$$

So we have $$C_P - C_V = \alpha^2 TV/\beta$$

This relation is valid for substances in all states of aggregation.

Related questions with answer:

Problem(1). Find out the value of $C_P - C_V$ for decane at 27^0C, given molar volume 106ml and $\alpha = 1 \times 10^{-3}$ K^{-1} and $\beta = 106 \times 10^{-6}$ atm^{-1}. (Ph.Ch.- D.N.Bajpai, page,155.)

Solution: $$C_P - C_V = \frac{\left(1\times 10^{-3}\right)^2 \times 300 \times 106}{106 \times 10^{-6}} \text{ (K}^{-1}\text{ ml mol}^{-1}\text{ atm)} = \frac{300 \times 106}{106} \text{(K}^{-1}\text{ml atm mol}^{-1}\text{)}$$

$$= 300 \text{ K}^{-1}. \text{ mol}^{-1} \times \frac{2}{82} \text{ cal} = 7.26 \text{ cal mol}^{-1}\text{K}^{-1}. \text{ (using 1 ml atm = 2/82 cal.).}$$

Expression of $\left(\partial U/\partial V\right)_T$

We have thermodynamic equation of state, $P + \left(\partial U/\partial V\right)_T = T\left(\partial P/\partial T\right)_V.$

So, $$\left(\partial U/\partial V\right)_T = T\left(\partial P/\partial T\right)_V - P.$$

This equation helps to calculate the value of $\left(\partial U/\partial V\right)_T$ for different gases.

(i) For ideal gas: $PV = nRT$ or, $P = nRT/V$ or, $\left(\partial P/\partial T\right)_V = nR/V.$

Thus, $\left(\partial U/\partial V\right)_T = T \times \frac{nR}{V} - P = \frac{nRT}{V} - P = P - P = 0$

So, $$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{---------------} \quad \text{for ideal gas.}$$

This means that the internal energy (U) of an ideal gas is independent of volume. Hence, we can say U is not a function of V for ideal gas and $U = f(T)$ only.

(ii) For vander Waals gas: For n moles gas, $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

or, $$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$ or, $$\left(\partial P/\partial T\right)_V = \frac{nR}{V - nb}$$

Putting in the expression of $\left(\partial U/\partial V\right)_T$, we get

$$\left(\partial U/\partial V\right)_T = \frac{nRT}{V - nb} - P = \left(P + \frac{an^2}{V^2}\right) - P$$

or, $$\left(\partial U/\partial V\right)_T = an^2/V^2 \quad \text{----------} \quad \text{vander Waals gas}$$

This relation shows that $\left(\partial U/\partial V\right)_T = (+)$ve and value decreases with increase of volume.

Isothermal expression of a vander Waals gas leads to increase of *U*.

BU'87, A vander Waals gas expands isothermally and reversibly from a volume of one lit to ten lit. Derive all necessary mathematical expression to calculate the internal energy change of the gas in calories.($a = 1.4$ atm lit^2 mol^{-2})

Solution: First derive $\left(\partial U/\partial V\right)_T = an^2/V^2$ as above.

Now, integrating the relation,

$$\int_{V_1}^{V_2} dV = an^2 \int_{V_1}^{V_3} \frac{dV}{V^2} \qquad \text{or,} \qquad U_2 - U_1 = -an^2\left[\frac{1}{V}\right]_{V_1}^{V_2}. \quad \text{Putting the values,}$$

$$\Delta U = 1.4 \,\text{atm lit}^2\,\text{mol}^{-2} \times (1\ \text{mol})^2\left[\frac{1}{1} - \frac{1}{10}\right]\text{lit}^{-1} = 1.4 \times \frac{9}{10}\ \text{lit atm} = 1.4 \times \frac{9}{10} \times \frac{2}{0.082}\ \text{cal}.$$

Or, $\Delta U = 30.73$ cal per mol of the gas,

ΔU for ideal and vander Waals gas

Internal energy change in terms of T and V.

$$\Delta U = nC_V\left(T_2 - T_1\right) \text{ for ideal gas}$$

and,

$$\Delta U = nC_V\left(T_2 - T_1\right) + an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right] \text{ for vander Waals gas.}$$

Provided no phase change or chemical transformation occurs.

BU'96 A student attempting to remember a certain formula comes up with $C_P - C_V = TV\alpha^m/\beta^n$, where m and n are certain integers whose values the student has forgotten. Use dimensional considerations to find m and n.

Solution: $\alpha^m/\beta^n = \dfrac{C_P - C_V}{TV}$ The dimension of $\alpha = $ K^{-1} and that of $\beta = \dfrac{L^2}{MLT^{-2}} = \dfrac{L}{MT^{-2}}$

So, $\alpha^m = $ K^{-m} and $\beta^n = $ L^{n}M^{-n}T^{2n}. Dimension of $LHS = \dfrac{K^{-m}}{L^n M^{-n} T^{2n}} = K^{-m}L^{-n}M^{n}T^{-2n}$

Dimension of RHS $= \dfrac{\text{K}^{-1}ML^2T^{-2}mol}{KL^3 mol^{-1}} = K^{-2}ML^{-1}T^{-2}$. Equating, we get m = 2 & n = 1.

Problem Calculate the difference between the molar heat capacities at constant pressure and at constant volume for copper at 20°C.
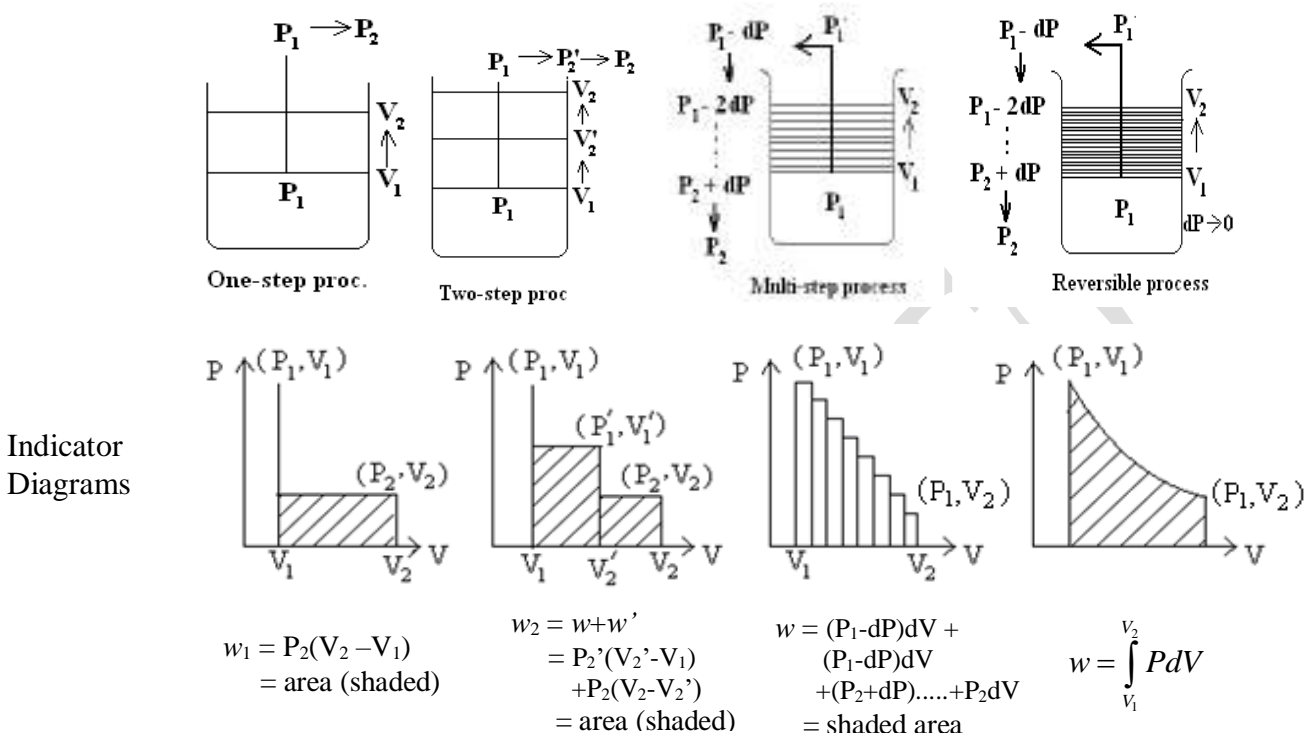
Given: $\alpha = 4.92 \times 10^{-5} K^{-1}$, $\beta = 7.0 \times 10^{-7} atm^{-1}$ and density of copper $= 8.96\ Kg\ dm^{-3}$.

[Answer: 0.654 J mol^{-1} K^{-1}]

Mechanical or pressure-volume work (*w*)

It is the work associated with the change in volume of a system against opposing pressure, $w = P_{opp}.\Delta V$, where P_{opp} is the pressure that opposes the change of V,

$$w = P_{opp}(V_2 - V_1)$$

Magnitude of *w* for specified volume change (say V_1 to V_2) depends on this opposing pressure.

One-step proc.	Two-step proc	Multi-step process	Reversible process

Indicator Diagrams

$$w_1 = P_2(V_2 - V_1)$$
$$= \text{area (shaded)}$$

$$w_2 = w + w'$$
$$= P_2'(V_2' - V_1)$$
$$+ P_2(V_2 - V_2')$$
$$= \text{area (shaded)}$$

$$w = (P_1 - dP)dV +$$
$$(P_1 - dP)dV$$
$$+ (P_2 + dP).....+P_2 dV$$
$$= \text{shaded area}$$

$$w = \int_{V_1}^{V_2} PdV$$

Since dP→0, P changes continuously, so summation is replaced by integration.

Magnitude of w is path function

This shows that magnitude of work done by a system increases with increase of number of steps that occurs for a specified volume change and maximum when the max process is reversible. Thus, *w* is a path function.

Sign Convention of w

$w = P_{opp}(V_2 - V_1)$ so, work done by the system is taken (+)ve and work done on the system is (−)ve.

Thus, for expansion of the gas, $w = (+)$ve since $V_2 \rangle V_1$

for compression of the gas, $w = (-)$ve since $V_2 \langle V_1$

Modern convention: $w = - P_{opp}(V_2 - V_1)$ so the sign of work done becomes opposite to the above conversion. However, we shall use the old convention only.

Expression of work done in reversible process:

Work done in reversible expansion is maximum

Reversible process is a multi-step process and in each step the working system attains equilibrium. Again the driving pressure is infinitesimally greater than the opposing pressure in each step and dP→0, i.e. pressure difference is infinitesimally small. If the pressure over the piston were kept greater than $P_1 - dP$, there obviously would be no expansion.

Therefore, the opposing pressure is always maximum in each step through out the whole process. Since $w = P_{opp}(V_2 - V_1)$ thus, for the same specified volume change ($V_1 \rightarrow V_2$), w = maximum as P_{opp} is maximum. Thus, work done by the system in reversible process is maximum and the

General expression of $w_{rev.}$

value is calculated as, $w_{rev} = \int_{V_1}^{V_2} PdV$.

Similarly, it can be shown that work done in compression of a gas (work done on the system) for same specified volume change in reversible process is minimum.

Work required in reversible compression is minimum

The pressure over the piston in this reversible compression is slightly greater then the opposing pressure. i.e. $P_2 + dP$ is infinitesimally greater than P_2. Thus, P_2 is minimum pressure below which there would be not be a reversible process.
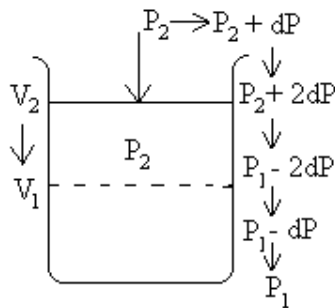
Thus in every step, the work required is minimum so, overall work done on the system is minimum in the reversible compression of a gas,

$w = P_2\, dV + (P_2 + dP)\, dV + (P_2 + 2dP)\, dV$ -------

$(P_1 - 2dP)\, dV + (P_1 - dP)dV$

$= \int_2^1 PdV = -\int_1^2 PdV$

When ideal gas is used, the equation is PV = nRT. Or, $P = \dfrac{nRT}{V}$.

Work done in reversible isothermal process

So, $w_{r,i} = \int_{V_1}^{V_2} PdV = nRT \int_{V_1}^{V_2} \dfrac{dV}{V}$, since the process isothermal. So, $w_{r,i} = nRT\, \ln \dfrac{V_2}{V_1}$.

Again as T is constant, so $\dfrac{V_2}{V_1} = \dfrac{P_1}{P_2}$.

So, $\qquad w_{r,i} = nRT\, \ln \dfrac{V_2}{V_1} = nRT\, \ln \dfrac{P_1}{P_2}$, -------id. gas, rev. isotherm. proc.

For vander Waals gas, $P = \dfrac{nRT}{V - nb} - \dfrac{an^2}{V^2}$ so, $w_{r,i} = \int_1^2 \dfrac{nRT}{V - nb} dV - \int_1^2 \dfrac{an^2}{V^2} dV$

Or, $w_{r,i} = nRT\, \ln \dfrac{V_2 - nb}{V_1 - nb} + an^2 \left(\dfrac{1}{V_2} - \dfrac{1}{V_1} \right)$ ----- vander Waals gas, rev. isotherm. proc.

Workdone in reversible adiabatic process

For ideal gas in reversible adiabatic process, $PV^\gamma = k, (cons\tan t)$ or, $P = {k}/{V^\gamma}$.

Therefore, $\qquad w_{r,a} = k \int_1^2 \dfrac{dV}{V^\gamma} = k \left[\dfrac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2} = \dfrac{1}{-\gamma+1} \left[P_2 V_2^\gamma . V_2^{-\gamma+1} - P_1 V_1^\gamma . V_1^{-\gamma+1} \right]$.

Or, $\qquad w_{r,a} = \dfrac{P_1 V_1 - P_2 V_2}{\gamma - 1}$ ----------- id. gas, rev. adiab. proc.

But, $\qquad P_1 V_1 = nRT_1 \qquad$ and $\qquad P_2 V_2 = nRT_2$,

so, $\qquad w_{r,a} = \dfrac{nRT_1 - nRT_2}{\gamma - 1} = \dfrac{nR}{{C_P}/{C_V} - 1}(T_1 - T_2)$. As, $C_P - C_V = R$,

so, $\qquad w_{r,a} = n C_V (T_1 - T_2)$ ---- id .gas, rev. adiab. proc.

This expression of $w_{r,a}$ is obvious as, for adiabatic process, q = 0, so 0 = dU + w

or, $\qquad w = -\,dU = -\,n C_V (T_2 - T_1)$.

So, $\qquad w_{r,a} = n C_V (T_1 - T_2)$ ---- id. gas, rev. adiab. proc.

and for n moles vander Waals gas, $\quad w = -\left[nC_V (T_2 - T_1) + an^2 \left(\dfrac{1}{V_1} - \dfrac{1}{V_2} \right) \right]$

or, $w_{r,a} = n C_V (T_1 - T_2) + an^2 \left(\dfrac{1}{V_2} - \dfrac{1}{V_1} \right)$ ---------- vander Waals gas, rev. adiab. proc.

Reversible cyclic process

     Let the process, for example, is isothermal reversible and 1 mole ideal gas as working substance. The work done, $w = w_1 + w_2$,

w_1 = work done in the forward process and w_2 = work done in the backward process.

$$w_1 = RT \ln \frac{V_2}{V_1} \qquad \text{and} \qquad w_2 = RT \ln \frac{V_1}{V_2}$$

So, $\quad w = RT \ln \dfrac{V_2}{V_1} + RT \ln \dfrac{V_1}{V_2}$ or, $\qquad w = RT \ln \dfrac{V_2}{V_1} - RT \ln \dfrac{V_2}{V_1} = 0$.

The net work done in the reversible cyclic process is zero and $w_1 = -\,w_2$.

This means that the original state of the system can be brought back without the aid of external agency and this is why it is called reversible process.

This can be compared by using indicator diagram from the area for the two type's curves of work done in reversible processes.

Comparison of $w_{r,i}$ and $w_{r,a}$
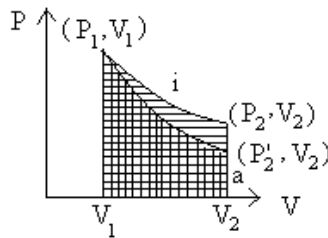
Indicator diagram

The ideal gas expands from volume V_1 to V_2 for two processes starting from the same initial position (P_1, V_1). $P_2 \rangle P_2'$, thus adiabatic curve is steeper than isothermal curve in the same P - V diagram.

The work done, $w_{r,i}$ = area shown by ' = ' and

$\qquad\qquad w_{r,a}$ = area shown by '||

It is evident that area under isothermal curve is greater than that under adiabatic curve. So, $w_{r,i} \rangle w_{r,a}$.

     The reason behind is that in isothermal process, energy is transferred from the surrounding and the system does the work. But in adiabatic process, work is done by the system at the expense of its own internal energy.

     This is why isothermal reversible process is preferred to obtain maximum work for a definite volume change of the system.

Work done in irreversible process:

General expression of w_{irr} isothermal process

     This process occurs against a constant opposing pressure, P_2 without the restriction of occurring in successive stages of infinitesimal amount. Thus, when a gas expands from V_1 to V_2 against constant opposing pressure P_2, the work done, $\qquad w_{irr} = P_2 (V_2 - V_1)$.

Since T is constant in the process, hence for ideal gas, $V_2 = nRT/P_2$, $V_1 = nRT/P_1$.

So, $w_{irr,i} = P_2 \left(\dfrac{nRT}{P_2} - \dfrac{nRT}{P_1} \right)$ Or, $w_{irr,i} = nRT \left(1 - \dfrac{P_2}{P_1} \right)$ --- id.gas, irrev. isotherm. proc.

Let the final temperature of the system in this irreversible adiabatic process is T_2'.

Then, $w_{irr,a} = nC_V (T_1 - T_2')$ which occurs at the cost of its internal energy of the system.

But this final temperature T_2' is calculated from the 1st law as,

$$0 = dU + w \qquad \text{or,} \qquad w = -dU \qquad \text{or,} \qquad P_2\, dV = -n\, C_V\, dT.$$

If the temperature changes from T_1 to T_2' and volume from V_1 to V_2, then,

$$P_2 (V_2 - V_1) = -nC_V (T_2' - T_1)$$

or, $\quad P_2 \left(\dfrac{nRT_2'}{P_2} - \dfrac{nRT_1}{P_1} \right) = -nC_V (T_2' - T_1)$ or, $\quad R \left(T_2' - T_1 \dfrac{P_2}{P_1} \right) = C_V (T_1 - T_2')$.
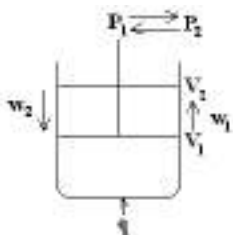
This relation can be used to calculate the final temperature (T_2') of the system.

Reshuffling the equation, it is possible to find an expression of T_2'.

$$T_2' = \dfrac{T_1}{C_P} \left(C_V + R \dfrac{P_2}{P_1} \right). \qquad \text{-------- --- id. gas, irrev. adiab. proc.}$$

Let us consider the irreversible expansion of a gas in a cyclic process consisting of one forward process and one backward process.

Work done in the forward process, $w_1 = P_2 (V_2 - V_1)$ and

work done in the backward process, $w_2 = P_1 (V_1 - V_2)$.

$$= -P_1 (V_2 - V_1).$$

Since $P_1 \rangle P_2$, hence $|w_2| \rangle |w_1|$.

Total work done in the irreversible cyclic process,

$$w = w_1 + w_2 = (P_2 - P_1)(V_2 - V_1) = (-)\text{ve}.$$

Work is required to bring the system back to its initial state. It means that the system cannot be restored to its original state without the aid of external agency and hence the name of the process is irreversible.
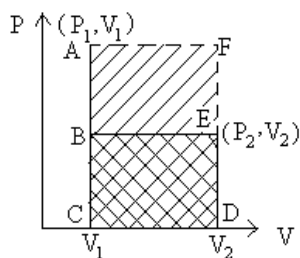
This can also be shown by the indicator diagram.

$w_1 = P_2 (V_2 - V_1) = $ area of BCDEB

$w_2 = -P_1 (V_2 - V_1) = $ area of ACDFA and

$w = -$ area of ACDFA + area of BCDEB

$\quad = -$ area of ABEFA.

$w_1 = $ ' // ' & $w_2 = $ '×'   This diagram also shows that $|w_2| \rangle |w_1|$.

Let us compare it by taking example of isothermal expansion of one mole ideal gas.

Using the expression of the work done (w), we get,

$$w_r = RT \ln \dfrac{P_1}{P_2} = RT \ln \left(1 + \dfrac{P_1 - P_2}{P_2} \right) = RT\, \dfrac{P_1 - P_2}{P_2} \quad \text{when } P_1 - P_2 \text{ is not very large.}$$

$$w_{irr} = P_2 (V_2 - V_1) = RT \left(1\, w_{irrev}\, \dfrac{P_2}{P_1} \right) = RT \left(\dfrac{P_1 - P_2}{P_1} \right). \text{ Since, } P_1 \rangle P_2, \text{ so } w_{rev} \rangle w_{irrev}$$
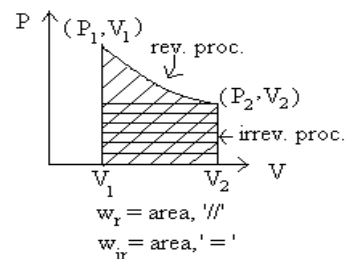
Again, $w_{rev} - w_{irrev} = RT \dfrac{P_1 - P_2}{P_2} - RT \left(\dfrac{P_1 - P_2}{P_1} \right) = RT (P_1 - P_2) \left(\dfrac{1}{P_2} - \dfrac{1}{P_1} \right)$

or, $\qquad w_{rev} - w_{irrev} = RT \left(\dfrac{(P_1 - P_2)^2}{P_1 P_2} \right) = (+)ve.$

So, $\qquad\qquad\qquad w_{rev} \rangle w_{irrev} .$

This can be shown by the indicator diagram also.

w_r = area, '//'
w_{ir} = area,' = '

A note for solving problems: Though various equations are formulated depending on conditions, they are not easy to remember while solving problems. We may summarize these into seven fundamental equations.

(1) The formula for expansion work, $\qquad w = P_{opposing} \times dV.$

(2) The mathematical form of the 1st law, $q = dU + w$

(3) The definition of enthalpy, $\qquad\qquad H = U + PV.$

(4) The definition of molar heat capacity, (a) $C_P = \left(\partial H / \partial T \right)_P$ and (b) $C_V = \left(\partial U / \partial T \right)_V$

(5) The change in internal energy and enthalpy of a system,

(a) $dU = nC_V\, dT + \left(\partial U / \partial V \right)_T dT$ and (b) $dH = nC_P\, dT + \left(\partial H / \partial P \right)_T dP$

IIT, KGP, 2000

One mole of steam is compressed reversibly to liquid water at its boiling point (100°C). The heat of vaporization of water at 100°C and 1atm pressure is 2258.1 Jg⁻¹.
Calculate each of the thermodynamic properties, (i) q, (ii) w, (iii) ΔU and (iv) ΔH.

Solution:

(i) q = heat of condensation per mole = -18×2258.1 J mol⁻¹ = -40.646 kJ mol⁻¹.

(ii) $w = P (\overline{V_l} - \overline{V_g}) = - P\overline{V_g}$ (neglecting $\overline{V_l}$) = $- RT = - 8.31 \times 373$ J mol⁻¹.

$\qquad = -3.099$ kJ mol⁻¹

(iii) $\Delta U = q - w = - 40.646 + 3.099$ kJ mol⁻¹ = $- 37.547$ kJ mol⁻¹.

(iv) $\Delta H = q_P = - 40.646$ kJ mol⁻¹.

Physical Chemistry –P C Rakhsit

(a) One mole of He at 27°C and 1atm is adiabatically reversibly compressed to a final pressure of 10atm. Evaluate the final temperature and also find out w, ΔU and ΔH.

(b) The same gas is compressed adiabatically against a constant pressure of 10 atm, the final pressure is 10 atm. Evaluate again the final temperature and the values of w, ΔU and ΔH.

Solution:

(a) $T_1 = 273 + 27 = 300$ K, $P_1 = 1$ atm, $P_2 = 10$ atm, $T_2 = ?$ $\gamma = 5/3$

(Since He is monatomic gas).

For the ideal gas in reversible adiabatic process,

$$T_2 = T_1 \left(P_2 / P_1 \right)^{\frac{\gamma-1}{\gamma}} = 300 \text{ K} \left(\frac{10\ atm}{1\ atm} \right)^{\frac{2}{5}} = 750\ K .$$

$\Delta U = nC_V (T_2 - T_1) = 1$ mol $\times$ 3 cal mol⁻¹ K⁻¹ (750 – 300) K = 1350 cal.

$\Delta H = nC_P (T_2 - T_1) = 1$ mol $\times$ 5 cal mol⁻¹ K⁻¹ (750 – 300) K = 2250 cal.

$w = - \Delta U = - 1350$ cal (Since the process is adiabatic).

(b) Let the final temperature is T_2'. So using the relation for irreversible adiabatic

process with ideal gas, $R\left(T_2' - T_1 \dfrac{P_2}{P_1}\right) = C_V (T_1 - T_2')$. Putting the values,

2 cal mol^{-1}K^{-1} $(T_2' - 300$ K $\times \dfrac{10\,atm}{1\,atm}) = 3$ cal mol^{-1}K^{-1} $(300$ K $- T_2')$ or, $T_2' = 1380$ K

$\Delta U = nC_V (T_2' - T_1) = 1$ mol $\times 3$ cal mol^{-1} K^{-1} $(1380 - 300)$ K $= 3240$ cal.

$\Delta H = nC_P (T_2' - T_1) = 1$ mol $\times 5$ cal mol^{-1} K^{-1} $(1380 - 300)$ K $= 5400$ cal.

$w = -\Delta U = -3240$ cal since the process is adiabatic.

(Note: T_2' is almost doubled for this irreversible process so w is high for compression).

Advanced
Physical
Chemistry
- D.N.Bajpai

One mole of an ideal gas at 300 K and 10 atm expands to 1 atm.
Calculate w, q, ΔU, ΔH for
(a) isothermal and reversible, (b) isothermal and irreversible,
(c) adiabatic and reversible   (d) adiabatic and irreversible.
Tabulate these results and state what important conclusions you can draw from these results. Plot P − V curves for adiabatic and isothermal changes. [Given, $C_V = 1.5R$].

Solution:

(a) $w_{rev,iso} = nRT \ln\left(\dfrac{P_1}{P_2}\right) = 1$ mol $\times 8.31$ J mol^{-1} K$^{-1} \times 300$ K $\ln \dfrac{10\,atm}{1\,atm} = 5744$ J

$\Delta U = nC_V \, dT = 0$ and $\Delta H = nC_P \, dT = 0$,

as, T = constant for this isothermal process. Therefore,

$q = \Delta U + w = 5744$ J.

(b) $w_{irrev.iso.} = nRT \left(1 - \dfrac{P_2}{P_1}\right) = 1\,mol \times 8.31\,J\,mol^{-1}K^{-1} \times 300\,K\left(1 - \dfrac{1\,atm}{10\,atm}\right) = 2244\,J$

for this isothermal process and ideal gas, $\Delta U = 0$ and $\Delta H = 0$.

$q = w = 2244$ J

(c) $T_2 = T_1 \times \left(\dfrac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = 300\,K\left(\dfrac{1\,atm}{10\,atm}\right)^{2/5} = 119.4\,K$. (As, $\gamma = {C_P}/{C_V} = {2.5R}/{1.5R} = {5}/{3}$).

$w_{rev,adiab} = nC_V (T_1 - T_2) = 1$ mol $\times 1.5 \times 8.31$ J mol^{-1} K^{-1} $(300 - 119.4)$K $= 2251$ J

$\Delta U = -w_{rev,adiab} = -2251$ J, (Since q = 0 for this adiabatic process).

$\Delta H = nC_P (T_2 - T_1) = 1$ mol $\times 2.5 \times 8.31$ J mol^{-1} K^{-1} $(119.4 - 300)$ K $= -3752$ J

(d) $R\left(T_2' - T_1 \dfrac{P_2}{P_1}\right) = C_V (T_1 - T_2')$ or, $R(T_2' - 300$ K $\times {1\,atm}/{10\,atm}) = 1.5R(300$K $- T_2')$

Or, $T_2' = 192$ K.   q = 0, (As this is an adiabatic process).

$w_{irrev,adiab} = nC_V (T_1 - T_2') = 1$ mol $\times 1.5 \times 8.31$ J mol^{-1} K^{-1} $(300 - 192)$ K $= 1447$ J

$\Delta U = -w_{irrev,adiab} = -1447$ J, (Since q = 0 for this adiabatic process).

$\Delta H = nC_P (T_2' - T_1) = 1$ mol $\times 2.5 \times 8.31$ J mol^{-1} K^{-1} $(192 - 300)$ K $= -2245$ J

In (a), $V_1 = \dfrac{nRT}{P_1} = \dfrac{1\,mol \times 0.082\,lit\,atm\,mol^{-1}K^{-1} \times 300K}{10\,atm} = 2.46\,lit$.

$V_2 = 10 \times 2.46 = 24.6$ lit.

In (c), $V_2' = \dfrac{nRT}{P_2} = \dfrac{1\,mol \times 0.082\,lit\,atm\,mol^{-1}K^{-1} \times 119.4K}{1\,atm} = 9.8\,lit$. And, $V_1 = 2.46$ lit.

Thus, for reversible isothermal process, $V_1 = 2.46$ lit and $V_2 = 24.6$ lit.

And, for reversible adiabatic process, $V_1 = 2.46$ lit and $V_2' = 9.8$ lit.

Table showing the results of calculation.

Process	w (J)	q (J)	ΔU (J)	ΔH (J)	T_2 (K)	V_2 (L)
Isothermal						
(a) rev.	5744	5744	0	0	300	24.6
(b) irrev.	2244	2244	0	0	300	24.6
Adiabatic						
(a) rev.	2252	0	–2252	–3753	119.4	9.8
(b) irrev.	1447	0	–1447	–2245	192.0	—
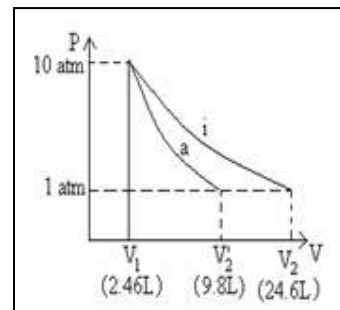
Conclusion:

(1) Work done in a reversible process (w_{rev}) is greater than that in an irreversible process (w_{irrev}).

(2) Work done in reversible isothermal process ($w_{rev,iso}$) is greater than that in reversible adiabatic process ($w_{rev,adiab}$).

(3) There occurs more rises in temperature in the irreversible adiabatic compression (T_2') than in reversible adiabatic compression (T_2).

(4) Final volume on reversible isothermal process (V_2) is greater than in reversible adiabatic process (V_2') for the same change of pressure.

      So adiabatic curve is steeper than isothermal curve in P–V diagram.

Physical
Chemistry
- G W Castellan

An ideal gas ($C_V = 2.5R$) is expanded adiabatically against a constant pressure of 1 atm until it doubles its volume. If the initial temperature is 25^oC and the initial pressure is 5 atm, calculate final temperature, then calculate q, w, ΔU and ΔH per mole of the gas for the transformation.

Solution: $T_2' = 274$ K, q = 0, w = 120 cal, ΔU = –120 cal mol^{-1}, ΔH = –168 cal.mol^{-1}.

Some more problems with solution in B.Sc. (Hons.) in BU/CU.

BU'1993

Problem (1): One mole of an ideal gas expands reversibly from a volume V_1 to V_2 obeying the relation PV^γ = constant. If T_1 = 300 K and T_2 = 200 K, calculate w. Given also that $C_V = 5R/2$, calculate Q, ΔU and ΔH.

Solution: Q = 0, ΔU = – 500 cal, ΔH = – 700 cal.

BU'1994

Problem (2): An ideal gas undergoes a reversible polytropic expansion according to the relation, $PV^n = C$ where C and n are constants, n $\rangle$ 1.

Calculate W for such an expansion if one mole of the gas expands from V_1 to V_2 and if T_1 = 300 K, T_2 = 200 K and n = 2.

Solution: $W = \int_1^2 PdV = C\int_1^2 \frac{dV}{V^n} = C\left[\frac{V^{-n+1}}{-n+1}\right]_{V_1}^{V_2} = \frac{C}{-n+1}\left(V_2^{-n+1} - V_1^{-n+1}\right)$

$= \frac{1}{-n+1}\left(CV_2^{-n+1} - CV_1^{-n+1}\right) = -\frac{1}{n-1}\left(P_2 V_2^n V_2^{-n+1} - P_1 V_1^n V_1^{-n+1}\right)$

$= -\frac{1}{n-1}(P_2V_2 - P_1V_1) = \frac{1}{n-1}(P_1V_1 - P_2V_2) = \frac{1}{n-1}(RT_1 - RT_2) = \frac{R}{n-1}(T_1 - T_2)$

Putting values given in Problem, W = $\frac{2}{2-1}(300 - 200)$ cal = 200 cal.

Problem (3): For a constant pressure process, $\Delta H = Q_P$. Does it follow that Q_P is a state function? Give reasons.

Solution: No, Q_P is not a state function. $Q_P = \Delta H = H_2 - H_1$.
H_2 is a function of the final state, and H_1 is a function of the initial state but $H_2 - H_1$ is neither the function of the final state nor the function of the initial state. Thus, Q_P is not a state function.

Problem (4): Calculate q, w , ΔU and ΔH for a reversible expansion at 300 K of 5 moles of an ideal gas from 500 ml to 1500 ml. What would be ΔU and w if the expansion occurs between the same initial and final states as before, but is done by expanding the gas in vacuum?

Solution: 1st case, q = 3,296.28 cal, w = 3,296.28 cal, $\Delta U = \Delta H = 0$.
2nd case, w = 0 and $\Delta U = 0$.

Problem (5)(i): Calculate the work done by a reversible isothermal expansion of 1 mole of a gas from V_1 to V_2 obeying the equation P (V− b) = RT.

(ii): Calculate the work done by an irreversible isothermal process for one mole of the same gas from V_1 to V_2 against a constant external pressure until the equilibrium is reached.

Answer: (i) $w_{rev,isotherm} = RT \ln \dfrac{V_2 - b}{V_1 - b}$. (ii) $w_{irrev,isotherm} = RT\left(1 - \dfrac{P_2}{P_1}\right)$..

Problem (6): Show that the work involved in an adiabatic expansion is than that in an isothermal process.

Answer: Let $w_{adiab} = P_2\left(V_2' - V_1\right)$ and $w_{isotherm} = P_2\left(V_2 - V_1\right)$ for the same change of pressure from P_1 to P_2 . But there will be greater volume change in the isothermal process than in adiabatic process, i.e. $V_2 \rangle V_2'$, hence, $w_{isotherm} \rangle w_{adiab}$.

THERMOCHEMISTRY

Introduction:

Exothermic & endothermic reactions

This chapter deals with the heat-change associated with a chemical reaction. When heat is evolved, Q = (–)ve and the reaction is called exothermic. When heat is absorbed, Q = (+)ve, it is called endothermic reaction. For example,

$$C + O_2 = CO_2 \; ; \; Q = (–)ve \quad and \quad N_2 + O_2 = 2NO \; ; \; Q = (+)ve$$
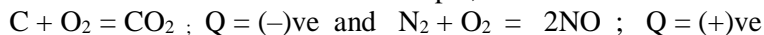
The former reaction is exothermic while the latter reaction is endothermic.

Heat change is associated with a chemical reaction

Since chemical reactions involve the breaking of old bonds and the making of new bonds, it is always associated with the heat changes.
The subject matter of this chapter is the consequences of first law of thermodynamics applied to chemical reactions.
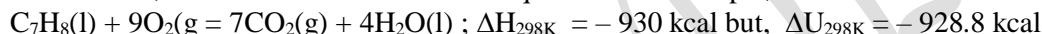
Heat of reaction

Heat of reaction is defined as the amount of heat change associated with a reaction as represented by the stoichiometric equation. As heat change depends on the physical state of the materials so these are also included in the chemical equations. For example,

$$N_2(g) + O_2(g) = 2NO(g); \; Q = 42 \text{ kcal but } \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) = NO(g); \; Q = 21 \text{ kcal}$$
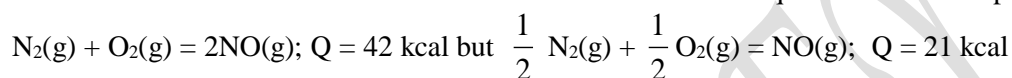
Two types of heat reactions

Heat of reaction is of two types: heat of reaction at constant pressure (Q_P) which is identified as ΔH and heat of reaction at constant volume (Q_V), identified as ΔU.
In the chemical equation when temperature, pressure, heat-change and physical states are included, it is called thermo-chemical equation. For example,
$$C_7H_8(l) + 9O_2(g = 7CO_2(g) + 4H_2O(l) \; ; \; \Delta H_{298K} = - 930 \text{ kcal but, } \Delta U_{298K} = - 928.8 \text{ kcal}$$

Now, ΔH of the reaction is called enthalpy of the reaction and as most reactions are carried out in open atmosphere or at constant pressure, enthalpy of reaction is commonly used to express the heat-changes of a reaction.

Relation between ΔH and ΔU of a reaction at constant temperature:

We have, by definition, $H = U + PV$ so for a chemical change, $\Delta H = \Delta U + \Delta(PV)$.
If the reacting components are assumed to obey the ideal gas equation, $PV = nRT$,

Ideal gaseous system is assumed.

$$\Delta H = \Delta U + (PV)_{Product} - (PV)_{Reactant}$$
$$= \Delta U + (nRT)_{Product} - (nRT)_{Reactant}$$
$$= \Delta U + (n_p - n_r) RT \quad \text{Or,} \quad \Delta H = \Delta U + \Delta n_g RT.$$

And, Δn_g = change in number of moles of the gaseous products and gaseous reactants.
For reactions with substances in condensed phases, $\Delta n_g = 0$ and $\Delta H = \Delta U$.

**Problem**: For the combustion of toluene (cited above), $\Delta n_g = 7 - 9 = - 2$ moles.
If ΔH is known then ΔU can be calculated.
So, $\Delta U_{298K} = \Delta H_{298K} - \Delta n_g RT = - 930 \text{kcal} - (-2 \text{ mol}) \times 2 \times 10^{-3} \text{ kcal mol}^{-1}\text{K}^{-1} \times 298\text{K}$
$$= - 928.8 \text{ kcal}.$$

This shows that difference of ΔH and ΔU is not very high.

Standard enthalpy of reaction (ΔH^o)

When the reacting components are in stable state and at unit activity (1 atm. pressure for ideal gaseous substances, 1 M for substances in ideal solution, and unity for pure solid and liquid states), the enthalpy of the reaction is called standard enthalpy (ΔH^o), at the specified temperature.

$$\text{For the reaction, } H_2(g) + \frac{1}{2} O_2(g) = H_2O(l) \; ; \; \Delta H^o_{298K} = - 68.3 \text{ kcal}$$
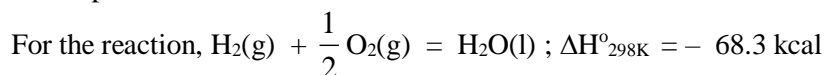
Laws of thermochemistry:

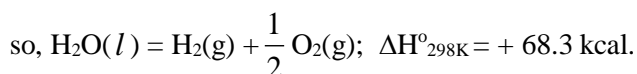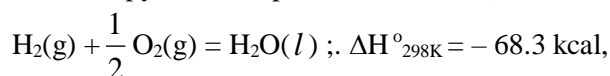There are two laws in thermochemistry. These are given below:

1st law : Law of Lavoisier and Laplace (1780):

Statement
"The enthalpy change of a chemical reaction in one direction is equal in magnitude but opposite in sign to that accompanying the same reaction in the reverse direction."

Thus, enthalpy of reaction in the formation of water (l) from $H_2(g)$ and $O_2(g)$ is exactly equal to the enthalpy of decomposition of water (l) into its elements but opposite in sign. Illustrated as,

Illustration
$$H_2(g) + \frac{1}{2} O_2(g) = H_2O(l) \;;. \Delta H^o_{298K} = -68.3 \text{ kcal,}$$

$$\text{so, } H_2O(l) = H_2(g) + \frac{1}{2} O_2(g); \; \Delta H^o_{298K} = +68.3 \text{ kcal.}$$

Consequence of the 1st law
The law is a consequence of 1st law of thermodynamics. H is a state function, so it depends on the states of the reacting system. Let us suppose, the reactants A and B first change into products C and D with enthalpy of reaction, ΔH_1 and when C and D give reactants A and B back, the enthalpy of reaction is ΔH_2. Thus, for the whole cycle,
$$\Delta H = \Delta H_1 + \Delta H_2 = 0 \text{ or, } \Delta H_1 = -\Delta H_2.$$

2nd law : Hess's law of constant heat summation (1940):

Statement
"For a chemical reaction, the net heat-change (ΔH or ΔU) will be the same whether the process occurs in one step or in several steps."

Illustration
Let a chemical reaction when occurs in one step, $A \rightarrow C \;; \Delta H = Q_1$.
But when the same reaction occurs in two steps, $A \rightarrow B \;; \Delta H = Q_2$
and $B \rightarrow C \;; \Delta H = Q_3$.
Then, according to the law, $\qquad\qquad\qquad Q_1 = Q_2 + Q_3$.
This law is also the consequence of the 1st law of thermodynamics.

Consequence of the 1st law
If the initial state and final state of a system due to a process are fixed, enthalpy-change or internal energy-change will also be fixed, independent of the intermediate steps that occur during the process. This is due to the fact that H and U are the state functions.
This law is sometimes used to calculate the enthalpy of a reaction which is difficult to determine by experiments.
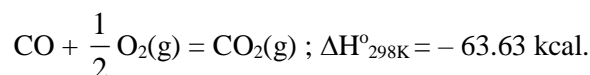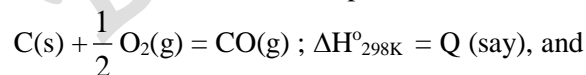
For example, $C(s) + \frac{1}{2} O_2(g) = CO(g)$, ΔH of the reaction is not possible to determine

Application of the law
experimentally as some amount of CO_2 always forms in association with CO.
However, the value of ΔH for the reaction can be calculated as follows:
$C(s) + O_2(g) = CO_2 \;; \Delta H^o_{298K} = -94.05 \text{ kcal,}$ when it occurs in a single step.
The same reaction can also occur in two steps.

$$C(s) + \frac{1}{2} O_2(g) = CO(g) \;; \Delta H^o_{298K} = Q \text{ (say), and}$$

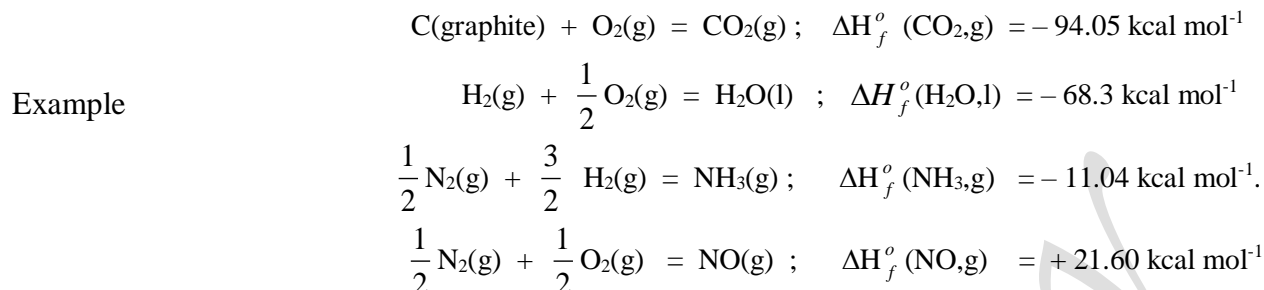$$CO + \frac{1}{2} O_2(g) = CO_2(g) \;; \Delta H^o_{298K} = -63.63 \text{ kcal.}$$

So, according to the law, $(-94.05 \text{ kcal}) = Q + (-63.63 \text{ kcal})$ or, $Q = -26.42 \text{ kcal.}$

Thus, $\qquad\qquad C(s) + \frac{1}{2} O_2(g) = CO(g); \Delta H = -26.42 \text{ kcal.}$

Various types of enthalpy of reaction:

Definition	**Enthalpy of formation:** It is the enthalpy change associated with the formation of one mole of a compound from its constituent elements in their stable state of aggregation. It is represented by ΔH_f.

When the elements are in their standard states, it is called standard enthalpy of formation (ΔH^o_f) at a specified temperature, generally at 25^oC. The examples are given here;

$$C(graphite) + O_2(g) = CO_2(g) ; \quad \Delta H^o_f \ (CO_2,g) = -94.05 \text{ kcal mol}^{-1}$$

Example

$$H_2(g) + \frac{1}{2} O_2(g) = H_2O(l) ; \quad \Delta H^o_f (H_2O,l) = -68.3 \text{ kcal mol}^{-1}$$

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) = NH_3(g) ; \quad \Delta H^o_f \ (NH_3,g) = -11.04 \text{ kcal mol}^{-1}.$$

$$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) = NO(g) ; \quad \Delta H^o_f \ (NO,g) = +21.60 \text{ kcal mol}^{-1}$$

Significance

Positive values of ΔH^o_f of a compound indicates that the compound is les stable than its constituents elements. While negative value of ΔH^o_f refers that the compound is more stable than its constituent elements. The former compounds may be called endothermic while the latter are exothermic.

Relation between std. enthalpy and std. enthalpy of formation of a compound:

Let us take that a compound C, which is formed from its constituent elements A and B by the reaction, $\quad\quad\quad\quad A + B \rightarrow C$

and, standard enthalpy of formation of C, $\Delta H^o_f \ (C) = \bar{H}^o_C - (H^o_A + H^o_B)$

However, the absolute value of enthalpies is not easily possible to determine, so usual convention is taken that standard enthalpy of an element in their stable state is zero at 25^oC temperature. That is, $H^o(element) = 0$ in its stable form at 25^oC.

$\Delta H^o_f (C) = \bar{H}^o_C$ So, $\quad\quad\quad H^o_A = 0$ and $H^o_B = 0$, so, $\Delta H^o_f (C) = \overline{H^o_C}$

The standard enthalpy of formation of a compound is equal to standard molar enthalpy of the compound.

This relation is widely used to calculate the standard enthalpy of a reaction which is otherwise not possible to determine experimentally.

Let us consider a reaction, $\quad\quad\quad \nu_1 A_1 + \nu_2 A_2 = \nu_3 A_3 + \nu_4 A_4$

            where, νs are stoichiometric coefficients and A's are reacting components.

Application

The enthalpy of the reaction is,

$$\Delta H^o = \{ \nu_3 \ \bar{H}^o_3 + \nu_4 \ \bar{H}^o_4 \} - \{ \nu_1 \bar{H}^o_1 + \nu_2 \ \bar{H}^o_2 \}$$

$$= \nu_3 \Delta H^o_f \ (A_3) + \nu_4 \Delta H^o_f \ (A_4) - \nu_1 \Delta H^o_f \ (A_1) - \nu_2 \Delta H^o_f \ (A_2)$$

Or, $\quad\quad\quad \Delta H^o = \sum \nu_i \ \Delta H^o_f \ (A_i).$ Where, $\nu_i = (+)$ve for the products, and

$$= (-)\text{ve for the reactants.}$$

Problems : Calculate the standard enthalpy (ΔH^o) of the following reaction.

$$Fe_2O_3 (s) + 3H_2(g) = 2Fe(s) + 3H_2O(l).$$
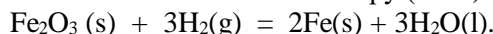
Given, $\Delta H^o_f \ (Fe_2O_3,s) = -824.2 \text{ kJ mol}^{-1}$ and, $\Delta H^o_f \ (H_2O, l) = -285.83 \text{ kJ mol}^{-1}$

Solution: Standard enthalpy of the reaction, taking std. enthalpy of H_2 and Fe as zero.

$$\Delta H^o = \sum \nu_i \Delta H^o_f \ (A_i). = 3\Delta H^o_f \ (H_2O,l) - \Delta H^o_f \ (Fe_2O_3,s)$$

$$= 3 (-285.83 \text{ kJ mol}^{-1}) - (-824.2 \text{ kJ mol}^{-1}) = -33.29 \text{ kJ}.$$
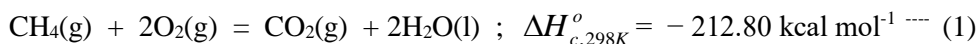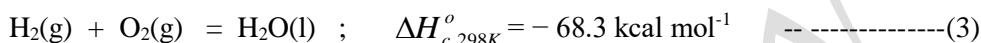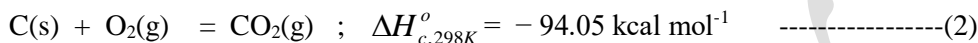
Enthalpy of combustion:

Definition

It is the enthalpy change associated with the complete combustion of one mole of a substance. When the enthalpy of combustion is measured at 1 atm pressure, it is called standard enthalpy of combustion (ΔH_c^o).

Standard enthalpy of combustion of CH_4 is −212 kcal/mole. It means that on complete combustion of CH_4, 212 kcal of heat is released per mole of CH_4 at constant pressure of 1 atm. and at a specified temperature.

The thermo chemical equation of combustion of different substances are given below:
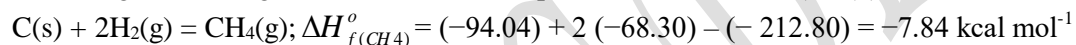
Example

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l) \; ; \; \Delta H_{c,298K}^o = -212.80 \text{ kcal mol}^{-1} \text{ --- (1)}$$

$$C(s) + O_2(g) = CO_2(g) \; ; \; \Delta H_{c,298K}^o = -94.05 \text{ kcal mol}^{-1} \text{ ------------------(2)}$$

$$H_2(g) + O_2(g) = H_2O(l) \; ; \; \Delta H_{c,298K}^o = -68.3 \text{ kcal mol}^{-1} \text{ ----------------(3)}$$

$$N_2(g) + O_2(g) = 2NO(g) \; ; \; \Delta H_{c,298K}^o = +43.2 \text{ kcal mol}^{-1} \text{ ------------------(4)}$$

Application − calculation of enthalpy of formation

Enthalpy of combustion data can be utilized to calculate the enthalpy of formation of some compounds that can not be determined experimentally.

For example, $\Delta H_{f(CH4)}^o$ can be calculated by using the enthalpy of combustion of $C(s)$, $H_2(g)$ and $CH_4(g)$. The mathematical operation is $(2) + 2 \times (3) - (1)$,

$C(s) + 2H_2(g) = CH_4(g); \Delta H_{f(CH4)}^o = (-94.04) + 2(-68.30) - (-212.80) = -7.84 \text{ kcal mol}^{-1}$

Thus, the standard enthalpy of formation of methane is −18.65 kcal mol^{-1}, though the reaction is not possible to perform in reality.

Importance of enthalpy of combustion data

Enthalpy of combustion has practical as well as theoretical importance. The purchaser of coal is interested in its enthalpy of combustion per ton. The dietician must know, among other factors, the number calories obtainable from the combustion of various foods. It is also used to estimate the flame temperature and to calculate the bond energies of a compound. In nutrition, the 'Calorie' refers to kcal.

Determination of enthalpy of combustion:

Heat of combustion is usually determined in a bomb-calorimeter at constant volume. Hence, it is internal energy of combustion. The bomb-calorimeter is internally enameled with platinum and capable of withstanding high pressure. It has capacity of about 400 cc

and fitted with pressure-tight screw cap.

A known weight of a sample is placed in a Pt-cup inside the calorimeter and is then filled with

Bomb-Calorimeter

oxygen at 20-30 atm. The combustion is initiated by a small electric current through the thin Pt-wire dipped into the sample. The substance on ignition gives large amount of heat which is measured by the rise in temperature of the water into which the bomb-calorimeter has been immersed before ignition. The heat capacities of the system is pre-determined by burning a standard substance (say, benzoic acid) of known heat of combustion.
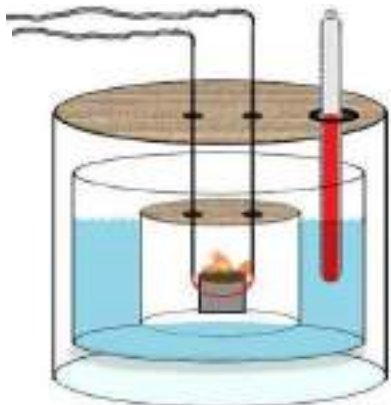
So, heat of combustion at constant volume (ΔU) =

$$\frac{Total\ heat\ capacity \times temperature\ rise}{Amount\ of\ the\ subs\tan ce\ taken\ in\ gm} \times molar\ mass\ of\ the\ substance.$$
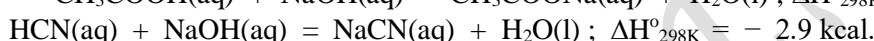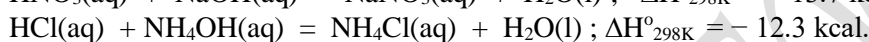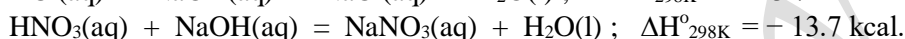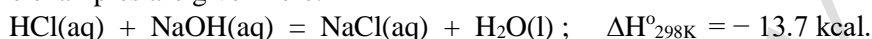
The enthalpy of combustion (ΔH) can be calculated by the use of the equation,

$$\Delta H = \Delta U - \Delta n_g RT .$$
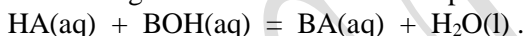
Enthalpy of neutralization:

Definition

It is the enthalpy change associated with the neutralization of one gram-equivalent of an acid by one gram equivalent of a base in their very dilute aqueous solution. Neutralization is an exothermic process.

Some examples are given here:

Example

$HCl(aq) + NaOH(aq) = NaCl(aq) + H_2O(l) ;\quad \Delta H^o_{298K} = - 13.7\ kcal.$

$HNO_3(aq) + NaOH(aq) = NaNO_3(aq) + H_2O(l) ;\ \Delta H^o_{298K} = - 13.7\ kcal.$

$HCl(aq) + NH_4OH(aq) = NH_4Cl(aq) + H_2O(l) ; \Delta H^o_{298K} = - 12.3\ kcal.$

$CH_3COOH(aq) + NaOH(aq) = CH_3COONa(aq) + H_2O(l) ; \Delta H^o_{298K} = - 12.6\ kcal.$

$HCN(aq) + NaOH(aq) = NaCN(aq) + H_2O(l) ; \Delta H^o_{298K} = - 2.9\ kcal.$

Two facts emerge from the examples cited above:

Constancy of enthalpy of neutralization of strong acid & base

(i) Enthalpy of neutralization of strong acid and strong base is found constant and equal to $- 13.7$ kcal irrespective of the nature of the strong acids and bases. This constancy of enthalpy of neutralization of strong acids and bases can be explained as follows:

$$HA(aq) + BOH(aq) = BA(aq) + H_2O(l) .$$

But strong acids and strong bases are completely dissociated in aqueous solution. So,

$$(H^+ + A^-) + (B^+ + OH^-) = (B^+ + A^-) + H_2O(l)$$
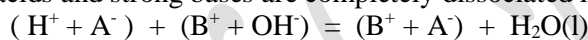
Canceling the like ions, we have, $H^+ + OH^- = H_2O(l)$.

Thus neutralization of string acid and strong base is reduced to formation of one mole water from H^+ and OH^-. Enthalpy-change will be the same for the same change of state for the reaction.

Enthalpy of dissociation of week acid or base

(ii) Again, if one (or both) is weak electrolyte, the enthalpy of neutralization is found less than $- 13.7$ kcal. This is explained by the fact that a portion of heat is required to dissociate the weak acid or base or both. For that reason, the enthalpy of neutralization is obtained less. This indirectly helps to calculate the heat of dissociation (or enthalpy of dissociation) of the weak acid or base. For example, enthalpy of dissociation of

$$HCN = (- 2.9\ kcal) - (- 13.7\ kcal) = 10.8\ kcal.$$

Enthalpy of solution: It is the enthalpy-change when one mole of a solute is dissolved in a specified amount of solvent.

Total enthalpy change when one mole solute is completely dissolved in a solvent is called integral enthalpy of solution. Let us illustrate the enthalpy of solution for HCl in aqueous solvent.

One mole solute HCl(g) when dissolved in

10 mol H_2O; $\Delta H^o_1 = - 16.5\ kcal\ mol^{-1}$

40 mol H_2O, $\Delta H^o_2 = - 17.4\ kcal\ mol^{-1}$

50 mol H_2O, $\Delta H^o_3 = - 17.5\ kcal\ mol^{-1}$

200 mol H_2O, $\Delta H^o_4 = - 17.7\ kcal\ mol^{-1}$

∞ mol H_2O, $\Delta H^o_\infty = - 18.0\ kcal\ mol^{-1}$
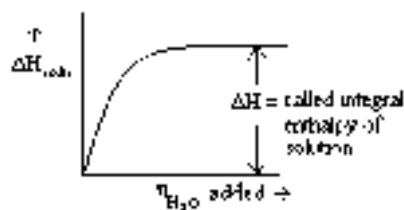
As more and more H_2O is added, ΔH increases, reaching to a maximum value at infinite dilution. Only then the solution is thermally complete.

This enthalpy of solution ($-$ 18.0 kcal mol^{-1}) is called integral enthalpy of solution.

Let, $\Delta H = f(n_1, n_2)$, subscript 1 is for solvent and 2 for solute.

So, $d(\Delta H) = \left[\dfrac{\partial(\Delta H)}{\partial n_1}\right] dn_1 + \left[\dfrac{\partial(\Delta H)}{\partial n_2}\right] dn_2$. This $\left[\dfrac{\partial(\Delta H)}{\partial n_1}\right]$ is called differential enthalpy of solution.

Bond energies:

> Bond energy of a given bond is defined as the average of energy required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state.

The bond energy differs from dissociation energy which is defined as the energy required to dissociate a given bond of some specific compound.

Let us consider O$-$H bond. The heat of dissociation of the O$-$H bond depends on the nature of molecular species from which the H-atom is being separated from O-atom.

Examples

For H$_2$O molecule, $H_2O(g) \rightarrow H(g) + OH(g)$; $\Delta H^o_{298K} = 119.95$ kcal mol^{-1}.

But to break the O$-$H bond in the hydroxyl radical requires a different quantity of heat.

$O-H(g) \rightarrow O(g) + H(g)$; $\Delta H^o_{298K} = 101.19$ kcal mol^{-1}.

The bond energy, ϵ_{OH} is defined as the average of these two values;

i.e. $\epsilon_{OH} = \frac{1}{2}(119.96 + 101.19) = 110.57$ kcal mol^{-1}

However, in diatomic molecules like H$_2$, bond energy and dissociation energy are identical.

Bond energy and enthalpy of combustion

Bond energy can be calculated from the enthalpy of combustion and the enthalpy of dissociation data:

For example, bond energy of C$-$H in CH$_4$(g) is obtained from the following reaction,

$CH_4(g) \rightarrow C(g) + 4H(g)$; $\epsilon_{C-H} = \frac{1}{4}(\Delta H)$

One specific example

The value of ΔH for the reaction can be calculated from the summation of the following equations.

$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l)$; $\Delta H^o_{298K} = -212.80$ kcal

$CO_2(g) \rightarrow C(graphite) + O_2(g)$; $\Delta H^o_{298K} = 94.05$ kcal

$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$; $\Delta H^o_{298K} = 136.64$ kcal

$2H_2(g) \rightarrow 4H(g)$; $\Delta H^o_{298K} = 208.38$ kcal

$C(graphite) \rightarrow C(g)$; $\Delta H^o_{298K} = 171.29$ kcal.

Adding these equations, we get, $CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta H^o_{298K} = 397.60$ kcal.

So, at 298K, we get, $\epsilon_{C-H} = \frac{1}{4}(397.60$ kcal$) = 99.4$ kcal mol^{-1}.

Bond energy and enthalpy of formation

Bond energy data can be utilized to calculate approximate enthalpy of formation of a compound of known structure.

Let us calculate the approximate enthalpy of formation of H$_2$O(g) from its constituent elements,

H$_2$(g) and O$_2$(g) according to the reaction, $H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(g)$.

The enthalpy of formation of H$_2$O(g),

$\Delta H_f(H_2O, g) = \epsilon_{H-H} + \dfrac{1}{2}\epsilon_{O=O} - 2\epsilon_{O-H} = 103.2 + \dfrac{1}{2} \times 118.0 - 2 \times 110.5 = -58.8$ kcal mol^{-1}.

Bond energy and enthalpy of reaction

Enthalpy of reaction can also be obtained from the bond energies of the reactants and products. Let us take the reaction,

$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$.

ΔH = ⟨ Energy required to break reactants into gaseous atoms ⟩

+ ⟨Energy released to form products from the gaseous atom ⟩

$= \{ 4\epsilon_{C-H} + \epsilon_{C=C} + \epsilon_{H-Cl} \} + \{ -5\epsilon_{C-H} - \epsilon_{C-C} - \epsilon_{C-Cl} \}$

$= (\epsilon_{C=C} + \epsilon_{H-Cl}) - (\epsilon_{C-H} + \epsilon_{C-C} + \epsilon_{C-Cl})$

$$= (147.0 + 103.2) - (98.8 + 83.1 + 78.5) = -10.2 \text{ kcal mol}^{-1}$$

.

Temperature dependence of the heat of reaction (Kirchhoff equation)

If we know the ΔH^o of a reaction at temperature, T_1, Kirchhoff's equation provides the calculation of ΔH^o of the same reaction at another temperature, T_2.

Representation of a chemical equation

Let us take the chemical reaction, $\quad v_1 A_1 + v_2 A_2 = v_3 A_3 + v_4 A_4$

or, $\quad 0 = -v_1 A_1 - v_2 A_2 + v_3 A_3 + v_4 A_4 \quad$ or, $\quad 0 = \sum v_i A_i$

where, v_i = stoichiometric coefficient = (+)ve for the products and (−)ve for the reactants.

Enthalpy of the reaction, $\Delta H^o = \left(v_3 \bar{H}_3^o + v_4 \bar{H}_4^o \right) - \left(v_2 \bar{H}_2^o + v_1 \bar{H}_1^o \right) = \sum v_i \bar{H}_i^o$

Since, P is fixed at the standard state value of 1 atm., differentiating with respect to T

at constant pressure, $\quad \left[\dfrac{\partial (\Delta H^o)}{\partial T} \right]_P = \sum v_i \left(\dfrac{\partial \bar{H}_i^o}{\partial T} \right)_P = \sum v_i C_{P,i}^o = \Delta C_P^o$,

called standard constant pressure molar heat capacity change of the process.

Integrating within limits, $\quad \displaystyle\int_{\Delta H_1^o}^{\Delta H_2^o} d(\Delta H^o) = \int_{T_1}^{T_2} \Delta C_P^o \, dT$.

General form of the Kirchoff equations

or, $\Delta H_2^o - \Delta H_1^o = \displaystyle\int_{T_1}^{T_2} \Delta C_P^o \, dT$. Similarly, $\Delta U_2^o - \Delta U_1^o = \displaystyle\int_{T_1}^{T_2} \Delta C_V^o \, dT$

Latter relation is for internal energy of the reaction with temperature.

(i) Over a short range of temperature-change, temperature dependence of ΔC_P^o can often be neglected and ΔC_P^o is assumed to be temperature independent. So,

When ΔC_P^o is T − independent

$$\Delta H_2^o = \Delta H_1^o + \Delta C_P^o (T_2 - T_1)$$

(ii) When ΔC_P^o depends on temperature, we first find its virial form (power series)

When ΔC_P^o is T − dependent

with T. $\quad C_{P,i}^o = a_i + b_i T + c_i T^2 + \dots$

and $\quad \Delta C_P^o = \sum v_i C_P^o = \sum v_i (a_i + b_i T + c_i T^2 + \dots)$

$\quad\quad\quad = \sum v_i a_i + \left(\sum v_i b_i \right) T + \left(\sum v_i c_i \right) T^2 + \dots$

$\quad\quad\quad = \alpha + \beta T + \gamma T^2 \dots,$

where $\alpha = \sum v_i a_i$, $\beta = \left(\sum v_i b_i \right)$ and $\gamma = \left(\sum v_i c_i \right)$.

Using this expression of ΔC_P^o, we get $\Delta H_2^o = \Delta H_1^o + \displaystyle\int_{T_1}^{T_2} (\alpha + \beta T + \gamma T^2 \text{-----}) \, dT$

Kirchhoff's equations

or, $\quad \Delta H_2^o = \Delta H_1^o + \alpha (T_2 - T_1) + \dfrac{\beta}{2} (T_2^2 - T_1^2)$.

The relation of internal energy of reaction with temperature is,

$$\Delta U_2^o = \Delta U_1^o + \alpha' (T_2 - T_1) + \dfrac{\beta'}{2} (T_2^2 - T_1^2).$$

These are the Kirchhoff's equations which relate the heat of reaction with temperature.

Problem (1)

For the reaction, $CO + \dfrac{1}{2} O_2 = CO_2$, $\Delta H = -67{,}650$ cal at 25^oC.

Calculate ΔH of the reaction at 100^oC. Given, $C_P(CO) = 6.97$, $C_P(CO_2) = 8.97$ and $C_P(O_2) = 7.0$ in cal mol^{-1}K^{-1}

Solution

The Kirchhoff equation is, $\Delta H_2 = \Delta H_1 + \Delta C_P (T_2 - T_1)$,

but, $\Delta C_P = \sum v_i C_{P,i} = C_P(CO_2) - C_P(CO) - \frac{1}{2} C_P(O_2)$

$\quad\quad = 8.97 - 6.97 - \frac{1}{2}(7.0) = -1.5$ cal K^{-1}. Thus,

$\Delta H_{373K} = \Delta H_{298K} + (-1.5)(T_2 - T_1) = -67{,}650$ cal $- 1.5(373 - 298)$ cal $= -67{,}762.5$ cal.

Problem (2)	Calculate the enthalpy–change at 1500 K for the reaction, $$2H_2(g) + O_2(g) = 2 H_2O(g).$$ Given that, $\Delta H_{300K} = 115.0$ kcal and the values of C_P (cal mol^{-1} K^{-1}) are for $H_2(g) = 6.95 - 0.0002\ T$, $O_2(g) = 6.10 + 0.0032\ T$ and $H_2O(g) = 7.19 + 0.0024\ T$. [C U' 1994]
Solution	$\Delta H_1 = \Delta H_{300K} = 115.0$ kcal. $\alpha = \sum v_i a_i = 2 \times 7.19 - 2 \times 6.95 - 6.10 = -5.62$ and $\beta = \sum v_i b_i = 2 \times 0.0024 - 2 \times (-0.0002) - 0.0032 = 2 \times 10^{-3}$. $\Delta H_{1500K} = \Delta H_{300K} + \alpha\,(T_2 - T_1) + \tfrac{1}{2}\,(T_2^2 - T_1^2)$ $\qquad = -115.0 \text{ kcal} + [(-5.62)(1500 - 300) + \tfrac{1}{2}\,(2 \times 10^{-3})(1500^2 - 300^2)] \times 10^{-3} \text{ kcal}$ $\qquad = -115.0 - 6.7 + 2.16 \text{ kcal}$ $\qquad = -119.54 \text{ kcal}.$
Problem (3)	Calculate the enthalpy of formation of NH_3, given the enthalpy of combustion of NH_3 and H_2 as -90.6 and -68.3 kcal mol^{-1} respectively. (BU'1986)

Solution	We require the enthalpy of the reaction, $\tfrac{1}{2}N_2 + (3/2)\ H_2 = NH_3$; $\Delta H = ?$
	      Given, (i) $NH_3 + (3/4)\ O_2 = \tfrac{1}{2}\ N_2 + (3/2)\ H_2O$; $\Delta H = -90.6$ kcal mol^{-1}
	            (ii) $H_2 + \tfrac{1}{2}\ O_2 = H_2O$; $\Delta H = -68.3$ kcal mol^{-1}.
	Following mathematical operations $(3/2) \times$ (ii) $-$ (i), we get,
	$(1/2)\ N_2 + (3/2)\ H_2 = NH_3$; $\Delta H = (-102.45) - (-90.6)$ kcal mol$^{-1} = -11.85$ kcal mol^{-1}.
	      Thus the enthalpy of formation of ammonia is -11.85 kcal mol^{-1}.

Problem (4)	Calculate the standard enthalpy of the reaction at 25°C, $$C_2H_4(g) + H_2O(l) = C_2H_5OH(l).$$ Given, $\Delta H_f^o\,(C_2H_4,g) = 12.50$, $\Delta H_f^o\,(H_2O,g) = -68.32$ and $\Delta H_f^o\,(C_2H_5OH, l) = -66.36$ in kcal mol^{-1}.
Solution	$\Delta H^o = \sum v_i\,\Delta H_f^o$ (i) $= \Delta H_f^o\,(C_2H_5OH, l) - \Delta H_f^o\,(C_2H_4,g) - \Delta H_f^o\,(H_2O,g)$ $\qquad = (-66.36) - (12.50) - (-68.32)$ kcal mol$^{-1} = -10.54$ kcal mol^{-1}. It is a hypothetical reaction, but its ΔH^o can be calculated by use of standard enthalpy of formation data.
Problem (5)	The enthalpy of neutralization of HCN by NaOH is -2900 cal. Calculate the enthalpy of ionization of one mole HCN. Given, enthalpy of the reaction, $H^+ + OH^- = H_2O$ is $-13{,}800$ cal. (BU'95)

Solution	Given, (i) $H^+ + OH^- = H_2O$; $\Delta H = -13{,}800$ cal
	            (ii) $HCN + (Na^+ + OH^-) = (Na^+ + CN^-) + H_2O$; $\Delta H = -2{,}900$ cal.
	  (ii) $-$ (i), we get, $HCN = H^+ + CN^-$; $\Delta H = (-2{,}900) - (-13{,}800)$ cal $= 10{,}900$ cal.

Problem (6)
 	
Solution
	The heat of formation of $NH_3(g)$ at constant pressure is 46.1 kJ mol^{-1} at 27°C.
	Calculate the heat of formation of $NH_3(g)$ at constant volume assuming ideal behavior. How would the value differ if the gases under consideration were vander Waals gas? (BU'1990)
	The equation for formation of $NH_3(g)$ is,
	$$\tfrac{1}{2} N_2(g) + \tfrac{3}{2} H_2(g) = NH_3(g).$$
	      $\Delta H = \Delta U + (PV)_{product} - (PV)_{reactant}$. Assuming ideal behavior, $PV = nRT$.
	      $\Delta H = \Delta U + \Delta n_g RT$, where, $\Delta n_g = n_P - n_R = 1 - \tfrac{1}{2} - \tfrac{3}{2} = -1$.
	The heat of formation at constant volume, $\Delta U = \Delta H - \Delta n_g RT$
	or, $\Delta U = -46.1$ kJ mol$^{-1} - (-1) \times 8.31 \times 10^{-3}$ kJ mol^{-1} K$^{-1} \times 300$K $= -43.609$ kJ mol^{-1}.
	2nd part: For vander Waals gas, $(PV)_{reactant} \rangle (PV)_{product}$ (Amagat's curve)

So in the equation, $\Delta H = \Delta U + [(PV)_{product} - (PV)_{reactant}]$,

we have, ΔU would be greater than that obtained by assuming ideal behavior.

Problem (7)

What will be the enthalpy of fusion of ice, ΔH_{fusion} at -10^oC

if, ΔH_{fusion} at 0^oC is 6.02 kJ mol^{-1}.

C_P(ice) = 37.66 J K^{-1} mol^{-1} and C_P(water) = 75.31 J K^{-1} mol^{-1} (Civil Service Exam.1999).

Solution

The Kirchhoff 'equation is ΔH_{fusion} (263 K) = ΔH_{fusion} (273 K) + ΔC_P (263 – 273)K.

The process is, ice → water, so $\Delta C_P = C_P$(water) – C_P(ice) = (75.31 – 37.66) J K^{-1} mol^{-1}.

Or, ΔC_P = 37.65 J K^{-1} mol^{-1} = 37.65 ×10^{-3} kJ K^{-1} mol^{-1} = 0.03765 kJ K^{-1} mol^{-1}

So, ΔH_{fusion} (263 K) = 6.02 kJ mol^{-1} + 0.03765 kJ K^{-1} mol^{-1} (263 – 273)K

$\qquad\qquad\qquad$ = 5.6435 kJ mol^{-1}.

Problem (8)

How much heat is used up in dissociating HBO_2? Use the following data:

(i) HBO_2 + NaOH → $NaBO_2$ + H_2O ; ΔH = − 10.0 kcal

(ii) $\qquad$ H^+ + OH^- → H_2O ; $\qquad\qquad$ ΔH = − 13.4 kcal.

State and explain the principle used in the calculation. (BU'1996)
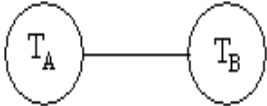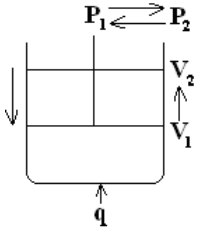
Solution

1st part: The equation (i), HBO_2 + (Na^+ + OH^-) = Na^+ + BO_2^- + H_2O ; ΔH = − 10.0 kcal.

Or, $\qquad\qquad\qquad$ HBO_2 + OH^- = BO_2^- + H_2O ; $\qquad$ ΔH = − 10.0 kcal.

Subtracting (ii) from this, we get

$\qquad\qquad\qquad$ HBO_2 → H^+ + BO_2^- ; ΔH = 3.4 Kcal..

$\qquad\qquad$ Hence, 3.4 kcal heat is used up in dissociating one mole of HBO_2.

2nd part: The principle used in the calculation is known as Hess's law of constant heat summation which states that for a given chemical process heat change will be the same whether the process is carried out in one or several steps.

According to the law, we can add or subtract the heat changes in the processes as it is, seen in the above calculation. In other words, thermodynamical equations can be treated as algebraical equation.

SECOND LAW OF THERMODYNAMICS

Limitation of the first law

The first law of thermodynamics states the equivalence of different forms of energy in the energy conversional process. In the process, if one form of energy disappears, an exactly equivalent amount of another form must reappear.
But it fails to state under what condition, this conversion of energy occurs.

Example for showing limitation

Let us explain this limitation of first law by taking the process of heat-flow. A and B are two metallic bodies of temperature T_A and T_B. These are connected by a thermal conducting wire. First law states that if Q amount of heat is lost by A, then exactly Q amount of heat is gained by B provided no heat is lost by any other processes.

Process of heat-flow

But first law fails to provide the answer if one asks the following questions relating to the process.

Limitation

(i)   Whether heat-flow would occur at all? (feasibility of the process)
(ii) If it would occur, then to what directions? (direction of the process)
(iii) To what extent, flow of heat would continue? (extent of the process).
First law remains silent about this feasibility, direction and extent of the process.

Statement of second law

However, second law of thermodynamics comes as rescue. It states that 'heat flows from higher temperature to lower temperature.' This simple statement of the second law can answer the above questions.

(i)   If $T_A \neq T_B$, the process of heat-flow is feasible. (feasibility).
(ii) If $T_A \rangle T_B$, heat will flow from A to B (direction).
(iii) When, $T_A = T_B$, heat will cease to flow (extent).

Clausius statement

Clausius thus stated the above form of the second law more elegantly as,
    "Heat, by itself, can not pass from lower temperature to higher temperature."

Different statements of second law.

Different scientists stated the law in different ways depending on the nature of the processes. But all these statements indicate the feasibility, direction and extent of a process. These different statements are listed below.
(1) Water flows from higher level to lower level.
(2) Air blows from higher barometric pressure to lower barometric pressure.
(3) Electricity flows from higher electric potential to lower electric potential.
(4) Chemical reaction occurs from higher chemical potential to lower chemical potential.
    Many other statements can be given to satisfy the requirements of the second law of thermodynamics.

Criteria of natural processes

The processes cited above are natural processes and these have two important criteria. These are given here.
(a) All natural processes are spontaneous and thermodynamically irreversible.
(b) All natural processes tend to attain equilibrium.

P – K statement

Now, let us consider the conversion of heat into mechanical work and the statement of Planck and Kelvin relating to this conversional process is given below.
    "Heat can not be completely converted into work. If it does so, the working system will suffer a permanent change."

Illustration of P-K statement

Let us explain the statement by taking an isothermal reversible expansion of one mole of ideal gas from volume V_1 to V_2 at temperature T.
The internal energy-change of the system,
$dU = C_V \, dT = 0$ as T = constant.
The gas is confined in a cylinder fitted with weightless, frictionless and movable piston.

From the first law,

$$q = dU + w', \text{ but } \quad dU = 0$$

$$\text{so,} \quad q = w' = RT \ln \frac{V_2}{V_1}.$$

It is seen that heat is completely converted into mechanical work but in doing so, the working system (here one mole gas) suffers a volume-change from V_1 to V_2 permanently.

If we try to remove the change by compressing the gas isothermally and reversibly from V_2 to V_1, then work required, $\quad w'' = RT \ln \frac{V_1}{V_2}$.

The net work obtained from the system without being suffered any permanent change,

$$w = w' + w'' = RT \ln \frac{V_2}{V_1} + RT \ln \frac{V_1}{V_2} = 0.$$

So the system, by isothermal reversible cyclic process, can produce no work from the supply of heat. If the process is not reversible, then also the system can not produce any positive work in the surrounding. Thus the P-K statement can also be stated as

"It is impossible for a system operating in a cycle and connected to a single reservoir (one temperature) to produce a positive amount of work in the surrounding."

Perpetual motion machine of the 2nd kind

This statement rejects the idea of possibility of constructing a perpetual motion machine of the 2nd kind. This machine was supposed to produce positive work by taking heat from the surrounding and continuously run for indefinite period of time. Thus, it was supposed to run the tram car (operating in cycle) by extracting heat from the atmosphere or to run a ship from the heat of the ocean. But P-K statement rejects such possibility since engine (operating in cycle) and heat source is at the same temperature (isothermal) and so it can not produce any positive work in the surrounding.

Condition for conversion of heat into mechanical work

Then the question is how the heat can be converted into mechanical work.
To convert heat into work two conditions are essentially required.
(1) There requires a mechanism or contrivance, called thermodynamic engine for the conversion of heat into work, the engine must work in cyclic fashion.
(2) The engine must operate between two heat reservoirs. It takes heat from the higher temperature reservoir (HTR), called heat source, and converts a portion of heat into mechanical work and rejects the rest heat to the lower temperature reservoir (LTR), called heat sink.

Schematically we can depict the process in the following way.

Efficiency of an engine
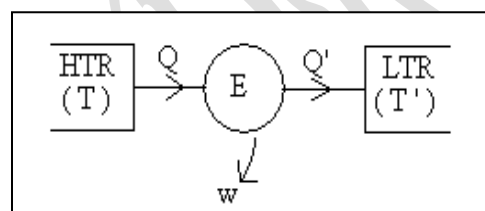
Q = heat taken by the engine from HTR (T)
Q' = heat rejected by the engine to LTR (T')

$$T \rangle T'$$

The efficiency of the engine, $\eta = \dfrac{energy\, output}{energy\, input}$.

Energy-balance shows that $Q - Q' = w$.

So, $\eta = \dfrac{work\, done\, by\, the\, engine\, (w)\, per\, cycle}{heat\, supplied\, to\, the\, engine\, (Q)\, per\, cycle}$. Or, $\eta = \dfrac{w}{Q} = \dfrac{Q - Q'}{Q} = 1 - \dfrac{Q'}{Q} \langle 1$

Formulation of efficiency of Carnot cycle

Sadi Carnot, a young French engineer in 1924 deduced theoretical maximum efficiency (η) of this idealized thermodynamic engine. The engine consists of four steps – all are reversible. It contains 1 mole ideal gas as working substance in a cylinder covered with a weightless, frictionless and movable piston. The engine works in cycle – two steps are expansions and two are compressions. The initial state of the gas is (P_1, V_1, T).
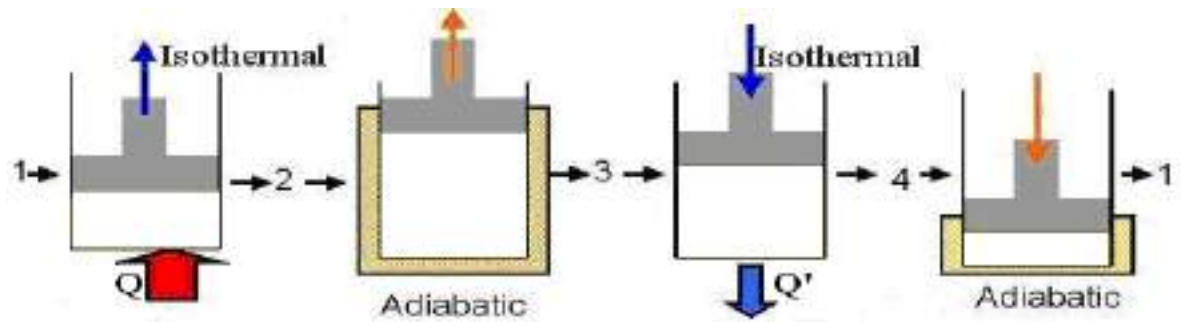
Step 1: Reversible isothermal expansion $(A \rightarrow B)$:

The engine is kept in contact with the higher temperature reservoir, at T.
(heat reservoir are devices which supply or absorb heat at constant temperature).
The gas is expanded isothermally and reversibly from volume V_1 to V_2.
The final state of the gas is (P_2, V_2, T). The engine absorbs heat Q from the HTR
and does work w_1.

$$Q = w_1 = RT \ln \frac{V_2}{V_1} \quad \text{-----(1)} \quad \text{since, dU} = 0 \text{ for ideal gas in isothermal process.}$$

Step 2: Reversible adiabatic expansion $(B \rightarrow C)$:

The engine is detached from HTR and kept insulated. The gas is expanded
reversibly and adiabatically from the state (P_2, V_2, T) to (P_3, V_3, T').
The gas suffers a fall in temperature $(T \rightarrow T')$. The work done by the engine in
this step is

$$w_2 = - dU = - C_V (T' - T). \text{ Or, } w_2 = C_V (T' - T) \quad \text{--------(2)}$$

Step 3: Reversible isothermal compression $(C \rightarrow D)$:

The engine is now brought in contact with LTR at temperature T' and the gas
is reversibly and isothermally compressed from V_3 to V_4. The state is changed
from (P_3, V_3, T') to (P_4, V_4, T'). The heat rejected by the engine to LTR is Q'.

Thus, $$Q' = w_3 = RT' \ln \frac{V_4}{V_3} \quad \text{------(3)}$$

Step 4: Reversible adiabatic compression $(D \rightarrow A)$

The engine is again detached from the LTR and kept insulated. The gas is
compressed reversibly and adiabatically from V_4 to V_1. The state is changed
from (P_4, V_4, T') to (P_1, V_1, T). The system comes back to its initial state.
So it works in cycle. Temperature is increased from T' to T.

The work done by the engine, $w_4 = - dU = - C_V (T - T')$ or, $w_4 = - C_V (T - T')$--- (4).

The total work done by the engine, $w = w_1 + w_2 + w_3 + w_4 = w_1 + w_3$, since $w_2 = - w_4$
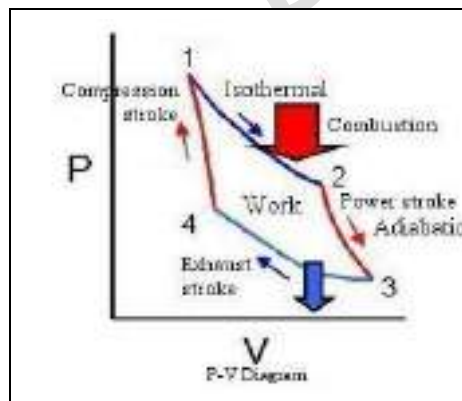
$$= RT \ln \frac{V_2}{V_1} + RT' \ln \frac{V_4}{V_3}.$$

But for two adiabatic and reversible processes
$B \rightarrow C$ and $D \rightarrow A$, we have the relation,
$T V_2^{\gamma-1} = T' V_3^{\gamma-1}$ --(a) and, $T V_1^{\gamma-1} = T' V_4^{\gamma-1}$ --(b)

Thus, $\dfrac{a}{b}$ gives $\dfrac{V_2}{V_1} = \dfrac{V_3}{V_4}$.

So $w = RT \ln \dfrac{V_2}{V_1} - RT' \ln \dfrac{V_3}{V_4} = RT \ln \dfrac{V_2}{V_1} - RT' \ln \dfrac{V_2}{V_1} = R\,(T - T')\,\ln \dfrac{V_2}{V_1}.$

But, $Q = RT \ln \dfrac{V_2}{V_1}.$ So the efficiency of the engine,

$$\eta = \frac{w}{Q} = \frac{T - T'}{T} \text{ or, } \eta = 1 - \frac{T}{T'}$$

This is the expression of maximum efficiency of Carnot engine.

Critical discussion on the efficiency of Carnot engine:

$$\text{We have, } \eta = 1 - \frac{T}{T'} = \frac{w}{Q} = \frac{T - T'}{T} \text{ or, } w = Q \times \left(1 - \frac{T'}{T}\right).$$

1. Perpetual motion of the first kind:
   If no heat is supplied to the engine, $Q = 0$ so, from above, $w = 0$.
   i.e. no engine can do any work if heat is not added to it.
   This explains the impossibility of perpetual motion of the 1st kind.

2. Perpetual motion of the 2ne kind:
   If $T = T'$, then also $w = 0$ i.e. if same heat source (single reservoir) is used,
   then $T = T'$, no engine can produce any positive work if it is connected to single
   reservoir and extracts heat from it.

3. Incompleteness of conversion of heat into work;
   $\eta = 1 - \dfrac{T}{T'}$ then, η can be only unity only when $T' = 0$ K or $T = \infty$.

   Both these conditions are never realized in practice, so $\eta < 1$ i.e. $w / Q \langle 1$ or, $w \langle Q$.
   It means that heat is not completely converted into work by an engine
   (engines work in cycle).

4. Unattainability of absolute zero temperature:
   Second law of thermodynamics states that $\eta \langle 1$ (P-K statement). The efficiency of
   the Carnot engine is always less than unity.

   $$\text{Thus } (1 - \frac{T}{T'}) \langle 1, \text{ so, } T' \text{ can never be equal to zero.}$$

   It means that 0K temperature can not be attained.

5. Comparison of efficiency:
   The efficiency of the engine, $\eta = 1 - \dfrac{T}{T'}$. So η can be increased either by lowering T'

   or increasing T or by both. If the efficiency of the engine is compared by decreasing
   the temperature of the sink (LTR) or increasing the temperature of the source (HTR) to
   the same extent, calculation shows that in the former attempt, η is higher.

   $$\text{When } T' \text{ is decreased by } dT', \ d\eta_1 = 0 - \frac{dT'}{T}$$

   When T is increased by dT, $d\eta_2 = 0 + \dfrac{T'}{T^2}\,dT$ but, $-dT' = dT$ so, $\dfrac{d\eta_1}{d\eta_2} = \dfrac{T}{T'} \rangle 1$.

Decreasing temperature of the LTR is more efficient than increasing temperature of the LTR. Though usual practice is to increase the temperature of the HTR keeping the LTR temperature fixed. High temperature boiler is used in steam engine for this purpose. A modern steam engine power plant uses high pressure boiler at 550°C and condenser at 40°C. $\eta = 1 - (\,313\,/\,823\,) = 62\%$. Actual η is obtained about 40%.

6. We have, $w = Q\,.\,\dfrac{T - T'}{T} = Q\,\dfrac{dT}{T}$. The engine converts $\dfrac{dT}{T}$ fraction of heat supplied (Q) into work

.

7. The efficiency (η) depends on temperature difference (dT) of source and sink and temperature of the source. It does not depend on the nature of the working substance used in the engine. Thus, instead of using ideal gas, if vander Waals gas (real gas) is used, the efficiency would be the same.
(See Physical Chemistry by Ira Levine p 79 for more details).

Problem (1): Calculate the efficiency (η) of steam engine working between 100°C and 27°C. Calculate the amount of work done and heat rejected to LTR if 1 kcal of heat is supplied to the engine.

Solution: $\eta = \dfrac{T - T'}{T} = \dfrac{373 - 300}{373} = 0.196 = 19.6\%$.

$$w = Q\,.\,\dfrac{T - T'}{T} = 10^3 \times 0.196 = 196 \text{ cal and } Q' = Q - w = 1000 - 196 = 804 \text{ cal.}$$

BU'1994 An ideal gas goes through a cycle consisting of alternate isothermal and adiabatic curves as shown in the following figures.
The isothermal processes proceed at the temperatures T_1, T_2 and T_3. Find the efficiency of such a cycle, if in each isothermal expansion, the gas volume increases in the same proportion.
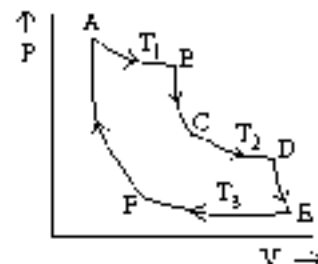
Solution: Work done in each step is given as follows:

Isothermal expansion A $\rightarrow$ B, $w_1 = Q_1 = RT_1 \ln (V_B/V_A)$ --- (1)

Adiabatic expansion B $\rightarrow$ C, $w_2 = C_V (T_1 - T_2)$ ------ (2).

Isothermal expansion C $\rightarrow$ D, $w_3 = Q_2 = RT_2 \ln (V_B/V_A)$ --- (3)

Adiabatic expansion D $\rightarrow$ E, $w_4 = C_V (T_2 - T_3)$ ------ (4)

Isothermal compression E $\rightarrow$ F, $w_5 = RT_3 \ln (V_F/V_E)$ -----(5)

Adiabatic compression B $\rightarrow$ C, $w_6 = C_V (T_3 - T_1)$ -----(6)

Total work done, $w = w_1 + w_2 + w_3 + w_4 + w_5 + w_6$

$$= w_1 + w_3 + w_5 \text{ as, } w_2 + w_4 + w_6 = 0.$$

Or, $w = RT_1 \ln(V_B/V_A) + RT_2 \ln (V_D/V_C) + RT_3 \ln (V_F/V_E)$.
But according to the condition, $V_B/V_A = V_D/V_C$.
So, $w = RT_1 \ln(V_B/V_A) + RT_2 \ln (V_B/V_A) + RT_3 \ln (V_F/V_E)$.
Using adiabatic relations, $T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1}$, $T_3 V_E^{\gamma-1} = T_2 V_D^{\gamma-1}$, $T_3 V_F^{\gamma-1} = T_1 V_A^{\gamma-1}$.
it is possible to find $V_F/V_E = (V_C/V_B)(V_A/V_D)$.
But $V_D/V_C = V_B/V_A$. Thus, $V_F/V_E = (V_A/V_B)(V_A/V_B) = (V_A/V_B)^2$.
Hence, $w = R(T_1 + T_2 - 2T_3) \ln (V_B/V_A)$.

Again total heat taken by the cycle, $Q = Q_1 + Q_2 = RT_1 \ln (V_B/V_A) + RT_2 \ln (V_B/V_A)$

or, $\qquad\qquad\qquad Q = R(T_1 + T_2) \ln (V_B/V_A)$.

Thus the efficiency of the cycle, $\eta = \dfrac{w}{Q} = \dfrac{T_1 + T_2 - 2T_3}{T_1 + T_2}$ or, $\eta = 1 - \dfrac{2T_3}{T_1 + T_2}$.

Refrigerator (R):
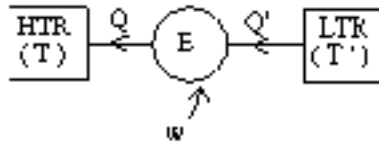
A refrigerator is a device that extracts heat from cold reservoir (LTR) and rejects to hot reservoir (HTR). The process of extraction of heat is called refrigeration.
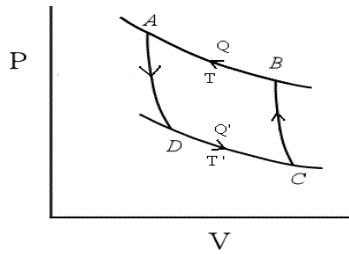
A Carnot refrigerator acts in the same fashion as that of Carnot engine but in reverse direction. It takes away heat (Q') from LTR, work (w) is supplied to it and finally it rejects heat (Q) to HTR. The refrigerator starts from D (shown in the indicator diagram). The sequence of the steps are given below:

Step 1: Reversible isothermal expansion at T' (D → A):

$$\text{Heat is taken from LTR} = Q' = w_1 = RT' \ln \frac{V_3}{V_4} \text{------ (1)}$$

Step 2: Reversible adiabatic compression (C → B):
Temperature increases from T' to T.
Work done $w_2 = C_V (T' - T)$ ------------------------------(2)

Step 3: Reversible isothermal compression at T (B→A):

$$\text{Heat rejected to HTR} = Q = w_3 = RT \ln \frac{V_1}{V_2} \text{------------(3)}$$

Step 4: Reversible adiabatic expansion (A → D):
Temperature decreases from T to T'.
Work done, $w_4 = C_V (T' - T)$ --------------------------- (4)

Adding, $w = w_1 + w_2 + w_3 + w_4 = w_1 + w_3$ since, $w_2 = - w_4$

$$w = RT' \ln \frac{V_3}{V_4} + RT \ln \frac{V_1}{V_2} = RT' \ln \frac{V_3}{V_4} - RT \ln \frac{V_2}{V_1}$$

$$= R (T' - T) \ln \frac{V_3}{V_4}$$

The efficiency of a refrigerator (the more heat it can extract, the more efficient the refrigerator is),

$$\psi = \frac{energy\ ouput\ per\ cycle}{energy\ input\ per\ cycle} = \frac{Q'\ (heat\ extracted)}{w\ (work\ \text{sup}\ plied)}$$

$$= (RT' \ln \frac{V_3}{V_4}) / [R (T' - T) \ln \frac{V_3}{V_4}] = \frac{T'}{T - T'} .. \text{ So, } \boxed{\psi = \frac{T'}{T - T'}.}$$

The capacity of refrigerator is expressed in terms of 'ton'. A 1-ton refrigerator extracts in a day an amount of heat just enough to freeze one ton of water at 32°F.

One short ton = 2000 pound (lb), latent heat of fusion of water = 144 Btu/lb

Heat extracted in one day = 144×2000 Btu / day $= \dfrac{144\ x\ 2000}{24\ x\ 60}$ Btu/min = 200 Btu / min.

Problem: What is the best efficiency of a refrigerator working between 20°C and –10°C? What minimum work has to be done to enable it to withdraw 1000 cal from –10°C and reject heat to the surroundings at 20°C?

Solution: The efficiency of the refrigerator, $\psi = \dfrac{T'}{T-T'} . = \dfrac{263}{293-263} = 8.8$.

Again, $\psi = Q'/w$ or, $w = Q'/w = 1000/8.8 = 114$ cal.

and, $Q = Q' + w = 1000 + 114$ cal $= 1114$ cal.

Various compression refrigerators:

For a good refrigerator, the heat transfer process in the refrigerator be at constant

$\psi = \dfrac{T'}{T-T'}$ .temperature by using vapor compression cycle of refrigeration. The working fluid

may be in the liquid and in the vap

Working substances like NH_3, CFC etc. are used
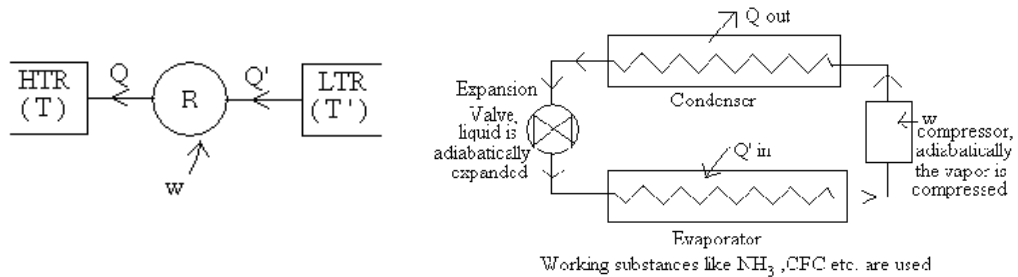
Steps used are given below:
1. The working substance in liquid phase at low P and T is passed through the evaporator at constant P. The liquid absorbs Q' heat from the surrounding cold temperature reservoir (LTR) at T' and turns into saturated vapor (D → C).
2. The above saturated vapor is compressed adiabatically and at high pressure and temperature to a super cooled vapor (C → B).
3. The vapor is then led though a coil immersed in the coolant at constant P, The vapor gives up Q amount of heat to the coolant at temperature T, and condensed to liquid state (B → A).
4. Now the liquid is adiabatically expanded by the valve. The liquid is at low T and P and ready for the next cycle of operation (A → D).

Heat pump: Heat pump (HP) is used to warm the house in the winter by refrigerating heat from outside or cool the house in the summer by refrigerating out heat from the house to the outside.

For heat pump, the efficiency

Interior of the house (T)
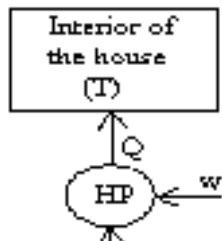
Outside of the house, T'
(LTR) and (T⟩ T').

$(\psi) = \dfrac{heat\ pumped\ inside\ the\ room}{work\ \sup plied}$

$= \dfrac{Q}{Q-Q'} = \dfrac{T}{T-T'}$

(See Ph. Ch - Castellan, p 163).

Problem: Calculate the minimum amount of work required to freeze 1 g of water at $0^{\circ}C$ by means of an ideal refrigerator that operates at $25^{\circ}C$. How much heat is rejected into the surrounding? **Answer**: $w = 7.33$ cal, heat rejected = 87.33 cal.

Carnot's theorem: Two important deductions, called Carnot's theorem are given below along with the proof.

(1) A reversible engine is more efficient than an irreversible engine and

(2) all reversible engines are equally efficient working between the same two temperature limits.

(1) Let us first prove the first theorem. Let two engines be considered with the following characteristics:
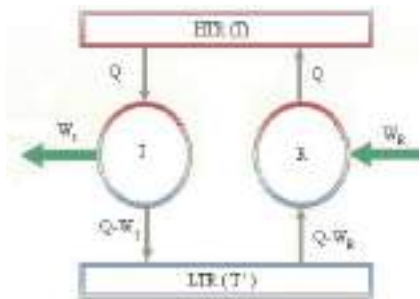
Irreversible engine (I):

Heat supplied = Q,   work done = w_1

Heat rejected   = $Q - w_1$.

Reversible engine (R):

Heat supplied = Q, work done = w_R,

Heat rejected = $Q - w_R$

We have to prove that $\eta_R \rangle \eta_I$.

But if it is not true, then let the reverse is true. i.e. $\eta_I \rangle \eta_R$ and so, $w_I \rangle w_R$

Since same amount of heat is supplied to the engines. Now let us prepare a couple engine in which I is acting as engine while R is acting as a refrigerator. From the diagram, it is clear that there is no loss of heat from the HTR. The couple takes heat

$(Q - w_R) - (Q - w_I) = w_I - w_R$ from the LTR.

The couple engine performs work = $w_I - w_R$. This shows that the couple engine converts heat into work completely leaving no change in the working system (here couple engine). This goes against the P—K statement of 2nd law of thermodynamics. Hence, η_I is not greater than η_R and

reverse is true i.e. $\eta_R \rangle \eta_I$.

(2) Now we prove the second theorem. In the same way as above, let us assume that the 2nd assertion is also false as we can show that it violates the 2nd law and thus first assertion is true.
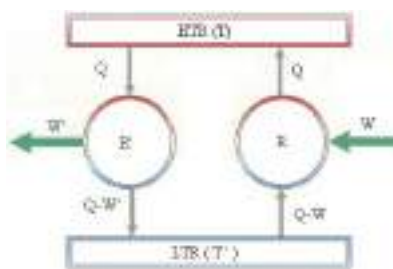
Let between two reversible engines, R' is more efficient i.e. $\eta_R' \rangle \eta_R$, hence $w' \rangle w$, since same amount of heat (Q) is given to the engines at the same two temperature limits. The composite engine takes heat from LTR = $(Q - w) - (Q - w')$

$$= w' - w$$

The composite engine does work = $w' - w$.

This shows that the couple engine converts heat into work completely by taking heat from LTR. This goes

against the P-K statement of the 2nd law. Thus assertion given is true

i.e. all reversible engines are equally efficient when working between the same two temperature limits.

Equivalence of the two statements of the 2nd law:

We have two famous statements of 2nd law: Clausius statement: 'Heat, by itself, can not pass from lower temperature to higher temperature.'

P-K statement: 'Heat can not be completely converted into work. If it does so, there will be a permanent change of the working system.'

These two statements seem to be widely different but it could be proved that they are equivalent. This is shown by using proper arguments as given here.

Let us consider one couple engine consisting of one engine (E) and one refrigerator (R) working between the same two reservoirs. Let the engine (E) obeys P-K statement i.e. the engine takes heat from HTR, part of heat it converts into work and the rest the engine rejects to LTR.
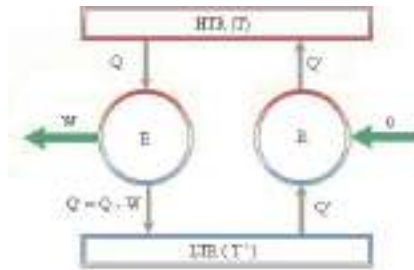
But the refrigerator (R) does not obey the Clausius statement i.e. it carries heat from LTR to HTR without having received any work. It can be shown that the couple engine does not obey the P-K statement.

As outlined above, the couple engine takes heat from HTR $= Q - Q'$.

But work done by the couple engine $=$ w.

Since $Q - Q' =$ w, this shows that couple engine converts heat into work completely by taking heat from HTR. This contradicts P-K statement. Though engine obeys P-K statement, refrigerator does not obey Clausius statement, result is that P-K statement is violated by the couple engine.
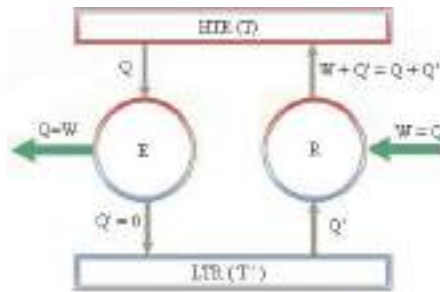
By the same way, it can be shown that if engine disobeys P – K statement but refrigerator obeys Clausius statement, result will be that Clausius statement is not obeyed by the composite engine.

The couple engine it transfers heat Q' from LTR to HTR and as $w - w = 0$, so no work is supplied to it.

Thus the engine and refrigerator together constitutes a self-acting device whose effect is to transfer heat (Q')from LTR to HTR. This couple engine violates the Clausius statement. So, the two statements of the 2nd law are equivalent

Kelvin scale of Temperature

(Thermodynamic scale): Lord Kelvin proposed a scale of temperature based on the efficiency of Carnot engine which does not depend on the nature of the thermometric substance used in the determination of temperature.

The efficiency of the engine, $\eta = \dfrac{w}{Q} = \dfrac{Q - Q'}{Q} = \dfrac{T - T'}{T}$ or, $\dfrac{Q}{Q'} = \dfrac{T}{T'}$. Heat change ratio is

proportional to temperature ratio. And $T = T' \times \dfrac{Q}{Q'}$. or, $T = 273.16 \text{ K} \times \dfrac{Q}{Q'}$

where, T' is assigned to the triple point of water which is 273.16 K. Q is the heat taken from HTR whose temperature (T) is to be determined. Q' is the heat rejected to the triple point of water which is acting as sink. Thus determination of temperature involves calorimetry instead of thermometry.

Again, $\eta = \dfrac{T - T'}{T} = 1 - \dfrac{T'}{T}$. The zero temperature in the scale is also the temperature of the

LTR of a reversible engine with efficiency of one i.e. capable of converting heat into work completely. This scale is made identical with absolute scale and each degree is equal to the Celsius degree.

Meaning of the term	The word 'entropy' means en → in, and trope → transformation i.e. in transformation. It is the property related to the tendency of the system towards transformation of states. 1st law introduces internal energy (U) while 2nd law leads to the introduction of entropy (S).
Different 2nd law statements under one umbrella	The 2nd law of thermodynamics has different statements depending on the various processes. All these different statements point out the feasibility, direction and extent of the processes. Clausius tried to unify the different statements under one umbrella in terms of new property, called entropy (S). Let us understand the criteria of spontaneity of a process through entropy.
Physical significance of entropy and criteria of spontaneity and equilibrium	Entropy measures the randomness or chaotic condition of a system. Higher the randomness, greater is the entropy. A system have tendency to pass spontaneously from a state of more orderliness to less orderliness, i.e. if a system is left to itself, it passes spontaneously (of its own accord) from less chaotic state to more chaotic state. The change of state (i.e. process) will stop when the system attains maximum chaotic condition. Thus we can say, a system changes its state of lower entropy to higher entropy and attains equilibrium when the entropy becomes maximum.

The above criterion of spontaneity of a process is valid for isolated system only. To include other type of systems, the criterion is that the net entropy (i.e. entropy of the universe) increases for spontaneous process and it becomes maximum when the process attains equilibrium.

Thus, it is, $\qquad \Delta S_{system} + \Delta S_{surrounding} = \Delta S_{universe} \geq 0.$

Inequality sign refers to the spontaneity and equality for equilibrium.

Statement of 2nd law in terms of entropy	All natural processes occur spontaneously and so net entropy of the universe is also increasing. Therefore, we can also write the statements of 1st and 2nd law as, 1. 1st law: The net energy of the universe is constant, and 2. 2nd law: The entropy of the universe is increasing.

Concept of entropy:

(1) ($dq_{rev.}$ / T) is perfectly differential but not $dq_{rev.}$:

It can be shown that $dq_{rev.}$ is not perfectly differential as it is not integrable and its value between two definite states depends on the path of the system. But (dq_{rev} / T) is perfectly differential and its value does not depend on the process of the system. This can be shown as follows.

Let one mole of ideal gas undergoes a change of state from (T_1, V_1) to (T_2, V_2) in a reversible process. The heat change that occurs is $dq_{rev.}$

$$\int_1^2 dq_{rev.} = \int_1^2 dU + \int_1^2 PdV = C_V \int_1^2 dT + \int_1^2 PdV = C_V (T_2 - T_1) + R \int_1^2 T \frac{dV}{V}.$$

But the second integral of the RHS of the equation can not be integrated until we know the relation between T and V. If T is kept constant, the integral will have one value and if T is not constant, it will give another value.

It means that $dq_{rev.}$ depends on the nature of the process. On the other hand.

$$\int_1^2 \frac{dq_{rev.}}{T} = C_V \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dV}{V} = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}.$$

Thus, the value of $\int_1^2 \frac{dq_{rev.}}{T}$ is definite between the two states (T_1, V_1) and (T_2, V_2).

So $(dq_{rev.} / T)$ is perfectly differential quantity and it is the difference of a certain fundamental property of the system. This property, Clausius called, entropy(S) and $(dq_{rev.} / T) = dS$.

(2) **Concept of entropy from Carnot cycle:**   Carnot cycle operates in reversible path.
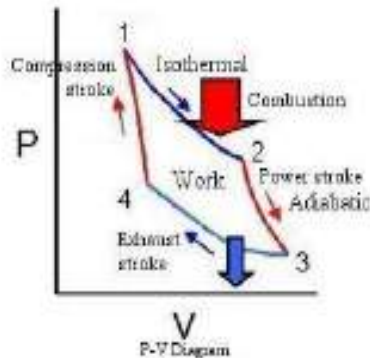
The efficiency of the Carnot engine, $\eta = \dfrac{w}{Q} = \dfrac{T - T'}{T}$

or, $\dfrac{Q - Q'}{Q} = \dfrac{T - T'}{T}$ or, $\dfrac{Q}{T} = \dfrac{Q'}{T'}$

Now let us consider the nature of the quantity, $\dfrac{heat\ change\ reversibly}{temperature}$

For change of state of the system, A→ C via B,
$$\dfrac{heat\ change\ reversibly}{temperature} = \dfrac{Q}{T} + 0 = \dfrac{Q}{T}\ .$$

Again, for the same change of state of the system, A→C via D,
$$\dfrac{heat\ change\ reversibly}{temperature} = 0 + \dfrac{Q'}{T'} = \dfrac{Q'}{T'}\ .$$

But from the Carnot cycle, we have deduced the relation, $\dfrac{Q}{T} = \dfrac{Q'}{T'}\ .$

Hence we can conclude that $\left[\dfrac{heat\ change\ reversibly}{temperature} \right]$ term is same for the change of the two definite states of the system and independent of path of the change.

Again, the term for the whole cycle, $\oint \dfrac{heat\ change\ reversibly}{temperature} = \dfrac{Q}{T} + 0 - \dfrac{Q'}{T'} + 0$

$$= \dfrac{Q}{T} - \dfrac{Q'}{T'}\ . \ = 0.$$

Since, Q' heat is rejected so it is (−) ve. Therefore, $\left[\dfrac{heat\ change\ reversibly}{temperature} \right]$

is a difference of some fundamental property and this property is a state function and called entropy of the system (S).

Calculation of entropy-change (ΔS)

(a) Clausius defined the entropy as a state function and its change between two states of

a system is, $dS = \dfrac{q_{rev.}}{T} = \dfrac{heat\ change\ that\ occurs\ \ reversibly}{temperature\ at\ which\ heat\ change\ occurs}$

When heat change occurs at different temperatures,

$$dS = \dfrac{q_1}{T_1} + \dfrac{q_2}{T_2} + \text{----} = \int_{T_1}^{T_2} \dfrac{q_{rev.}}{T}, \ \text{since T changes continuously.}$$

Problem (1)

In the reversible phase change, heat-change occurs at constant temperature.
One mole of ice melts into liquid water at 0°C and 1 atm. pressure.
1 mole ice (0°C, 1 atm)   →   1 mole of water (0°C, 1 atm).
Initial state (S_1)   ΔS   Final state (S_2)

Hence, $\Delta S = S_2 - S_1 = \dfrac{q_{rev.}}{T} = (18 \times 80) / 273$ cal K^{-1} = 5.27 cal K^{-1}.

This shows that $S_2 > S_1$ i.e. randomness in liquid water is greater than in solid water. It is also important to note that we determine only the entropy-change and not the absolute entropy values.

This is just like the case of the internal energy (U) whose change is determined by adiabatic work, but whose absolute values are undefined. The absolute value of entropy could only be determined with the help of third law of thermodynamics.

When heat-change occurs at different temperature.

Problem (2)

One mole of water is heated reversibly from 27°C to 37°C at 1 atm pressure.

$$\text{1 mole water (27}°\text{C, 1 atm)} \quad \rightarrow \quad \text{1 mole of water (37}°\text{C, 1 atm)}$$
$$\text{Initial state (S}_1\text{)} \qquad \Delta S \qquad \text{Final state (S}_2\text{)}$$

Solution

$$\Delta S = \int_{T_1}^{T_2} \frac{q_{rev.}}{T} = nC_P \int_{300K}^{310K} \frac{dT}{T} = 1 \text{ mol} \times 18 \text{ cal mol}^{-1}K^{-1} \times \ln \frac{310K}{300K} = 0.59 \text{ cal } K^{-1}$$

The result shows that $\Delta S = $ (+)ve. Hence, $S_2 \rangle S_1$ i.e. entropy increases with rise in temperature.

(b) Absorption of heat increases the entropy of the system while evolution of heat decreases its entropy.

(c) Reversible adiabatic process is isentropic. For reversible adiabatic process, $q_{rev} = 0$ so, $dS = 0$. This means that entropy remains constant for a reversible process in isolated system. This is why it is called isentropic process.

Relation of entropy with internal energy and enthalpy of the system.

(Basic thermodynamic equations).

1st law states, $q_{rev.} = dU + PdV$ while   2nd law states, $dS = q_{rev.}/T$.
Combining the two, we have $TdS = dU + PdV$
        or, $dU = TdS - PdV$ ------ (1)

Again, $H = U + PV$ or, $dH = dU + PdV + VdP = TdS + VdP$.
         Thus, $dH = TdS + VdP$ ----- (2)

These two relations, called basic thermodynamic equations. These are of immense help for formulating different relations.

Entropy and unavailable energy (Illustration through Carnot cycle):

From Carnot cycle, $\dfrac{Q}{T} = \dfrac{Q'}{T'}$, where, Q amount of heat is supplied to the engine from the source (HTR at temperature, T and it rejects Q' amount of heat to the sink (LTR).

The Carnot engine utilizes only $(Q - Q')$ amount of heat into useful work.

So this energy (Q') out of supplied heat (Q) is not used for doing mechanical work, and the engine rejects it to the sink.

Therefore the unavailable energy (Q') at $T' = T' \times \dfrac{Q}{T} = T' \times \Delta S$

So unavailable energy (Q') = temperature at which the unavailable energy is considered
                           $\times$ entropy increase due to heat take-up.

Thus when a system absorbs a certain amount of heat in a process, a part of the absorbed heat is utilized for producing work while the rest heat goes to increase the randomness of molecular motion which increases the entropy of the system. It is the randomness of molecules which is responsible for incomplete conversion of heat into work.

Thus entropy-increase of a system measures the unavailable energy for doing useful work and this leads to the degradation of energy or run-down ness of the system.

Formulation of expressions of entropy-change in different processes.

ΔS of ideal gas

(A) Entropy-change of a system in reversible process.

The basic thermodynamic equation is, $dU = TdS - PdV$.

But for n moles ideal gas, $dU = nC_V\, dT$. Substituting these and rearranging we get,

$$dS = nC_V \frac{dT}{T} + \frac{P}{T}dV = nC_V \frac{dT}{T} + nR\frac{dV}{V} \text{ as, } \frac{P}{T} = \frac{nR}{V}$$

Replacing (P / T) and integrating within limits we get, $\int_{S_1}^{S_2} dS = nC_V \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$

$$\Delta S = nC_V\, \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1} \quad\text{-------- id. gas, rev. proc. ---------- (1)}$$

This is entropy-change of the system for the change of state (T_1, V_1) to (T_2, V_2) and C_V is assumed to be independent of T for small change of temperature.

If we use 2nd basic equation, $dH = TdS + VdP$ and insert $dH = nC_P dT$

we get, $\Delta S = nC_P \ln\frac{T_2}{T_1} - nR \ln\frac{P_2}{P_1}$ ----(2) This is the expression for ΔS of the system for the

change of state (T_1, P_1) to (T_2, P_2) in reversible process involving ideal gas.

For isothermal process, $T_1 = T_2$,

$$\Delta S = nR \ln\frac{P_1}{P_2} \quad\text{and}\quad \Delta S = nR \ln\frac{V_2}{V_1} \quad.,----- (3) \qquad \text{id. gas, isotherm. rev. proc}$$

For isochoric process, $V_1 = V_2$, $\quad \Delta S = nC_V \ln\frac{T_2}{T_1}$ ---------- id. gas, rev. isochor. proc.

and for isobaric process, $P_1 = P_2$, $\quad \Delta S = nC_P \ln\frac{T_2}{T_1}$ ---------- id. gas, rev. isobar. proc.

ΔS of a system in reversible adiabatic process for ideal gas

Reversible adiabatic process is called isoentropic process and $\Delta S = 0$. Thus for a change of state from (T_1, V_1) to (T_2, V_2) of a system containing n moles ideal gas in reversible adiabatic process,

$$0 = nC_V \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1} \text{ Or, } R \ln\frac{V_2}{V_1} = -C_V \ln\frac{T_2}{T_1}.$$

This leads to the fact that entropy-change due to volume-change compensates that due to temperature-change in the reversible adiabatic process of an ideal gas.

Again this relation shows that for reversible adiabatic expansion $(V_2 \rangle V_1)$, temperature of the system falls $(T_1 \rangle T_2)$.

And reversible adiabatic compression leads to increase of temperature.

We can also find the T-V relation from the above deduction.

$$\frac{R}{C_V} \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2} \quad\text{but}\quad \frac{R}{C_V} = \frac{C_P - C_V}{C_V} = \gamma - 1 \quad\text{so,}\quad (\gamma - 1)\ln\frac{V_2}{V_1} = \ln\frac{T_1}{T_2}$$

or, $\quad \ln\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \ln \frac{T_2}{T_1}$ or, $\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_2}{T_1}$

or, $T_1 V_1^{\gamma-1} = T_2\, V_2^{\gamma-1}$ -------- for ideal gas in reversible adiabatic process.
This is our required relation.

ΔS for reversible phase change of a pure substance

Change of a pure substance from one phase to another at constant temperature and pressure occurs reversibly. For example, phase change of ice to liquid water occurs at 0°C and 1 atm

pressure. Heat change in the process at constant pressure is equal to the enthalpy change for this type of phase transformation and
$$\Delta S = \frac{\Delta \overline{H}_\epsilon}{T_\epsilon}$$

where, ΔH_ϵ is the enthalpy change at the transition temperature (T_ϵ),

For vaporization of a liquid at its boiling point, $\quad \Delta S = \frac{n\overline{L}_v}{T_b}$.

For the process of fusion of a solid at the melting point, $\quad \Delta S = \frac{n\overline{L}_m}{T_m}$

and for freezing of liquid its freezing point, $\quad \Delta S = -\frac{n\overline{L}_f}{T_f}$.

If q_{rev} heat is taken by the system from the surrounding reversibly at constant T, exactly same amount of heat is lost by the surrounding.

Entropy-change of the universe in reversible process

Thus, $\quad \Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0$

This can also be proved by the use of Carnot cycle. Here, system is Carnot cycle which is operating in cycle so, $\Delta S_{syst} = 0$. The surrounding constitutes HTR and LTR.

$$\Delta S_{surr} = \Delta S_{HTR} + \Delta S_{LTR} = -\frac{Q}{T} + \frac{Q'}{T'} = 0. \quad \text{Since,} \quad \frac{Q}{T} = \frac{Q'}{T'}.$$

This concludes that entropy-change of the universe (net entropy-change) in reversible process (equilibrium process) is zero. When a process occurs reversibly, it proceeds through infinitesimally equilibrium steps. So, the criterion of a process to be at equilibrium, is $\Delta S_{univ} = 0$. However, if the system is an isolated one, then $\Delta S_{surr} = 0$ always and so, $\Delta S_{syst} = 0$
i.e. $\Delta S_{syst} = 0$ --------- rev. proc. isolated syst.

(B) Entropy-change of a system in irreversible processes:

Entropy (S) is a state function and so the entropy-change of a system between two fixed states will be same irrespective of the process ─ reversible or irreversible.

Method of calculation of ΔS in irreversible process
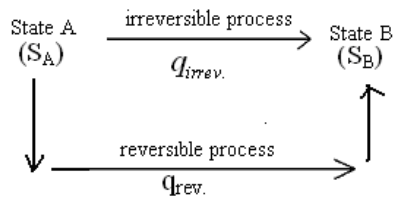
$S_B - S_A = \Delta S$ will be the same for both the processes.

But according to Clausius definition,

$$\Delta S = \frac{q_{rev}}{T} \text{ and not equal to } \frac{q_{irrev}}{T}.$$

To evaluate entropy-change of a system in an irreversible process, a reversible path is assumed between the same two given states of the system. In this reversible path, heat absorbed at each point is divided by the temperature and the quotients are summed up to get the entropy-change of the system between the two given states in the irreversible path.

Example: Entropy-change in irreversible phase-change of a pure substance.
Let us consider the phase transition of 1 mole of super cooled water at – 10°C and 1 atm pressure into ice that occurs suddenly and spontaneously (irreversible process)
[C U'2000]

$$H_2O\ (l) \xrightarrow[\text{irreversible proc.}]{\Delta S} H_2O\ (s)$$
$$-10^0C(-263K) \qquad\qquad -10^0C(-263K)$$
$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

rev. path $\quad \Delta S_1 = C_{P_2} \ln \dfrac{273}{263}$

$$= 18 \times 0.037$$
$$= 0.67 \text{ cal K}^{-1}\text{mol}^{-1}$$

rev. path $\quad \Delta S = C_{P_3} \ln \dfrac{263}{273}$

$$= 9 \times (-0.037)$$
$$= -0.34 \text{ cal K}^{-1}\text{mol}^{-1}$$

$$H_2O\ (l) \xrightarrow[\Delta S_2 = -\bar{L}_f\big/T_e]{\text{rev. path}} H_2O(s)$$
$$0^0C(273K) \qquad\qquad 0^0C(273K)$$

$$= -\frac{18 \times 80}{273} = -5.27 \text{ cal K}^{-1}mol^{-1}$$
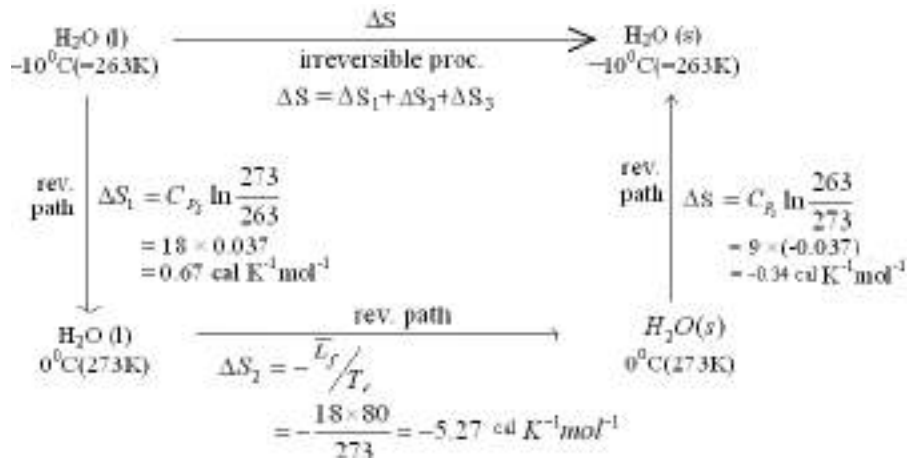
Thus the entropy-change for this irreversible process of phase transition is
$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 0.67 - 5.27 - 0.34 = -\ 4.94 \text{ cal K}^{-1} \text{ mol}^{-1}.$$

ΔS of a system in irreversible process of 1 mole ideal gas

When a system changes its states from (T_1, V_1) to (T_2, V_2) in reversible adiabatic process

The relation, $\qquad R \ln \dfrac{V_2}{V_1} = -\ C_V \ln \dfrac{T_2}{T_1}$ holds.

However, if the system proceeds from the same initial state (T_1, V_1) (by irreversible adiabatic process) to the final volume V_2, the final temperature becomes different and let it be T_2'.

If reversible path is assumed for the change of state from (T_1, V_1) to (T_2', V_2),

$$\Delta S = C_V \ln \frac{T_2'}{T_1} + R \ln \frac{V_2}{V_1} = C_V \ln \frac{T_2'}{T_1} - C_V \ln \frac{T_2}{T_1}.$$

But it could be shown that $T_2' \rangle T_2$ from the assertion, $w_{r,a} \rangle w_{ir,a}$

$$\text{or, } C_V (T_1 - T_2) > C_V (T_1 - T_2') \qquad \text{or, } \qquad T_2' \rangle T_2$$

Thus, $\qquad \Delta S = (+)\text{ve} \qquad\qquad \text{i.e.} \qquad \Delta S > 0$ ------ irrev. adiab. proc., id. gas.

Entropy of the system increases in this process.

So, irreversible adiabatic process in not isentropic and it leads to increase of entropy.

For adiabatic process in isolated system,

This can also be shown by assertion that $\Delta S_{univ} \rangle 0$ for process occurring spontaneously (i.e. irreversibly). as there is no interaction with the surroundings.

Adiabatic process occurs in isolated system which has no interaction with the surroundings.

Hence, $\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} \rangle 0$. But, $\Delta S_{surr} = 0$, So, $\Delta S_{univ} = \Delta S_{syst} \rangle 0$,

$$\text{thus } \Delta S_{syst} \rangle 0 \text{ ------------ isolated syst. irrev. adiab. proc.}$$

Clausius inequality and ΔS of the Universe in irreversible process:

Let us first see what is meant by Clausius inequality. For an irreversible Carnot cycle (in which let one step is irreversible), the efficiency is less than that of a reversible Carnot engine working between the same two temperature limits.

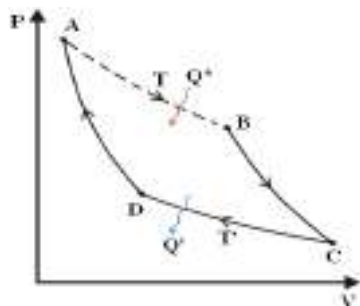i.e. $\quad \eta_{ir} \langle \eta_r$. But, $\quad \eta_r = \dfrac{T - T'}{T} \qquad$ and $\quad \eta_{ir} = \dfrac{w_{ir}}{Q^*} \quad$ or, $\eta_{ir} = \dfrac{Q^* - Q'}{Q^*}$,

where, $\quad Q^* =$ irreversible heat-change $\quad$ and $\quad Q' =$ reversible heat-change.

Irreversible path is shown by dotted line and reversible path by solid lines.

$$\frac{T - T'}{T} \rangle \frac{Q^* - Q'}{Q^*} \quad \text{or,} \quad \frac{Q^*}{T} \langle \frac{Q'}{T'}.$$

Thus, $\dfrac{Q^*}{T} \langle dS \quad$ or, $\quad TdS \rangle Q^*.$

So in general, entropy-change of a system is always greater than (irreversible heat-change / temperature)

i.e. $\qquad dS \rangle (q_{irrev} / T).$

Clausius inequality

This is called Clausius inequality.

The relation helps to find out the criteria of spontaneity of a process.
Now we see the entropy-change of the universe in an irreversible process.
Taking the example of the above irreversible Carnot cycle,

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr},$$

here, $\quad \Delta S_{syst} = \Delta S_{engine} = 0$, as it works in cycle.

$\Delta S_{Universe}$ in an irreversible process.

$$\Delta S_{surr} = \Delta S_{HTR} + \Delta S_{LTR} = -\frac{Q^*}{T} + \frac{Q'}{T'} = (+)ve,$$

since, $\qquad \dfrac{Q'}{T'} \rangle \dfrac{Q^*}{T}$

For reservoir (which is large heat-content), $\quad \Delta S = \dfrac{heat - change \ irreversibly}{temperature}$ (granted).

Therefore, $\qquad \Delta S_{univ} \rangle 0$ for irreversible process (which is spontaneous also).
The criteria of spontaneity (irrev.) and equilibrium (rev.) of a process is

$$\Delta S_{net} \geq 0$$

inequality sign refers for spontaneous and equality sign for equilibrium processes.

Limitation of the criteria of spontaneity of a process, $\Delta S_{net} \geq 0$

For a spontaneous process, net entropy will increase and attains maximum when the process reaches equilibrium.
Though the criterion appears simple but it poses difficulty to calculate ΔS_{surr}, as the process is occurring in the system only. So this criterion is rarely used in actual calculation for spontaneity of a process.
We shall seek criteria of spontaneity of a process in terms of the change of other thermodynamic property of the system.
In the universe, thousands of natural processes are happening and for that the entropy of the Universe is also increasing. The chaotic condition or randomness of the Universe is also increasing. The unavailable energy for doing useful work in the Universe is also increasing due to these natural (irreversible) processes. When the entropy of the Universe attains maximum, there will be no available energy for doing useful work.
All the natural processes will attain equilibrium and there will be death of the Universe.

Speculation for death of the Universe

Some examples for $\Delta S_{universe}$ of spontaneous processes:

(1) Irreversible (spontaneous) flow of heat:
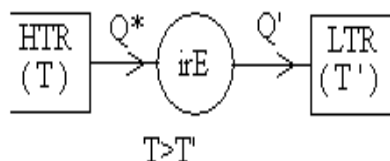   Let a small amount of heat, q flows from HTR at temperature T to LTR at temperature T'.
   Temperature is assumed to be not affected by this small heat-transfer.

$$\Delta S_{univ} = \Delta S_{HTR} + \Delta S_{LTR} = -\frac{q}{T} + \frac{q}{T'} = q\left(\frac{1}{T'} - \frac{1}{T}\right) = (+) \text{ ve, since } T \rangle T'.$$

This is definitely an irreversible process and $\Delta S_{univ} \rangle 0$ for the process.

(2) Joules free expansion of ideal gas:
   Let n moles of an ideal gas is expanded against vacuum (P = 0) under insulated condition.
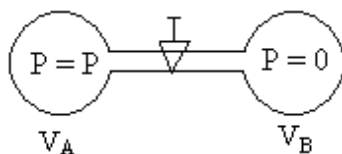
For the process, $w = P_{ext.} \, dV = 0$, $q = 0$.
The expansion is irreversible and so spontaneous.
From the 1st law of thermodynamics of ideal gas,
$q = n \, C_V \, dT + w$. Since $q = 0$ and $w = 0$,
$dT = 0$ and T is constant i.e. isothermal process.
The system thus moves from (T, V_1) to (T, V_1+V_2),

The entropy-change for the process,

$$\Delta S_{syst} = nR \ln \frac{V_1 + V_2}{V_1} \text{ and } \Delta S_{surr} = 0 \text{ as no heat-change occurs between system}$$

and surrounding. $$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} = nR \ln \frac{V_1 + V_2}{V_1} \rangle 0.$$

Thus for this spontaneous process also, $\Delta S_{univ} \rangle 0$.

Physical significance of entropy:

Calculation shows that entropy of a substance increases when it changes from solid to liquid to gas. If we consider from the molecular point of view, then randomness or chaotic condition of the molecules are also increasing from solid to liquid to gas. This promptly suggests that entropy is a measure of randomness of the system.

As randomness increases, entropy is also increased.

Randomness or chaotic condition of the molecules is expressed by a term, called thermodynamic probability (W). It is the number of ways the molecules can be arranged in different energy cells of the system. As the randomness of the molecules increases, the thermodynamic probability also increases. Therefore, we can build up a relation between entropy (S) and probability (W) of a system.

Planck's relation, $S = k \ln W$
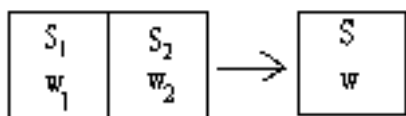
So we can write the relation as $S \, \alpha \, f(W)$.
Let two systems containing identical particles are mixed up to give total entropy S and probability W.
Since entropy is an additive but probability is a multiplicative property so, $S = S_1 + S_2$ and $W = W_1 \times W_2$.

Therefore, $S \, \alpha \, f(W_1 \times W_2)$ but $S_1 \, \alpha \, f(W_1)$ and $S_2 \, \alpha \, f(W_2)$,
Hence, $f(W_1 \times W_2) = f(W_1) + f(W_2)$.
To satisfy this mathematical condition, the function must be logarithmic and so $S \, \alpha \ln W$
or, $S = k \ln W$.   This proportionality constant is Boltzmann constant.
When a solid is at 0 K and attains perfectly crystalline structure, $W = 1$ and $S = 0$.
This is the third law of thermodynamics.

Problem (1)

What would a Carnot cycle look like in a T – V diagram? Label the states and various processes involved. What does the enclosed area signify?   [BU'91, m = 2+3+2]

Answer:
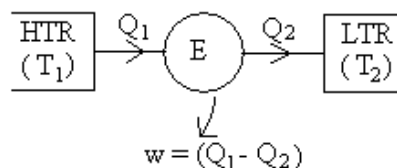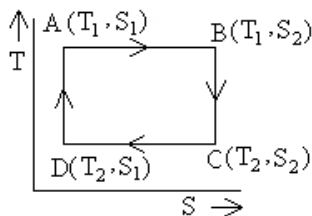
It looks like a rectangle. The various states involved are listed below:
(i) Reversible isothermal expansion of 1 mole ideal gas: T_1 remains constant but entropy increases from S_1 to S_2

(ii) Reversible adiabatic expansion: entropy remains constant but temperature falls from T_1 to T_2

(iii) Reversible isothermal compression at T_2: temperature remains constant at T_2 but entropy decreases from S_2 to S_1

(iv) Reversible adiabatic compression: entropy remains constant at S_1 but temperature increases from T_2 to T_1. The cycle is complete.

The enclosed area (ABCD) = BC × AB = $(T_1 - T_2) \times (S_2 - S_1) = T_1 \Delta S - T_2 \Delta S$
$$= Q_1 - Q_2 = w.$$

So the enclosed area signifies the total work done by the Carnot cycle.

Problem (2)

Show that isobaric temperature coefficient of entropy, $(\partial S / \partial T)_P$ is greater than isochoric temperature coefficient of entropy, $(\partial S / \partial T)_V$. And plot S vs. T curves for
(i) reversible isothermal, (ii) reversible adiabatic, (iii) reversible isobaric and (iv) reversible isochoric processes, using ideal gas.

Answer:
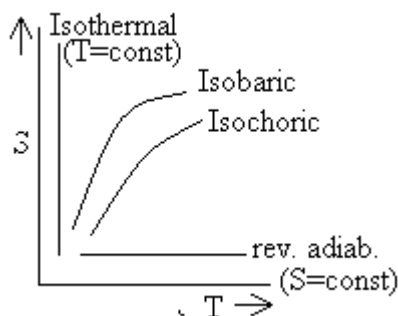
(i) S increases at T so S vs. T plot is vertically straight line.

(ii) S is constant with increase of T, so S vs. T is horizontal straight line

(iii) We have basic thermodynamic equation,
$$dH = TdS + VdP.$$
For 1 mole ideal gas, $dH = C_P dT$.
Thus, $C_P dT. = TdS + VdP$.
Or, $(\partial S / \partial T)_P = C_P / T$
So, S increases with T at constant P with (–) ve curvature.

(iv) Another basic equation is $dU = TdS – PdV$.

Putting $dU = C_V dT$, we get, $C_V dT = TdS – PdV$
$$\text{or, } (\partial S / \partial T)_V = C_V / T.$$

S increases with T at constant V with (–) ve curvature.
Since $C_P \rangle C_V$, so $(\partial S / \partial T)_P \rangle (\partial S / \partial T)_V$.

Isobaric curve is steeper than isochoric in the S – T diagram.

The plots S vs. T for isobaric and isochoric processes produce curve with decreasing slope as T increases. The curvature of the plots are $(\partial^2 S / \partial T^2)_P = – C_P / T^2$ and $(\partial^2 S / \partial T^2)_V = – C_V / T^2$, both are (–)ve.

Problem (3)

Calculate the entropy-change when Argon at 25°C and 1.00 atm pressure in a container of volume 500 ml is allowed to expand to 1000 ml and is heated simultaneously at 100°C. (C_V = 12.48 J mol^{-1} K^{-1} for Argon at 25°C and 1 atm). [IISc'03, adm. to MSc. m=5].

Solution

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad \text{for n moles of ideal gas.}$$

= 1 mol×12.48 J mol^{-1}K^{-1} ln $\frac{373K}{298K}$ +1 mol×8.31 J mol^{-1}K^{-1} ln $\frac{1000\ ml}{500\ ml}$ = 8.55 J K^{-1}.

Problem (4)

For NH_3, $C_P = 6.2 + 7.9 \times 10^{-3}$ T cal mol^{-1}K^{-1}. Assuming ideal behavior, estimate the entropy-change in heating 34 gm of the gas from a volume 100 lit at 300 K to a volume of 60 lit at 800 K.

Solution

Since 34 gm = 2 moles and $C_V = C_P – R = (6.2 + 7.9 \times 10^{-3}$ T – 2) cal mol^{-1}K^{-1}
$$= 4.2 + 7.9 \times 10^{-3} \text{ T cal mol}^{-1}\text{K}^{-1}.$$

$dS = nC_V (dT/ T) + nR (dV/ V)$
= 2 mol×(4.2 + 7.9 ×10^{-3} T cal mol^{-1}K^{-1})(dT / T)+2 mol×(2 cal mol^{-1}K^{-1}) (dV / V),
Integrating within limits,

$$\int_1^2 dS = 8.2 \int_1^2 \frac{dT}{T} + 15.8 \times 10^{-3} \int_1^2 dT + 4 \int_1^2 \frac{dV}{V}$$

or, $\qquad$ $S_2 - S_1 = 8.2 \ln \dfrac{T_2}{T_1} + 15.8 \; 10^{-3} \, (T_2 - T_1) + 4 \ln \dfrac{V_2}{V_1}$

or, $\quad \Delta S = 8.2 \ln (800/300) + 15.8 \times 10^{-3} (800 - 300) + 4 \ln (60 \text{ lit} / 100 \text{ lit}) = 14.1 \text{ cal K}^{-1}$.

Problem (5)	A certain mass of an ideal gas expands into vacuum to twice its initial volume. Calculate ΔU and ΔS for the process. $\qquad$ [BU, 1999, Q 7(a), m = 2+2]
Solution	It the free expansion of ideal gas against vacuum ($P = 0$) $\quad$ so, $w = P_{ext} (V_2 - V_1) = 0$. This expansion occurs without any heat exchange (Joule's expansion), so, $\qquad$ q = 0. Therefore using 1st law of thermodynamics, $q = \Delta U + w$ $\qquad\qquad$ or, $\quad 0 = \Delta U + 0$ or, $\qquad \Delta U = 0$. Again for ideal gas $\Delta U = n C_V dT = 0$ but $T =$ constant. So, the process is also isothermal.. The entropy change of the process, $\Delta S = R \ln (V_2 / V_1) = 2 \text{ cal mol}^{-1}\text{K}^{-1} \ln (2V_1/ V_1)$ $\qquad\qquad$ or, $\Delta S = 2 \ln 2 \text{ cal mol}^{-1}\text{K}^{-1}$ $\quad$ or, $\Delta S = 1.386 \text{ cal mol}^{-1}\text{K}^{-1}$.
Problem (6)	(i) Use the appropriate statement of the Carnot theorem to establish Clausius inequality, $\oint \dfrac{dq_{irrev}}{T} \langle 0 .$ $\qquad\qquad$ [CU'93, Q5(a), m = 4]
Answer:	The Carnot theorem which may be used to prove the Clausius inequality is that 'A reversible engine is more efficient than an irreversible engine working between the same two temperature limits.' Let dq_{irrev} amount of heat is taken by the irreversible engine from the HTR at T irreversibly and dq_{rev} heat is given out by the engine reversibly to the LTR at T'. Then it is possible to show that $\qquad \dfrac{dq_{irrev}}{T} \langle \dfrac{dq_{rev}}{T'}$. $\quad$ But, $\quad \dfrac{dq_{rev}}{T'} = dS$, $so \; \dfrac{dq_{irrev}}{T} \langle dS$. Thus for the cyclic integral, $\oint \dfrac{dq_{irrev}}{T} \langle \oint dS, \; but \oint dS = 0, \; hence \oint \dfrac{dq_{irrev}}{T} \langle 0$.

Helmholtz Free Energy or Work Function (A)

Definition	This thermodynamic property is a derived one and is defined as, $A = U - TS$ Since U, T and S are all state functions, so A is also a state function and perfectly differential quantity. U and TS are energy terms so A is also an energy term. Further, U = internal energy of the system while TS = unavailable energy for doing useful work. So, $A = U - TS$ = part of the internal energy of the system which is available for doing useful work.
Physical significance	Let us consider, a system changes its state by an isothermal reversible process. So the change of A of the system is, $\quad \Delta A = \Delta U - T\Delta S$, $\quad$ since, $\quad \Delta T = 0$ for isothermal process. But, $\quad T\Delta S = Q_{rev.} = \Delta U + w_{max}$, as reversible isothermal process produces maximum work. Therefore, $\quad \Delta A = \Delta U - (\Delta U + w_{max.})$ or, $\quad -\Delta A = w_{max.}$ ----- rev. isotherm. proc. The result signifies that the decrease of work function of a system is equal to the maximum work done by the system in reversible isotheral process. Thus, A measures the working ability of a system. Greater the value of A, greater amount of work the system can do. If a system does work, its value of A decreases. When the process is only reversible isothermal, the system can do maximum work. For other processes, $\quad -\Delta A \neq w_{max.}$ $\quad$ and $\quad -\Delta A > w$. That is, there will be same drop of A of the system but work done becomes less.
Basic thermo-dynamic equation	We have, $\quad\quad A = U - TS$, $\quad$ on complete differentiation. $dA = dU - TdS - SdT$. But, $TdS = dU + PdV$, when work is considered only mechanical. So, $\quad\quad dA = dU - (dU + PdV) - SdT$ $\quad$ or, $\quad\quad dA = -SdT - PdV$. This is also one basic thermodynamic equation and is widely used for formulating different thermodynamic relations.
Expression for calculation of ΔA	(1) When the process is reversible and isothermal, $dT = 0$, the above equation becomes $dA = -PdV$. $\quad$ If the ideal gas is used, $\quad P = -\dfrac{nRT}{V}$ $\quad$ so, $\quad dA = -nRT\,\dfrac{dV}{V}$. Integrating within limits, $\displaystyle\int_1^2 dA = -nRT\int_1^2 \dfrac{dV}{V}$ $\quad$ or, $\quad A_2 - A_1 = -nRT\ln\dfrac{V_2}{V_1}$. Thus, $\quad\quad\quad\quad \Delta A = nRT\ln\dfrac{V_2}{V_1}$ ------------- id. gas, rev. isotherm. proc.
Work function and temperature	(2) When the process is isochoric, $dV = 0$ $\quad$ so, $\quad\quad dA = -SdT$ or, $(\partial A/\partial T)_V = -S$. Since, entropy (S) of a system is always a (+)ve quantity, so, $\quad\quad\quad\quad\quad\quad (\partial A/\partial T)_V = (-)$ve. This implies that work function of a system is always decreased with rise in temperature. Further, $S_{gas} > S_{liquid} > S_{solid}$, hence we can infer that decrease of A per degree increase of T is highest for gaseous substance, lowest for solid and in-between for liquid. This is also in conformity with our physical experience. As T increases, randomness increases, working ability decreases. The above basic equation also leads to the fact that for a reversible isochoric isothermal process, $\quad\quad\quad\quad dA = 0$ as $\quad dT = 0$ $\quad$ and $\quad dV = 0$. $\quad\quad$ This draws interest when a chemical process occurs at constant T and V, $\Delta A = 0$, the process is at equilibrium.
Thermodynamic definition of entropy (S) and pressure (P)	Again, entropy (S) and pressure (P) of a system can be defined from the use of the basic equation. $\quad\quad\quad\quad\quad\quad S = -(\partial A/\partial T)_V$ i.e., entropy (S) of a system is its decrease of A per unit increase of T at constant V. Likewise, S is defined as, $\quad P = -(\partial A/\partial V)_T$,

Definition	It is also a derived very powerful thermodynamic property. It is defined as, $G = H - TS$. Since H, T and S are all state functions, so G is also a state function and perfectly differential quantity.

Again, H and TS are energy terms, so G is also an energy term of the system.

In the similar way as A, G is also defined as the part of enthalpy (total heat-content) of the system that is available for doing useful work by the system.

Physical significance	Let us consider a system is undergoing a reversible isothermal and isobaric change (viz. reversible phase-change of a substance at constant T and P). The change in G of the system, $\Delta G = \Delta H - T\Delta S$. But $H = U + PV$ so, $\Delta H = \Delta U + P\Delta V$ since, T and P are constants.

Thus, $\Delta G = (\Delta U + P\Delta V) - T\Delta S$. Again, $T\Delta S = \Delta U + w$.

This work may be partly mechanical or partly non-mechanical or fully mechanical or fully non-mechanical. Putting the terms,

$\Delta G = (\Delta U + P\Delta V) - (\Delta U + w) = P\Delta V - w$. or, $-\Delta G = w - P\Delta V = w_{non-mechanical}$.

$-\Delta G = w_{non-mechanical}$ --------------- rev. isotherm. isobaric proc.

This implies that decrease of free energy of a system in reversible isothermal isobaric process is equal to the non-mechanical work done by the system.

When a voltaic cell is full-charged, its G is maximum, but as it gives electrical energy when used, its G is decreased and when the cell is totally exhausted, its G becomes minimum.

When the process is not reversible isothermal and isobaric, there occurs same decrease of G but $w_{non-mech}$ becomes less between the two specified states.

i.e., $-\Delta G > w_{non-mech.}$

By definition, $G = H - TS = U + PV - TS$ which on complete differentiation,

$dG = dU + PdV + VdP - TdS - SdT$. But, $TdS = dU + PdV$.

Substituting, we get another basic thermodynamic equation,

$dG = VdP - SdT$.

Basic thermo-dynamic equations	So far we have formulated four basic equations. These are: (1) $dU = TdS - PdV$. (2) $dH = TdS + VdP$. (3) $dA = -SdT - PdV$. (4) $dG = -SdT + VdP$

Calculation of ΔG of a process	The basic equation is, $dG = -SdT + VdP$, so, for a reversible isothermal and isobaric process (reversible phase-change at constant T and P), $\Delta G = 0$. Thus for ice $\rightarrow$ water at 0^oC and 1 atm pressure, $\Delta G = 0$ and $G_{ice} = G_{water}$ exists so long transition of ice to water continues.

ΔG of a system for pressure-change in reversible isothermal	(1) For reversible isothermal process, $dG = VdP$. When n moles of ideal gas is used in the system, $V = \dfrac{nRT}{P}$, so $dG = nRT\,\dfrac{dP}{P}$. Integrating within limits, $\displaystyle\int_1^2 dG = nRT\int_1^2 \dfrac{dP}{P}$ $G_2 - G_1 = nRT \ln\dfrac{P_2}{P_1}$ or, $\Delta G = nRT \ln\dfrac{P_2}{P_1}$ ---- id. gas, rev. isotherm. proc.

This relation can be used to calculate ΔG of a system.

When $P_1 = 1$ atm (standard state), $G_1 = G^o$ (standard free energy of the system), the relation becomes,

$G = G^o + nRT \ln P$,

where, G is the free energy of the system at pressure P.

This shows that G varies linearly with lnP. Dividing by n, $(G/n) = (G^o/n) + RT \ln P$

This (G/n) is the molar free energy and Lewis called it 'chemical potential' and is denoted by μ.
So, $\mu = \mu^o + RT \ln P$, here, μ^o = Standard chemical potential
and it depends only on T of the system.
More precisely, it should be written as, $\mu(T, P) = \mu^o(T) + RT \ln P$

Chemical potential of a pure substance

The gas flows from higher pressure to lower pressure spontaneously. The above equation suggests that the gas will flow from a state of higher chemical potential to a state of lower chemical potential and the process will stop when chemical potential becomes equal.

Like other kinds of potential – electrical, gravitational, magnetic etc., chemical potential (μ) is always in the direction from high to low potential.

Free energy and temperature

(2) For isobaric process, $dP = 0$ and so, $(\partial G/\partial T)_P = -S = (-)ve$.
This means that with rise of temperature (T), free energy (G) of the system will decrease i.e. amount of available energy for doing non-mechanical work will also decrease.
With similar arguments as in work function, we can conclude that the decrease of G per unit increase of T is highest for gaseous substances and lowest for solid substances.

Definition of V and S in terms of free energy

The volume (V) and entropy (S) of a system are defined as,
$$V = (\partial G/\partial P)_T \quad \text{and} \quad S = -(\partial G/\partial T)_P.$$
These are the definitions of V and S in terms Gibb's free energy of the system.
The relations also states that G will increase with increase of P at constant T and
G will decrease with increase of T at constant P.

Problem (1)

Calculate the change in Gibbs free energy for a process carried out from 300 K to 500 K at constant pressure. Given, $S_T = 50 + 12 \ln T$. [NET—CSIR, UGC].

Solution

The basic equation is, $dG = -SdT + VdP$, P is constant so, $dP = 0$.
The equation is then $dG = -SdT = -(50 + 12 \ln T) dT$. Integrating within limits,

$$\int_1^2 dG = -50 \int_1^2 dT + 12 \int_1^2 \ln T \, dT.$$

or, $G_2 - G_1 = -50(T_2 - T_1) - 12[(T_2 \ln T_2 - T_2) - (T_1 \ln T_1 - T_1)]$
or, $\Delta G = -50(500-300) - 12[(500 \ln 500 - 500) - (300 \ln 300 - 300)] = -24,352$ cal.

Problem (2)

The temperature of one mole of N_2 gas at 2 atm pressure is raised from 300 K to 400 K. Calculate ΔG for the process if entropy of N_2 gas is given by $S = A + B \ln T$ with A = 25 J/K and B = 29 J/K. (Ans. – 19,494 J) [BU'91, Q 10(b), m = 10]

Problem (3)

Point out whether for an ideal gas the following are an enthalpy or an entropy effect:
(i) increase of μ with increase of P at constant T
(ii) decrease of μ with increase of T at constant P [BU'97, Q 9(b), m = 4]

Answer:
(i) We have $\left(\frac{\partial \mu}{\partial P}\right)_T = \overline{V}$ as, $\overline{V}$ of a substance is always (+)ve hence $\left(\frac{\partial \mu}{\partial P}\right)_T = (+)ve$.

It is definitely an entropy effect as with increase of P, ($\overline{V}$) decreases and entropy decreases due to less randomness of the system, non-mechanical working ability (μ) is increased.

(ii) $\left(\frac{\partial \mu}{\partial T}\right)_P = -\overline{S} = (-)ve$, it is obviously an entropy effect.

We have by definition, $G = H - TS$, and $-S = (\partial G/\partial T)_P$, so eliminating S, we get, $\quad G = H + T(\partial G/\partial T)_P$ ---------(1).

By similar way, we may get, $\quad A = U + T\,(\partial A/\partial T)_V$ ------ (2).

Gibbs-Helmholtz equations for a single substance

These two equations are called Gibbs Helmholtz equations and applied to a given state of the system.

However, equation (1) can be written in the following form also.

$$-H = -G + T\left(\frac{\partial G}{\partial T}\right)_P , \qquad \text{dividing by } T^2, \qquad -\frac{H}{T^2} = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P = \left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_P.$$

$$\text{Or,} \quad H = -T^2\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_P. \quad \text{Again, } H = \left[\frac{\partial\left(G/T\right)}{\left(-\partial T/T^2\right)}\right]_P \quad \text{or,} \quad H = \left[\frac{\partial\left(G/T\right)}{\partial\left(1/T\right)}\right]_P \text{ ----- (3).}$$

Since, H is a state function, so RHS of the equation is also a state function.

These relations are used for a pure substance or system in a given state.

Gibbs-Helmholtz equations for a system in isothermal isobaric process

Now let us consider, the system undergoes a change of isothermal isobaric process, and for that, $\quad \Delta G = \Delta H - T\,\Delta S$, but, $\quad -S_1 = (\partial G_1/\partial T)_P \quad$ and $\quad -S_2 = (\partial G_2/\partial T)_P$,

where, S_1 and S_2 are the entropies of the system in the initial and final states,

G_1 and G_2 are their corresponding free energies.

$$\text{So,} \qquad -(S_2 - S_1) = \left[\frac{\partial(G_2 - G_1)}{\partial T}\right]_P \quad \text{or,} \quad -\Delta S = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P.$$

Replacing ΔS,

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \text{ --------- isotherm. isobar. proc.} \qquad (4)$$

This equation is very important and it is specially called Gibbs Helmholtz equation.

Rearranging, we can get,

$$-\frac{\Delta H}{T^2} = \left[\frac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P \qquad \text{and} \qquad \Delta H = \left[\frac{\partial\left(\Delta G/T\right)}{\partial\left(1/T\right)}\right]_P. \text{ ----------------(5)}$$

Similar equations with ΔA and ΔU can be formulated in the similar way:

$$-\Delta S = \left[\frac{\partial(\Delta A)}{\partial T}\right]_V , \quad \Delta A = \Delta U + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V , \quad -\frac{\Delta U}{T^2} = \left[\frac{\partial\left(\Delta A/T\right)}{\partial T}\right]_V \text{ and } \Delta U = \left[\frac{\partial\left(\Delta A/T\right)}{\partial\left(1/T\right)}\right]_V.$$

Applications

These equations are useful to calculate ΔG at a given temperature if it is known at other temperature.

If ΔH is assumed to be independent of T, then the plot of $(\Delta G/T)$ vs.$(1/T)$ gives a straight line with slope of ΔH.

ΔG, ΔS and ΔH of a reaction can be calculated from the measurement of potential of galvanic cell by the use of the above relations. If n gm equivalent chemical change occurs in the galvanic cell of potential E_{cell}, then the electrical energy produced from the cell is nFE, where F is one faraday (96,500 C /mol.). The above thermodynamic properties of the cell reaction can be calculated by using the following relations.

$$\Delta G = -\,nFE_{cell}, \qquad \Delta S = -\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = nF\left(\frac{\partial E_{cell}}{\partial T}\right)_P \quad \text{and} \quad \Delta H = nF\left[T\left(\frac{\partial E_{cell}}{\partial T}\right)_P - E_{cell}\right].$$

Problem (1)	Calculate ΔG per mole for freezing of super cooled water at $-5^{\circ}C$, given latent heat of fusion of ice = 1440 cal mol^{-1}.

Solution We have, $-\dfrac{\Delta H}{T^2} = \left[\dfrac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P$ or, $d\left(\dfrac{\Delta G}{T}\right)_P = -\dfrac{\Delta H}{T^2}\,dT$. Integrating within limits and

assuming ΔH independent of T, $\displaystyle\int_1^2 d\left(\dfrac{\Delta G}{T}\right) = -\Delta H\int_1^2\dfrac{dT}{T^2}$ or, $\dfrac{\Delta G_2}{T_2} - \dfrac{\Delta G_1}{T_1} = \Delta H\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$.

At $0^{\circ}C$ (273 K), the process is reversible phase change at constant T and P, so, $\Delta G_1 = 0$.

Therefore, $\dfrac{\Delta G_2}{T_2} = \Delta H\left(\dfrac{1}{T_2} - \dfrac{1}{273}\right)$ or, $\dfrac{\Delta G_2}{268} = -1440\left(\dfrac{1}{268} - \dfrac{1}{273}\right)$,

since latent heat for freezing of water $= -1440$ cal mol^{-1}.

Thus, $\Delta G_2 = -1440 \times 268 \times \dfrac{5}{268\times 273}$ cal mol^{-1}, Or, $\Delta G_2 = -26.37$ cal mol^{-1}.

Problem (2)	For a certain reaction, $\Delta G = -a + bT\ln T$ where a and b are constants. Express ΔH as function of T. [Brilliant Tutorials]

Answer From the relation, we have, $\dfrac{\Delta G}{T} = -\dfrac{a}{T} + b\ln T$, so $\left[\dfrac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P = -\dfrac{\Delta H}{T^2}$.

Or, $-\dfrac{\Delta H}{T^2} = \dfrac{\partial}{\partial T}\left(-\dfrac{a}{T} + b\ln T\right) = \dfrac{a}{T^2} + \dfrac{b}{T} = \dfrac{a+bT}{T^2}$. Comparing we get, $-\Delta H = a + bT$.

Problem (3)	Calculate ΔG for the formation of $H_2O(l)$ from its elements at $25^{\circ}C$, $\Delta H_f = -286$ kJ. Entropies of $H_2(g)$, $O_2(g)$ and $H_2O(l)$ are respectively 130.6, 205.0 and 70.3 J K^{-1}mol^{-1}. [Brilliant Tutorials]

Solution The reaction for the formation of water is, $H_2(g) + \frac{1}{2} O_2(g) = H_2O(l)$;

$\Delta S = \sum \gamma_i \overline{S_i} = -130.6 - \frac{1}{2} \times 205.0 + 70.3 = -162.8$ J K^{-1}.

But $\Delta G = \Delta H - T\Delta S = -286$ kJ $- 298$ K $\times (-162.8 \times 10^{-3}$ kJ K$^{-1}) = -237.5$ kJ.

Problem (4)	For a certain reaction, ΔG (in cal/mole) = 13,580 + 16.1 T logT $-$ 72.59 T. Find ΔS and ΔH of the reaction at $27^{\circ}C$. [CU' 87, Q 6(c), m = 4]

Solution Given, $\Delta G = 13{,}580 + (16.1/2.303)$ T lnT $- 72.59$ T $= 13{,}580 + 6.99$ T lnT $- 72.59$ T.

At $27^{\circ}C$, $\Delta S = -\left[\dfrac{\partial\left(\Delta G\right)}{\partial T}\right]_P = -[0 + 6.99 + 6.99\,\ln T - 72.59] = 25.82$ cal K^{-1} mol^{-1}.

$\Delta G = 13{,}580 + 16.1 \times 300\,\log 300 - 72.59 \times 300 = 3{,}763.83$ cal mol^{-1}.
$\Delta H = \Delta G + T\,\Delta S = 3{,}767.5 + 300 \times 25.73 = 11{,}509.88$ cal mol^{-1}

Problem (5)	The free energy change, ΔG accompanying a given process is -20.5 Kcal mol^{-1} at $25^{\circ}C$, while at $35^{\circ}C$ it is -20 Kcal mol^{-1} at constant pressure. Calculate the approximate entropy change, ΔS and the change in heat content, ΔH for the process a $30^{\circ}C$. [CU'88]

Solution $\Delta S = -\left[\dfrac{\partial\left(\Delta G\right)}{\partial T}\right]_P = -\left[\dfrac{\Delta G_2 - \Delta G_1}{T_2 - T_1}\right] = -\left[\dfrac{-20.0 + 20.5}{10}\right] = -0.05$ KcalK^{-1}mol^{-1}.

At $30^{\circ}C$, $\Delta G = -20.25$ Kcal mol^{-1}. Again, $\Delta H = \Delta G + T\Delta S$.
Putting the values, we get, $\Delta H = -20.25 + 303 \times (-0.05) = -35.40$ Kcal mol^{-1}.

Maxwell's relationships

Basic equations in thermo-dynamics

We have four basic equations which are the basis of formulation of the Maxwell's relations. These are:

(1) dU = TdS – PdV,   (2) dH = TdS + VdP,
(3) dA = – SdT – PdV,   (4) dG = – SdT + VdP,

Each basic equation will produce one relation. Let us formulate one such relation from the basic equation (1),   dU = TdS – PdV

This gives $(\partial U/\partial S)_V = T$. Differentiating again with respect to V at constant S,

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S \text{-------- (A).}$$

Again from the basic equation, we can write, $(\partial U/\partial V)_S = -P$. Differentiating with respect to S at constant V, we have

$$\frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V \text{ ----- (B)}$$

Since U is a state function and so it obeys Euler's reciprocal relation, $\dfrac{\partial^2 U}{\partial V \partial S} = \dfrac{\partial^2 U}{\partial S \partial V}$.

Equating, we get the relation, $\left(\partial T/\partial V\right)_S = -\left(\partial P/\partial S\right)_V$

By similar procedure, we can formulate other relations ─ one from each basic equation. These are given here:

Four Maxwell's relations.

(1) dU = TdS – PdV, $\left(\partial T/\partial V\right)_S = -\left(\partial P/\partial S\right)_V$.

(2) dH = –TdS + VdP, $\left(\partial T/\partial P\right)_S = \left(\partial V/\partial S\right)_P$.

(3) dA = – SdT – PdV $\left(\partial P/\partial T\right)_S = \left(\partial S/\partial V\right)_T$.

(4) dG = – SdT + VdP, $\left(\partial V/\partial T\right)_P = -\left(\partial S/\partial P\right)_T$.

These relations are obtained from the mathematical theorem, dz = M dx + N dy

and z, M and N are all functions of x and y, then $\left(\partial M/\partial y\right)_x = \left(\partial N/\partial x\right)_y$.

A short-cut way to bring out the relations is given as:
If S and P are in quotient, then put (–)ve sign in the term.
These relations do not refer to a process but express relations which hold at equilibrium state of a system. These relations are very useful as it provides relationships between measurable quantities (LHS) with immeasurable quantities (RHS).
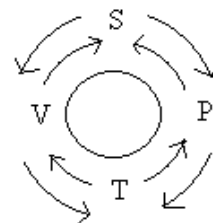
Formulation of thermodynamic equations of state

Application of Maxwell's relations

(1) We have basic equation, dU = TdS – PdV. Dividing by dV at constant T, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P.$$ But Maxwell's relation is $\left(\partial P/\partial T\right)_S = \left(\partial S/\partial V\right)_T$.

Substituting, we get the relation, $\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial P}{\partial T}\right)_V - P.$

This is one thermodynamic equation of state.

(2) Another basic equation is dH = TdS + VdP. Dividing by dP at constant T

and using Maxwell's relation, we have $\left(\dfrac{\partial H}{\partial P}\right)_T = T\left(\dfrac{\partial S}{\partial P}\right)_T + V$.

But Maxwell's relation is $-\left(\partial V/\partial T\right)_P = \left(\partial S/\partial P\right)_T$. Using the relation, we get,

$$\left(\dfrac{\partial H}{\partial P}\right)_T = -T\left(\dfrac{\partial V}{\partial T}\right)_P + V \ .$$

This is another thermodynamic equation of state.

U and H are functions of T only for ideal gas

If we calculate $(\partial U/\partial V)_T$ for ideal gas using the above equation, then we find $(\partial U/\partial V)_T = 0$ and for vander Waals gas, $\qquad (\partial U/\partial V)_T = an^2/V^2$.
This predicts that U = f (T) only and independent of V for ideal gas
but, $\qquad\qquad$ U = f (T,V) for vander Waals gas and U is a function of T and V.

Again, $\qquad \left(\dfrac{\partial H}{\partial P}\right)_T = 0$ for ideal gas so, H = f (T) only.

But for vander Waal's gas, $\qquad \left(\dfrac{\partial H}{\partial P}\right)_T = b - \dfrac{2a}{RT} + \dfrac{3abP}{R^2T^2}$

and so H = f (T,P), that is H is a function of T and P.

Problem (1)

Show that the total differential of entropy in terms of temperature and volume can be

expressed by the equation, $\qquad dS = \dfrac{C_V}{T}dT + \dfrac{\alpha}{\beta}dV$. $\qquad$ [Civil Service Exam, 01]

Answer:

$S = f (T,V) \qquad$ so, $\qquad dS = \left(\dfrac{\partial S}{\partial T}\right)_V dT + \left(\dfrac{\partial S}{\partial V}\right)_T dV$.

But Maxwell's relation is $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V = \dfrac{\alpha}{\beta}$. And the basic equation is dU = TdS – PdV.

Taking for one mole ideal gas, $dU = C_V dT$, the equation becomes $\ C_V\ dT = T\ dS - P\ dV$

or, $\left(\dfrac{\partial S}{\partial T}\right)_V = \dfrac{C_V}{T}$. Putting these expressions, we get, $\ dS = \dfrac{C_V}{T}dT + \dfrac{\alpha}{\beta}dV$. (Shown)

Problem (2)

By integration of $\left(\partial A/\partial V\right)_T = -P$, Derive an expression for work function (A) of vander Waals gas (include integration constant).

Answer:

For 1 mole vander Waals gas, $P = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$. So, $\qquad \int dA = -RT\int\dfrac{dV}{V-b} + a\int\dfrac{dV}{V^2}$

Rearranging and integrating we get, $\qquad$ A = −RT ln(V − b) + (a/V) + IC

Problem (3)

Find the value of $\left(\partial S/\partial V\right)_T$ for vander Waals gas.

Answer:

Maxwell relation gives, $\left(\partial S/\partial V\right)_T = \left(\partial P/\partial T\right)_V$. For 1 mole vander Waals gas, $P = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$.

So, $\qquad \left(\partial S/\partial V\right)_T = \left(\partial P/\partial T\right)_V = \dfrac{R}{V-b} + 0$. $\qquad$ Therefore, $\qquad \left(\partial S/\partial V\right)_T = \dfrac{R}{V-b}$.

Problem (4)

Derive an expression for the change in entropy for the isothermal expansion of 1 mole vander Waals gas from V_1 to V_2.

Answer: The expression for the entropy change in isothermal expansion is $\left(\frac{\partial S}{\partial V}\right)_T$.

In the problem (3), we have already deduced, $\left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{V-b}$, so $dS = R\frac{dV}{V-b}$.

Integrating within limits, $\int_1^2 dS = R\int_1^2 \frac{dV}{V-b}$ or, $S_2 - S_1 = \left[\ln(V-b)\right]_{V_1}^{V_2}$ or, $\Delta S = R \ln \frac{V_2 - b}{V_1 - b}$.

This is the expression of entropy change in isothermal expansion of 1 mole vander Waals gas from V_1 to V_2.

Problem (5) Derive expressions for $\left(\frac{\partial S}{\partial V}\right)_T$ and $\left(\frac{\partial S}{\partial T}\right)_V$ and show that they are always (+)ve. What do the results signify? [BU'90, Q 9(b), m = 4+1]

Answer: From Maxwell's relation, we get, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = (+)ve.$

Thus P increases with rise of T always at constant V.

Again, $dU = TdS - PdV$ or, $C_V dT = TdS - PdV$

or, $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} = (+)ve$ always, as C_V and T both are (+)ve quantity.

The results signify that isothermal expansion of a gas always leads to increase of entropy and isochoric increase of temperature also results in increase of entropy.

Problem (6) Justify /criticize the following $\left[\frac{\partial\left(G/T\right)}{\partial\left(1/T\right)}\right]_P$ is a state function. [BU'93, Q 7(c) m = 3]

Solution The above term is equal to H and H is a state function so the term is also a state function.

Problem: (7) An adiabatic transformation is always an isoentropic. Justify / criticize. [BU'94, Q 12(c) m = 4]

Answer: The statement is wrong. Only reversible adiabatic process is isentropic ($\Delta S = 0$), but irreversible adiabatic process leads to increase of entropy ($\Delta S > 0$) so it is not isentropic. (See the Text, page   ).

Problem (8) An ideal gas is expanded under the condition PV^γ = constant. Will the entropy of the system increase, decrease or remain the same? Justify tour answer. [CU'94, Q 4(a), m=2]

Answer: The relation is valid only for reversible adiabatic process for which $\Delta S = 0$. So, the entropy will remain same.

Problem (9) The maximum useful work obtained in a process is given by the relation
(A) $\Delta H - T\Delta S$ (B) $\Delta U - T\Delta S$ (C) $\Delta H + T\Delta S$ (D) $\Delta U + T\Delta S$ [CSIR-UGC NET]
Ans. (B).

Problem (9) Amongst the quantities q_{rev}, w, q_{rev}/T and $q_{rev} - w$, the state functions are
(A) q_{rev}/T, $q_{rev} - w$ (B) q_{rev}, $q_{rev} - w$ (C) q_{rev}, q_{rev}/T (D) q_{rev}/T, w. [CSIR-UGC NET]
Ans. (A).

Thermodynamic criteria for a spontaneous and equilibrium process.

Rev. process is an equilibrium process	Thermodynamic principles provide conditions for physico-chemical equilibrium and spontaneous processes. Various properties like U, H, S, A and G can be chosen for stipulating these conditions. The condition for reversible process is also a necessary and sufficient condition for equilibrium. In fact, a reversible process consists of a very large number of equilibrium stages.
Irrev. process is a spontaneous process	A spontaneous process is one which takes place of its own accord; it is an irreversible process which ends towards an ultimate state of equilibrium.
Clausius inequality	Let us take a system in which an infinitesimal irreversible process is taking place and the system is kept in contact with a reservoir at temperature T. The quantity q* (small heat change) is exchanged with the reservoir. Since the process is irreversible, the entropy-change (dS) for the system must be greater than q*/T i.e., $dS > q*/T$ (Clausius inequality) or, $T\,dS > q*$ or, $TdS - q* > 0$. If the system does only pressure-volume work then $q* = dU + PdV$. Hence, the Clausius inequality can be expressed as, $TdS - dU - PdV > 0$
Single equation for the condition of spontaneity and equil^m. of a process	This inequality is always applicable if the process is spontaneous (which is irreversible) and work is only mechanical. But when the process is under equilibrium, which is thermodynamically reversible, the inequality sign is replaced by equality sign and the above relation becomes $$T\,dS - dU - P\,dV = 0.$$ When both the stages of a system are considered simultaneously, we may write $$T\,dS - dU - P\,dV \geq 0$$
Criteria in terms of U	Now if volume and entropy of the system is kept constant when the process occurs within it, $$(dU)_{S,V} \leq 0.$$ Thus, for spontaneity of a process occurring at constant S and U, the internal energy decreases and at equilibrium, U attains minimum (dU = 0). This is the familiar condition for a conservative mechanical system that stable state is one of lowest internal energy.
Criteria in terms of H	The Clausius inequality is $T\,dS - dU - P\,dV \geq 0$ or, $dU + P\,dV - T\,dS \leq 0$ or, $d(U+PV)_{S,P} \leq 0$ or, $dH_{S,P} \leq 0$. The significance is same as that is used in case of $dU_{S,V} \leq 0$.
Criteria in terms of S	If volume and internal energy of the system remain constant during the process (the system is isolated as $q = dU + PdV = 0$), Or, $(dS)_{U,V} \geq 0$. For the spontaneous process, entropy of the isolated system (in which the process is occurring) is increasing (dS > 0). When the process in the system attains equilibrium, entropy becomes maximum (dS = 0). However, if the system is not isolated (i.e U and V do not remain fixed), the entropy-change of the surrounding must also be taken into account. The condition then becomes $$dS_{univ} \geq 0.$$
Criteria in terms of A	If T and V are kept constant during the process occurring in the system, the above starting relation becomes, $d(TS - U)_{T,V} \geq 0$ or, $d(U - TS)_{T,V} \leq 0$ or, $(dA)_{T,V} \leq 0$ For a spontaneous process, A of the system decreases and attains minimum at equilibrium.

Criteria in terms of G

When a process occurs in a system at constant T and P (most physico-chemical changes happen under this condition), the criteria of spontaneity and equilibrium is expressed in terms of free energy (G) of the system.

We have the general condition, $TdS - dU - PdV \geq 0$ or, $dU + PdV - TdS \leq 0$

or, $\qquad d(U + PV - TS)_{T,P} \leq 0 \qquad$ or, $\quad d(H - TS)_{T,P} \leq 0$

or, $\qquad dG_{T,P} \leq 0$

This states that for a spontaneous process occurring at constant T and P, free energy (G) of the system decreases and attains minimum when the process reaches equilibrium.

Each condition stated above represents the mathematical form of 2nd law of thermodynamics since they state the feasibility, direction and extent of a process.

The above relations are deduced for small changes, hence for finite or macroscopic changes, d is replaced by Δ. These relations are thus,

$\qquad \Delta U_{S,V} \leq 0, \qquad \Delta H_{S,P} \leq 0, \qquad \Delta S_{U,V} \geq 0, \qquad \Delta A_{T,V} \leq 0, \qquad$ and $\qquad \Delta G_{T,P} \leq 0.$

It is interesting to note that the thermodynamic properties of the system are increasing in a spontaneous process then attaining maximum at equilibrium or decreasing to attain minimum value.

However, the condition of spontaneity of a process does not say anything about the rate of occurring the process.

Special consideration of the criteria for spontaneity and equilibrium of a process at constant T and P

This condition is deduced as, $\Delta G_{T,P} \leq 0$. This can be obtained alternatively as follows:

$\qquad G = H - TS$ or, $dG = dH - T\,dS$ at constant T.

But, $\qquad dH = q_P$ at constant P $\qquad$ so, $\qquad dG = q - TdS = q - q_{rev}$

Now two possibilities may be considered.

$\qquad$ When the process is at equilibrium, $\quad q = q_{rev}$ and $\quad dG = 0.$

But when the process is spontaneous, $\quad q = q_{irrev}$ and $\qquad dG = q_{irrev} - q_{rev}$

But, $\quad q_{rev} \rangle q_{irrev}$ for the same change of state of the system. $\qquad$ Thus, $\qquad dG < 0.$

Thus, $\qquad$ for finite reversible process, $\quad \Delta G_{T,P} = 0,$

The initial state and final state exist at equilibrium with each other with no net change of G. And for finite irreversible (spontaneous) process, $\quad \Delta G_{T,P} < 0$ i.e., G is decreasing .

When stated jointly, $\qquad \Delta G_{T,P} \leq 0.$

The inequality sign refers for spontaneous change and equality sign for equilibrium.

This condition is useful since the most chemical reactions occur at constant T and P.

Comparison of S and G criteria for spontaneity and equilibrium of a process

The free energy criteria for spontaneous change and equil[m]. are more useful than the entropy criteria. Let us remember these criteria, $\Delta S_{U,V} \geq 0$ and $\Delta G_{T,P} \leq 0$. It is difficult to keep the internal energy (U) of a system constant, whereas the temperature and pressure can easily be kept constant. Hence is the greater utility of the criteria in terms of G. Another point is that for a system at constant U and V is an isolated system.

But for other system, the entropy criterion is $(\Delta S_{syst.} + \Delta S_{surr.}) \geq 0$. So to use the entropy criteria, we must make measurements not only of the system but also of the surroundings.

But the latter measurement is not so easy. Hence the entropy criterion is not quite useful. For free energy criteria, only ΔG of the system is to be measured at constant T and P.

Problem

The 2nd law states that the entropy of universe (system + surrounding) increases in a spontaneous process, $(\Delta S_{system} + \Delta S_{surrounding}) \geq 0$. Give arguments that at constant T and P, $\Delta S_{surr.}$ is related to the system enthalpy-change by $\Delta S_{surr.} = -\Delta H_{syst.} / T$.

Hence come to the conclusion that $-\Delta G_{T,P} \geq 0$ for spontaneous process. [BU'97, Q9(c), m=5].

Answer:

For heat-change at constant T and P between system and surrounding is $\quad \Delta H_{syst.} + \Delta H_{surr.} = 0$

or, $\qquad \Delta H_{syst} + T\,\Delta S_{surr.} = 0 \qquad$ or, $\qquad \Delta S_{surr.} = -\Delta H_{syst} / T.$

Again, $\qquad (\Delta S_{syst.} + \Delta S_{surr.}) \geq 0 \qquad$ or, $\quad (\Delta S_{syst} - \Delta H_{syst} / T) \geq 0$

or, $\qquad -(\Delta H_{syst} - T\,\Delta S_{syst}) \geq 0 \qquad\qquad$ or, $\qquad -\Delta G_{T,P} \geq 0.$ at constant T and P.

Evaluation of ΔG of a process:

ΔG of a system in a process is evaluated by the relation, $\Delta G = \Delta H - T\Delta S$,

Evaluation of ΔH & ΔS

T and P constancy are omitted due to simplicity of the term, ΔG. But T and P constant terms are implied.

ΔH is evaluated by the use of bond energies of the products and reactants or calorimetric estimation or use of Van't Hoff equation or emf measurement of cell in which the reaction occurs.

ΔS is calculated from the third law of thermodynamics or by emf measurement of cell.

Critical discussion on the spontaneity and equil^m. of a process at constant T and P

We have, $\Delta G = \Delta H - T\Delta S$, when $\Delta G < 0$, the process occurs spontaneously.

Thus, (1) When ΔH of the process = (—)ve and ΔS = (+)ve, $\Delta G \langle 0$ always.

The reactions of this type occurs spontaneously always.

(2) When ΔH = (—)ve but ΔS = (—)ve, i.e. exothermic reaction with decrease of randomness. $\Delta G \langle 0$ only when $|\Delta H| \rangle |T\Delta S|$. This type of reactions favors at low T. For example, $2H_2(g) + O_2(g) = 2 H_2O(l)$.

(3) When ΔH = (+)ve and ΔS = (+)ve, i.e. endothermic with increase of randomness due to the reactions. $\Delta G \langle 0$ only when $|\Delta H| \langle |T\Delta S|$. This type of reactions favors at high T. The thermal dissociation of the gaseous substances is this type of reaction, $PCl_5(g) = PCl_3(g) + Cl_2(g)$.

(4) When ΔH = (+)ve and ΔS = (–)ve, $\Delta G \rangle 0$ always, so endothermic reactions with decrease of randomness will never happen.

Some examples

(A) Feasibility of the process, $A + A = A_2$ (dimerisation) with ΔH = 0.

$\Delta G = \Delta H - T\Delta S$, but ΔH = 0 and ΔS = (–)ve, since two molecules unite to give one molecule, randomness decreases. Thus, $\Delta G \rangle 0$ always and the reaction is not feasible.

(B) Spontaneous vaporization of water at constant T and 1 atm pressure.

For spontaneous vaporization of any liquid at constant T and P, the condition is $\Delta G \langle 0$ and at equilibrium, $\Delta G = 0$. Since, $\Delta G = \Delta H - T\Delta S$, so for $\Delta G \leq 0$, the condition is $\Delta H - T\Delta S \leq 0$ or, $T \geq \Delta H / \Delta S$

For vaporization of water, $\Delta H = 18 \times 540$ cal mol^{-1} and $\Delta S = 26$ cal mol^{-1}K^{-1}.

Putting the values, $T \geq (18 \times 540 / 180)$ K or, $T \geq 373.16$ K or, $T \geq 100^oC$.

The condition implies that so long T remains 373.16 K (100°C), the liquid water and vapor remains equilibrium but when T exceeds 373.16 K vaporization starts spontaneously. Calculation is made when P = 1 atm. That is when water is heated above its boiling point, it vaporizes spontaneously.

(C) Feasibility study of the reaction, $C(s) + H_2O(g) + CO(g) + H_2(g)$ at 100°C and 1000°C . (Given, ΔH = 31,400 cal and ΔS = 32 cal mol^{-1})

Let us study the feasibility of the reaction at 100°C (=373 K). We have, $\Delta G = \Delta H - T\Delta S$.

So, $\Delta G = 31,400 - 373 \times 32$ cal = + 19,464 cal. The reaction does not occur at 100°C.

At 1000°C (=1273 K), $\Delta G = 31,400 - 1273 \times 32$ cal = – 9,336 cal.

The reaction is feasible at 1000°C.

Reasons for assuming ΔH & ΔS independent of T

It is to be noted that both at 100°C and 1000°C, same values of ΔH and ΔS are inserted in the calculation of ΔG, though they vary with T. But variation of ΔG with T is very high in comparison to that of ΔH and ΔS with T. This is why, for approximate computation of ΔG, the values of ΔH and ΔS are taken independent of T. So, ΔH and ΔS of the reaction are determined at any convenient T and are used in calculation of ΔG at the required T

(D) Study of the reaction: $NH_3(g) + HCl(g) \overset{low\,T}{\underset{high\,T}{\Longleftrightarrow}} NH_4Cl(s)$.
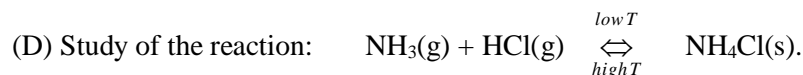
Forward reaction is exothermic, $\Delta H = (-)ve$, as bonds are formed. Again when the reaction proceeds. $\Delta S = (-)ve$, two gaseous molecules unite to give one solid molecule of NH_4Cl. Randomness decreases. Thus for $\Delta G \langle 0$, we need $|\Delta H| \rangle |T \Delta S|$.

<center>The reaction is favored at low T.</center>

Again, backward reaction is endothermic, as heat is required to break the bond of NH_4Cl, $\Delta H = (+)ve$ and $\Delta S = (+)ve$, as randomness increases.

<center>Thus, for $\Delta G \langle 0, |\Delta H| \langle |T \Delta S|$. The reaction favors at high T.</center>

Problem (1)

Give qualitative arguments to explain the fact that for the reaction, $N_2(g) \Longleftrightarrow 2N(g)$, ΔG^o at very low T is positive while its value is negative at very high T.   [BU'92, m = 4].

Answer:

For the reaction, $\Delta H^o = (+)ve$, endothermic, heat is required to break the bond of $H_2(g)$. $\Delta S^o = (+)ve$, randomness increases as one molecule is dissociating into two atoms. Thus, $\Delta G^o = \Delta H^o - T\Delta S^o$, at low T, $\Delta H^o \rangle T\Delta S^o$ and ΔG^o is positive.

<center>But at high T, $T\Delta S^o \rangle \Delta H^o$ and ΔG^o is negative.</center>

Problem (2)

At 27°C and 1 atm pressure, will the vaporization of liquid water be spontaneous?
<center>(Given, $\Delta H = 9,710$ cal mol^{-1} and $\Delta S = 26$ cal mol^{-1} K^{-1})</center>

Solution

<center>$\Delta G = \Delta H - T\Delta S = (9,710 - 300 \times 26)$ cal mol^{-1} = 1910 cal mol^{-1}.</center>
Since $\Delta G > 0$ at 27°C and 1 atm pressure, the vaporization of liquid water is not spontaneous.

First-order phase transition:

The phase-changes of a pure substance such as sublimation, melting, vaporization etc. are called first order phase transition. These transitions are associated with an abrupt change of first order derivative of free energy. Though G changes continuously but $\left(\partial G/\partial P\right)_T$ and $\left(\partial G/\partial T\right)_P$ will change discontinuously at the point of transition when plotted against T.
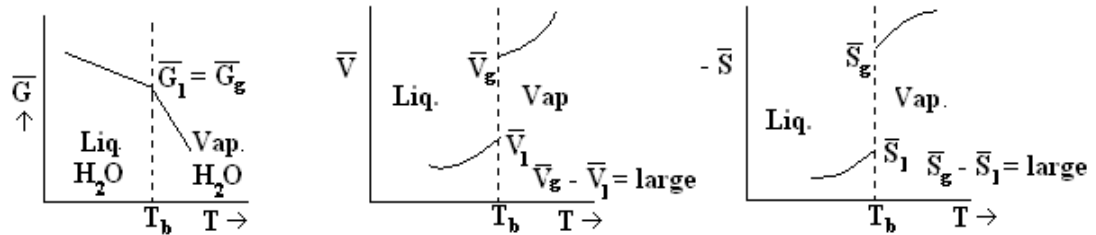
The basic equation is $d\bar{G} = -\bar{S}dT + \bar{V}dP$ so, $\left(\partial \bar{G}/\partial P\right)_T = \bar{V}$ and $-\left(\partial \bar{G}/\partial T\right)_P = \bar{S}$.

Three criteria of the first-order phase transition, phase α → phase β are given as:

(i) $\bar{G}_\beta = \bar{G}_\alpha$ (ii) $\bar{V}_\beta - \bar{V}_\alpha \neq 0$ and   (iii) $\bar{S}_\beta - \bar{S}_\alpha \neq 0$.

The difference of $\bar{V}_\beta$ and $\bar{V}_\alpha$ or, $\bar{S}_\beta$ and $\bar{S}_\alpha$ are very large.

These criteria are shown by the following diagram of vaporization of water at its boiling point.

On the other hand, there are some cases of transitions where second order derivative of free energy of the substance changes abruptly. For example, change of ferromagnetic material to paramagnetic material at the Curie point, liquid He II to liquid I at the λ-point etc.

Clapeyron Equation (effect of P on the transition temperature):

If two phases of a pure substance are in equilibrium with each other, they have same molar free energy at that T and P. when P is changed at constant T, or T is changed at constant P, one of the phases will disappear. But if T and P are both changed in such a way as to keep the two molar free energies (chemical potentials) equal to each other, the two phases will continue to co-exist and remain equilibrium.

Thus for two phases α and β of the substance at equilibrium, we have $\bar{G}_\alpha = \bar{G}_\beta$. If T and P are changed so that equilibrium is maintained, then, $d\bar{G}_\alpha = d\bar{G}_\beta$.

Derivation of the equation.

But, $d\bar{G} = \bar{V}\,dP - \bar{S}\,dT$ hence, $\bar{V}_\alpha\,dP - \bar{S}_\alpha\,dT = \bar{V}_\beta\,dP - \bar{S}_\beta\,dT$.

Or, $$\frac{dP}{dT} = \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} = \frac{\Delta \bar{S}}{\bar{V}_\beta - \bar{V}_\alpha}$$

But for the phase-change at constant T and P, $\Delta \bar{S} = \Delta \bar{H}/T$,

where, $\Delta \bar{H}$ = molar latent heat transition or molar enthalpy of transition.

Therefore, $$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T\left(\bar{V}_\beta - \bar{V}_\alpha\right)}.$$ This is called Clapeyron equation.

However molar properties can be replaced and then Clapeyron equation becomes

$$\frac{dP}{dT} = \left(\frac{\Delta H}{T(V_\beta - V_\alpha)} \right).$$

Alternative derivation from Maxwell relation.

From Maxwell's relation, we get $\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$.

When two phases are in equilibrium (say, liquid and vapor), the vapor pressure is independent of the mass and hence volume. So, $\left(\frac{\partial P}{\partial T} \right)_V = \frac{dP}{dT}$.

Again, if we consider latent heat of transition, L as nearly constant, independent of T, then

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{dS}{dV} = \frac{L}{T\left(V_\beta - V_\alpha \right)}.$$

Therefore the Clapeyron equation is $\frac{dP}{dT} = \left(\frac{\Delta H}{T(V_\beta - V_\alpha)} \right)$

Sign of $\frac{dP}{dT}$ depends on the sign of L and $(V_\beta - V_\alpha)$

Vaporisation of liquids

(1) For vaporization of liquid, L = (+)ve and $(V_\beta - V_\alpha) = (V_g - V_l) = $ (+)ve,

hence $\frac{dP}{dT} = $ (+)ve. This signifies that the vapor pressure of a liquid increases with temperature. It also states that the boiling point of a liquid increases with increase of pressure.

Melting of solid

(2) For melting of paraffin or any solid except ice, L = (+)ve and $(V_l - V_s) = $ (+)ve,

hence $\frac{dP}{dT} = $ (+)ve so melting point of paraffin increases with increase of pressure.

Melting of ice ─ a special

(3) For melting of ice, L = (+)ve and $(V_l - V_s) = $ (─)ve, since $V_{ice} > V_{water.}$

This indicates that $\frac{dP}{dT} = $ (─)ve, indicating that melting point of ice decreases with increase of pressure

.

Clausius Clapeyron equation:

Clausius simplified the relation for sublimation and vaporization processes by assuming that vapor obeys perfect gas equation and neglecting the molar volume of the liquid or solid in comparison to that of the vapor. For the process of vaporization, the

Equation for vaporization and sublimation

Clapeyron equation is $\frac{dP}{dT} = \left(\frac{\bar{L}_V}{T(\bar{V}_g - \bar{V}_l)} \right).$

Since $\overline{V_g} \rangle\rangle \overline{V_l}$, hence $\frac{dP}{dT} = \frac{\bar{L}_V}{T\bar{V}_g} = \frac{\bar{L}_V \times P}{RT^2}$. Separating the variables and integrating,

we get, $\int \frac{dP}{P} = \frac{\bar{L}_V}{R} \int \frac{dT}{T^2}.$ Or $\ln P = - \frac{\bar{L}_V}{R} \cdot \frac{1}{T} + $ C (IC).

When integrated within limits, we get, $\ln \frac{P_2}{P_1} = \frac{\bar{L}_V}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right).$

This is Clausius-Clapeyron equation or simply called Clausius equation.

$\bar{L}_V$ is assumed to be independent of T.

Utility of the equation	Using this relation, it is possible to calculate the latent heat of vaporization or latent heat of sublimation from the vapor pressure at two temperatures.
However if $\overline{L}_V$ of the process is known, vapor pressure at a given temperature can also be calculated if that at other temperature is known.

Trouton's rule: From the relation, $\quad \ln P = -\dfrac{\overline{L}_V}{R}.\dfrac{1}{T} + C,$

we can put P = 1 atm, when $T = T_b$ (normal boiling point). Thus, $0 = -\dfrac{\overline{L}_V}{R}.\dfrac{1}{T_b} + C$

or, $\quad \dfrac{\overline{L}_V}{T_b} = RC = \text{constant} \approx 21$ (Approx.) for non-associated simple liquids.

Reason in support of the rule	Trouton made an important generalization from experimental observation that the ratio of molar heat of vaporization to the normal boiling point is constant for simple and non-associated liquids and the constant is about 21 cal mol^{-1}K^{-1}.
The rule also states that molar entropy-change of vaporization at normal boiling point is same and is about 21 cal mol^{-1}K^{-}1.
That is, $\quad \left(\Delta \overline{S}\right)_{vap.\,at\,normal\,BP} \approx 21$ for all simple and non-associated liquids.
This consistency of entropy of vaporization from liquids to vapor is readily understood from Boltzmann hypothesis relating entropy to disorder. The change from liquid to vapor leads to increased disorder. The entropy of vaporization is at the critical temperature because liquids behave alike not only at their T_C but also equal fraction of their T_C. Hence different liquids should have same entropy of vaporization at their boiling point provided there is no association or dissociation upon vaporization.

Problem (1)	The vapor pressure of water is 23.75 torr at 25°C and 760 torr at 100°C. What will be the heat of vaporization? [Civil Service Exam. 2003]
Solution	Clausius Clapeyron equation is, $\quad \ln \dfrac{P_2}{P_1} = \dfrac{\overline{L}_V}{R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)$

or, $\ln \dfrac{760}{23.75} = \dfrac{\overline{L}_V}{2}\left(\dfrac{373 - 298}{373 \times 298}\right)$, or $\overline{L}_V = \dfrac{2 \times 373 \times 298}{75}\ln\dfrac{760}{23.75} = 10,272.8 \, cal\,mol^{-1}$.

Problem (2) Solution	Calculate the boiling point of water at a pressure of 75 cm of Hg, given that latent heat of vaporization is 540 cal mol^{-1}.
We know that boiling point of water is 100°C when the pressure is 76 cm of Hg.
Putting the values in the Clausius equation, we have, $\quad \ln\dfrac{76}{75} = \dfrac{18 \times 540}{2}\left(\dfrac{1}{T} - \dfrac{1}{373}\right)$
Solving the equation, we get the BP of water is 372.63 K = 99.63^{o}C at 75 cm of Hg

Problem (3)	If the rate of change of vapor pressure of water with respect to T is 2.7 cm of Hg per degree around 100°C, Calculate the molar volume of liquid water (given specific volume of water vapor = 1674 cc gm^{-1}). Calculate also the boiling point of water at a pressure of 75 cm of Hg. [BU'91, Q 7(b) m = 6+3]
Solution:	Given, $\dfrac{dP}{dT} = 2.7$ cm of Hg per degree around 100°C. Putting the values in the Clapeyron

equation, $\dfrac{dP}{dT} = \dfrac{l_V}{T(v_g - v_l)}$ or, $2.7 \times 13.6 \times 980$ dyne cm^{-2} K^{-1} = $\dfrac{536 \times 4.18 \times 10^7 \, erg \, gm^{-1}}{373 K^{-1}(1674 cc \, gm^{-1} - v_l)}$.

Calculation gives v_l = 5 cc/gm. So molar volume of liquid water = 5 $\times$18 = 90 cc/mole.

2nd part:　　　　given, $\dfrac{dP}{dT}$ = 2.7 cm of Hg per degree around 100ºC

or,　　　$\dfrac{P_2 - P_1}{T_2 - T_1}$ = 2.7 cm of Hg/ºC, Putting the values, $\dfrac{76 - 75}{100 - t_1}$ = 2.7　or,　t$_1$ = 99.63ºC

Problem (4)

Derive Clapeyron equation and show that it can be represented by the equation,

$P = P^* \exp[(-\Delta H_{vap} / R)\{\dfrac{1}{T} - \dfrac{1}{T*}\}]$. For liquid – vapor boundary assuming ideal gas behavior

and making certain approximation.　　　[Civil service Exam, 2001]

Answer :　　Derive Clausius equation, $\ln \dfrac{P*}{P} = \dfrac{\Delta H_{vap}}{R}\{\dfrac{1}{T} - \dfrac{1}{T*}\}$ and get the required form.

Problem (5)

At the normal melting point of NaCl 801ºC, its enthalpy of fusion is 28.8 kJmol^{-1}. the density of solid is 2.165 gm cm^{-3} and that of the liquid is 1.733 gm cm$^{-3.}$ What is the increase of pressure needed to raise the melting point by 1.00 ºC.

[IISc, Bangalore, adm. test for Int. Ph. D.]

Solution :

The process is melting,　　NaCl (s)　→　NaCl (l).

In the Clapeyron equation, dT = 1.00K,　T = 273+801=1074K, ΔH_m = 28.8 kJ mol^{-1} . dP = ?

$$dP = dT \times \dfrac{\Delta \bar{H}_m}{T\left(\bar{V}_l - \bar{V}_s\right)} = 1\,K \times \dfrac{28.8\,kJ\,mol^{-1} \times 10^{10}\,erg\,kJ^{-1}}{1074K\left(\dfrac{1}{1.733} - \dfrac{1}{2.165}\right) \times 58.5\,cc\,mol^{-1}}$$

$$= 3.98 \times 10^7\,dyne\,cm^{-2} = \dfrac{3.98 \times 10^7}{76 \times 13.6 \times 981}\,atm.$$

Problem (6)

Average value of enthalpy of vaporization (kJ / mole) of water between 363K and 373K
　　　is (a) 42.50　(b) 40.80　　(c) ─ 40.65　　(d) – 40.80.
Given vapor pressure of water at 363K & 373K are 529 Torr & 760 Torr.

Solution :　The correct answer is (b). Use Clausius equation to get the answer.

Problem (7)

At 373.6 K and 372.6 K, vapor pressure of water is 1.018 and 0.982 atm respectively.
Calculate the molar entropy of vaporization and ΔV, the change of volume per mole when
liquid water vaporizes at 373 K. Assume that the vapor behaves ideally.

[B U, 1994 & 1996]

Solution :　Clausius equation (assuming vapor behaving ideally) is

$$\ln \dfrac{P_2}{P_1} = \dfrac{\bar{L}_V}{R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right). \text{ Putting the values given, } \ln \dfrac{1.018}{0.982} = \dfrac{\bar{L}_V}{2}\left(\dfrac{1}{373.6 \times 372.6}\right)$$

or, $\overline{L}_V$ = 10,023.7 cal mol^{-1} ,　$\Delta \bar{S} = \dfrac{\overline{L}_V}{T} = \dfrac{10,023.7}{373}$ = 26.87 cal K^{-1}mol^{-1}.

Now the Clapeyron equation is $\dfrac{\Delta P}{\Delta T} = \dfrac{\Delta \bar{S}}{\Delta \bar{V}}$　or, $\dfrac{(1.018 - 0.982)\,atm}{1\,K} = \dfrac{26.87\,cal\,K^{-1}mol^{-1}}{\Delta \bar{V}}$

or,　　　　　$\Delta \bar{V} = \dfrac{26.87}{0.036} \times \dfrac{0.082}{1.987}\,lit\,mol^{-1}$ = 30.8 lit mol^{-1} .

BU'2008, Q 1(g)

"The Clausius-Clapeyron equation is a special case of the van't Hoff
equation for liquid-vapor equilibrium." ─ Justify or criticize. (2).

Answer:　The van't Hoff equation is, $\dfrac{d \ln K_P}{dT} = \dfrac{\Delta H}{RT^2}$, where ΔH is the enthalpy of the reaction and K$_P$ is

the equilibrium constant of the reaction.

But for the liquid-vapor equilibrium, the Clausius-Clapeyron equation is given by,

$\dfrac{d \ln P}{dT} = \dfrac{\Delta H}{RT^2}$, here P is the equilibrium pressure and ΔH is also the enthalpy of vaporization. Thus the statement is correct.

BU'2008, Q 4(b) With increase of pressure, the melting temperature of paraffin increases but that of ice decreases. ─ Explain. (2).   Answer: See the Text, page 63.

BU'94 Q 3 (a) Deduce thermodynamically the first order phase transition. Give illustrations.

Establish the relation $\left(\dfrac{\partial P}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial V}\right)_T$. Hence deduce the Clapeyron equation. (4+4+4)

Answer: See the Text, page.

(b) Calculate the freezing temperature of water if the pressure be increased by 1 atm, given L = 80 cal/gm, $\rho_{ice(0^o C)} = 0.9168 \, gm/cc$ and $\rho_{H_2O(0^o C)} = 0.9998 \, gm/cc$. (4).

Solution: For the process water → ice, the Claypeyron equation is $\dfrac{dP}{dT} = \left(\dfrac{\Delta H}{T(V_{ice} - V_{water})}\right)$.

$$\dfrac{1 \, atm}{dT} = \left(\dfrac{-80 \, cal \, gm^{-1}}{273 \, K (\dfrac{1}{0.9168} - \dfrac{1}{0.9996}) cc \, gm^{-1}}\right), \ dT = \dfrac{1 atm \times 273 K (1.0907 - 1.0004) cc \, gm^{-1}}{-80 \, cal \, gm^{-1}}$$

or, $dT = \dfrac{1 \times 76 \times 13.6 \times 981 \, dyne \, cm^{-2} \times 273 K (1.09075 - 1.0004) cc \, gm^{-1}}{-80 \times 4.18 \times 10^7 \, erg \, gm^{-1}} = -0.075 \, K.$

Thus the freezing point of water becomes ─ 0.075°C if pressure is increased by 1atm.

BU'96 Q 5(a). If in a phase transition the first order partial derivative of G with respect to temperature and pressure change continuously in going from one phase to the other, will it be possible to obtain the Clapeyron equation? Give reasons for your answer. (4).

Answer: It is not possible to obtain Clapeyron equation.

The equation is, $\dfrac{dP}{dT} = \dfrac{S_\beta - S_\alpha}{V_\beta - V_\alpha}$. But, $\left(\dfrac{\partial G}{\partial P}\right)_T = V$ and $\left(\dfrac{\partial G}{\partial T}\right)_P = -S.$

As $\left(\dfrac{\partial G}{\partial P}\right)_T$ and $\left(\dfrac{\partial G}{\partial T}\right)_P$ change continuously in going from one phase to the other,

so V and S will change continuously and at the transition point, $V_\beta = V_\alpha$ and $S_\beta = S_\alpha$.

Putting in the Clapeyron equation, RHS of the equation becomes meaningless.

Experiment

Let us imagine a cylinder thermally insulated and equipped with two non-conducting pistons on opposite sides of a porous wall. This wall may be porous plug of narrow constriction or a series of small holes. Between the left hand piston and the wall, there is 1 mole gas at a pressure P_1 and volume V_1.

$P_1 > P_2$

| P_1 | P_2 |

$V_1 \uparrow V_2$
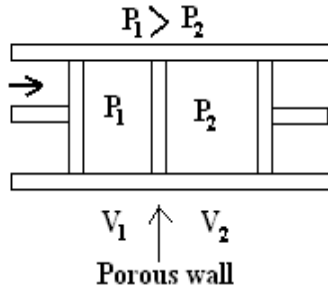
Porous wall

The gas passes through the porous wall against the constant pressure P_2. This is a throttling expansion.

This process is slow and it allows the gas to be slowly forced from one chamber to another. The pressure equilibrium is maintained in each chamber.

Let the volume of the gas after passing through the wall be V_2. The initial equilibrium state of the gas is (P_1, V_1) and final equilibrium state becomes (P_2, V_2).

However, it is an irreversible process since the gas expands against constant external pressure.

Joule Thomson effect:

Experimental results show that when most gases, in a compressed condition are allowed to expand through orifice or throttle under adiabatic enclosure, they undergo cooling.

However, H_2 and He are warmed up at room temperature by such process.

This is known as Joule Thomson effect.

Inversion temperature (T_i):

Experiment shows that temperature-dependence of this expansion effect switch over from cooling to heating as temperature is increased. There is a temperature, characteristic of the gas, below which the gas cools down but above which it is heated up by this J-T expansion. This temperature is called 'inversion temperature' of the gas. For H_2, it is 193 K and for He, it is 53 K. Below these temperatures, the gases can be cooled down by such expansion.

Let 1 mole gas is expanded under this adiabatic process.

Thermodynamic condition of the experiment:

⁻rom first law of thermodynamics, $q = dU + w$, but, $q = 0$.

The change in internal energy, $dU = U_2 - U_1$.

The work done, $$w = \int_{V_1}^{0} P_1 dV + \int_{0}^{V_2} P_2 dV = -P_1 V_1 + P_2 V_2$$

since P_1 and P_2 remain constant during the process.

Therefore, $0 = (U_2 - U_1) + (P_2 V_2 - P_1 V_1) = (U_2 + P_2 V_2) - (U_1 + P_1 V_1) = H_2 - H_1$ or, $H_1 = H_2$

or, $\Delta H = 0$.

It means that the process is isenthalpic.

This states that the initial enthalpy and final enthalpy of the gas are equal.

However, one is not entitled to say that the enthalpy remains constant during the process.

One is not sure to the enthalpy of the intermediate stages of this non-equilibrium (irreversible) process. In plotting a throttling process on any diagram, the initial and final equilibrium states are known and so may be represented by points. However, the intermediate states are not known and so can not be plotted.

Joule Thomson Coefficient (μ_{JT})

In order to quantify the temperature change due to the pressure change of the gas, we can define a term, called Joule Thomson coefficient, μ_{JT}.

It is defined as, $$\mu_{JT} = \left(\partial T / \partial P \right)_H.$$

It is an intensive property since it is the ratio of infinitesimal changes of two intensive properties.

$P_1 > P_2$, so, $dP = P_2 - P_1 = (-)$ve, hence for cooling effect, $T_1 > T_2$ and $\mu_{JT} = (+)$ve.

Similarly, for heating effect, $T_1 < T_2$ and $\mu_{JT} = (-)$ve.

When there is no effect, $T_1 = T_2$ and $\mu_{JT} = 0$.

Therefore,   when $T \langle T_i$, $\mu_{JT} = (+)$ve , and when $T \rangle T_i$, $\mu_{JT} = (-)$ve

and at $T = T_i$, $\mu_{JT} = 0$

We have enthalpy, $H = f(T, P)$. On partial differentiation,

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

Concept of inversion temperature (T_i): C_P = constant pressure molar heat capacity of the gas which is undergoing the J T expansion.

For this process, $dH = 0$

hence, $0 = C_P\, dT + \left(\dfrac{\partial H}{\partial P}\right)_T dP$ or, $\left(\dfrac{\partial T}{\partial P}\right)_H = -\dfrac{1}{C_P}\left(\dfrac{\partial H}{\partial P}\right)_T$.

But $\left(\dfrac{\partial T}{\partial P}\right)_H = \mu_{JT}$ so, $\mu_{JT} = -\dfrac{1}{C_P}\left(\dfrac{\partial H}{\partial P}\right)_T$.

Again, $H = U + PV$.

So, $\mu_{JT} = -\dfrac{1}{C_P}\left(\dfrac{\partial(U + PV)}{\partial P}\right)_T = \left[-\dfrac{1}{C_P}\left(\dfrac{\partial U}{\partial V}\right)_T\left(\dfrac{\partial V}{\partial P}\right)_T\right] + \left[-\dfrac{1}{C_P}\left\{\dfrac{\partial(PV)}{\partial P}\right\}_T\right]$

This relation of μ_{JT} consists of two parts.

(a) For ideal gas, $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$ and $\left\{\dfrac{\partial(PV)}{\partial P}\right\}_T = 0,$ hence $\mu_{JT} = 0$.

This means that ideal gas does not undergo any J T effect.

(b) For real gas, $\left(\dfrac{\partial U}{\partial V}\right)_T = (+)$ve always, and $\left\{\dfrac{\partial V}{\partial P}\right\}_T = (-)$ve.

Hence 1st term $= (+)$ve always and it is practically independent of P. But value of PV decreases with increase of P at low T (below the Boyle temperature, T_B of the gas) and low P.

So, $\left\{\dfrac{\partial(PV)}{\partial P}\right\}_T = (-)$ve, and 2nd term is also then $(+)$ve.

Therefore, $\mu_{JT} = (+)$ve i.e. there is cooling effect of the gas.

But at high P even at low T, PV increases with increase of P

so $\left\{\dfrac{\partial(PV)}{\partial P}\right\}_T = (+)$ve and 2nd term $= (-)$ve.

When the magnitude of the 2nd term exceeds the 1st term,

$\mu_{JT} = (-)$ve, and there will be heating effect.

However, when T is high (above T_B), PV increases with increase of P always and

$\left\{\dfrac{\partial(PV)}{\partial P}\right\}_T = (+)$ve always , 2nd term becomes $(-)$ve. When the 2nd term dominates over

the 1st, $\mu_{JT} = (-)$ve. There occurs heating effect.

So to conclude, heating effect of the gas in this process may occur at high T and ordinary P or at high P at ordinary T.

Hence in between the cooling effect and heating effect of the gas, there might be temperatures depending on P at which $\mu_{JT} = 0$.

These temperatures are called 'inversion temperatures' (T_i).
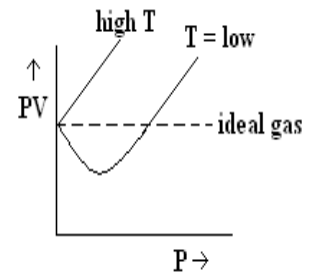
The 2nd thermodynamic equation of state is, $\left(\dfrac{\partial H}{\partial P}\right)_T = -T\left(\dfrac{\partial V}{\partial T}\right)_P + V.$

Expression of μ_{JT} :

Again, $\quad \mu_{JT} = -\dfrac{1}{C_P}\left(\dfrac{\partial H}{\partial P}\right)_T \qquad$ or, $\qquad \mu_{JT} = \dfrac{1}{C_P}\left[T\left(\dfrac{\partial V}{\partial T}\right)_P - V\right].$

This is the general expression of μ_{JT}

(a) For ideal gas, the equation of state is PV = RT for 1 mole gas. So, V = RT/P

or, $\left(\partial V / \partial T\right)_P = R/P$ or, $T\left(\partial V/\partial T\right)_P = RT/P = V.$ Therefore, $\mu_{JT} = \dfrac{1}{C_P}\left(V - V\right) = 0.$

This shows that ideal gas will not suffer any J T effect.

(b) For one mole of vander Waals gas, the equation of state is $(P + a/V^2)\,(V - b) = RT.$

Or, $PV - Pb + (a/V) - (ab/V^2) = RT.$ The (a /V) and (ab / V²) are correction terms, their values are very small, hence to replace V, ideal gas equation can be employed

i.e. $\quad V = (RT / P).\qquad$ Thus, $PV - Pb + \dfrac{aP}{RT} - \dfrac{abP^2}{R^2T^2} = RT$

or, $\quad V - b + \dfrac{a}{RT} - \dfrac{abP}{R^2T^2} = \dfrac{RT}{P}$ --(A)

or, $\quad V = \dfrac{RT}{P} + b - \dfrac{a}{RT} + \dfrac{abP}{R^2T^2} \qquad$ or, $\left(\partial V/\partial T\right)_P = \dfrac{R}{P} + 0 + \dfrac{a}{RT^2} - \dfrac{2abP}{R^2T^3}$

or, $\quad T\left(\partial V/\partial T\right)_P = \dfrac{RT}{P} + \dfrac{a}{RT} - \dfrac{2abP}{R^2T^2}.$ Replacing $\dfrac{RT}{P}$ from equation (A), we get

$T\left(\partial V/\partial T\right)_P = V - b + \dfrac{2a}{RT} - \dfrac{3abP}{R^2T^2} \qquad$ or, $\quad T\left(\partial V/\partial T\right)_P - V = \dfrac{2a}{RT} - b - \dfrac{3abP}{R^2T^2}.$

Thus, $\qquad \mu_{JT} = \dfrac{1}{C_P}\left(\dfrac{2a}{RT} - b - \dfrac{3abP}{R^2T^2}\right)$ --------- (B)

At low pressure of the gas, $\dfrac{3abP}{R^2T^2}$ can be neglected and the expression becomes,

$$\mu_{JT} = \dfrac{1}{C_P}\left(\dfrac{2a}{RT} - b\right) \quad ----- \ (C)$$

This shows the advantage for μ_{JT} for liquefaction of gases. μ_{JT} is linearly related with reciprocal of T. Hence, lower the temperature of the gas, larger is the drop in temperature for a given pressure-change.

(i) At the inversion temperature, i.e. $T = T_i$, $\mu_{JT} = 0$, putting in equation (C),

$0 = \dfrac{1}{C_P}\left(\dfrac{2a}{RT} - b\right).$ Or, $T_i = \dfrac{2a}{Rb}.$

This is the expression of inversion temperature of the gas obeying vander Waals equation.

(ii) When $T \langle\ T_i$, $\dfrac{2a}{RT} \rangle\ b$, $\mu_{JT} = (+)$ve, there will be cooling effect.

Intermolecular forces of attraction dominates over the repulsive forces (size effects).

So, during expansion, the intermolecular separation increases and in this process, the molecules have to work against the attractive forces. A part of the internal energy of the gas is utilized for this work and the temperature falls.

(iii) When $T \rangle T_i$, $b \rangle \dfrac{2a}{RT}$ and $\mu_{JT} = (-)$ve. Intermolecular repulsive forces (size effects) dominate over the attractive forces in the gas under this situation and there is warming on expansion. For H_2 and He, a is very small and hence at room temperature,

$$\frac{2a}{RT} \langle \text{ b and } \mu_{JT} = (-)\text{ve, so occurs heating effect.}$$

Problem: Calculate inversion temperature of N_2 gas, given that for the gas, a = 1.40atm lit^2 mol^{-2} and b = 0.039 lit mol^{-1}.

Solution: We have the expression, $T_i = \dfrac{2a}{Rb} = \dfrac{2 \times 1.40\, atm lit^2\, mol^{-2}}{0.083\, lit\, atm\, mol^{-1}\, K^{-1} \times 0.039\, lit\, mol^{-1}} = 875$ K
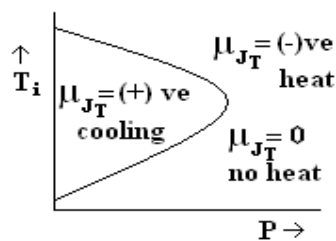
More than one inversion temperature:

We have expression (B), $\mu_{JT} = \dfrac{1}{C_P}\left(\dfrac{2a}{RT} - b - \dfrac{3abP}{R^2 T^2} \right)$

At high P, $\dfrac{3abP}{R^2 T^2}$ can not be neglected. So at $T = T_i$, $\mu_{JT} = 0$

so, $0 = \dfrac{1}{C_P}(\dfrac{2a}{RT_i} - b - \dfrac{3abP}{R^2 T_i^2})$.

Or, $0 = \dfrac{2a}{RT_i} - b - \dfrac{3abP}{R^2 T_i^2}$ or, $b - \dfrac{2a}{RT_i} + \dfrac{3abP}{R^2 T_i^2} = 0$.

Multiplying T_i^2, we get, $bT_i^2 - \dfrac{2a}{R}T_i + \dfrac{3abP}{R^2} = 0$.

This is a quadratic equation of T_i.
Hence there should be two inversion temperatures of the gas. This situation is also realized by experiment with N_2 gas. The above equation contains two variables T_i, P and they are interrelated. So if P is changed, T_i is also changed. We can plot T_i against P, the curve will be parabolic. Thus we see that at every pressure (initial) of the gas, there exist two inversion temperatures – higher T_i and lower T_i below lower T_i there will be heating and above higher T_i there will be also heating.
Only when the initial temperature is below higher T_i and above lower T_i,

$$\mu_{JT} = (+)\text{ve} \quad \text{and} \quad \text{cooling occurs.}$$

As the pressure increases, the separation between the two inversion temperatures decreases and at a certain pressure, P_2 the two become equal. When the pressure increases further, no more inversion phenomenon is possible and $\mu_{JT} = (-)$ve. The area enclosed by the parabola represents 'cooling zone' on J T expansion, while the area outside the curve corresponds to 'warming zone'.

Calculation of two T_i of a gas Let for a vander Waals gas, $a = 1.4\ atm\ lit^2 K^{-2}$ and $b = 0.04\ lit\ mol^{-1}$. Calculate the inversion temperatures of the gas at 10 atm pressure.

We have the equation, $bT_i^2 - \dfrac{2a}{R}T_i + \dfrac{3abP}{R^2} = 0$. Now putting the values, we get

$$0.04T_i^2 - \frac{2 \times 1.4}{0.082} T_i + \frac{3 \times 1.4 \times 0.04 \times 10}{(0.082)^2} = 0.$$

Solving the equation, we have, $T_i = 846.4\,K$ and 7.38 K.

When we use the relation, $T_i = \dfrac{2a}{Rb}$ and put the values, we get $T_i = 853.6\,K$.

So the $T_i = 853.6\,K$ is the higher inversion temperature of the gas.

Difference between adiabatic cooling and J T cooling:	(1) Adiabatic cooling occurs due to decrease of internal energy of the gas by the adiabatic cooling But J T cooling occurs due to also decrease in internal energy of the gas for doing work intermolecular attraction when the intermolecular separation is increased for this against expansion. (2) Adiabatic cooling occurs for both ideal and real gas at any experimental temperature. But J T cooling occurs only for real gas and that also when the experimental temperature is below its inversion temperature. There is no J T cooling for ideal gas since it has no intermolecular attraction.

Problem (1)

For CO_2(g) at 300 K and 1 atm pressure, $\left(\dfrac{\partial H}{\partial P}\right)_T = -10.2$ cal mol^{-1} atm^{-1} and

$C_P = 8.919$ cal mol^{-1} K^{-1}. Calculate the J T coefficient (μ_{JT}) of the gas at the given T and P. [C U, 1990]

Solution :

We have the relation $\mu_{JT} = -\dfrac{1}{C_P}\left(\dfrac{\partial H}{\partial P}\right)_T$

$$= -\frac{1}{8.919 \; cal \; mol^{-1} \; K^{-1}} \times (-10.2 \; cal \; mol^{-1} \; atm^{-1})$$

$$= 1.1436 \text{ K atm}^{-1}.$$

Problem (2)

Find out the relation between μ_{JT} and $\left(\dfrac{\partial H}{\partial P}\right)_T$. μ_{JT} for a vander Waals gas is given by

$\mu_{JT} = \dfrac{1}{C_P}\left(\dfrac{2a}{RT} - b\right)$. Calculate the value of ΔH in calorie for te isothermal

(300 K) compression of 1 mole of N_2 from 1 to 500 atm. (a = 1.34atm lit^2 mol^{-2} and b = 0.039 lit mol^{-1}) [C U, 1986]

Solution :

For the answer of 1st part, see the text.

The relation is $\mu_{JT} = -\dfrac{1}{C_P}\left(\dfrac{\partial H}{\partial P}\right)_T$ or, $\left(\dfrac{\partial H}{\partial P}\right)_T = -C_P \times \mu_{JT} = -\left(\dfrac{2a}{RT} - b\right)$.

$$\int_1^2 dH = -\left(\frac{2a}{RT}\right)\int_1^2 dP \quad \text{or,} \quad \Delta H = -\left(\frac{2a}{RT} - b\right).(P_2 - P_1)$$

$$= \left(\frac{2 \times 1.34}{0.083 \times 300} - 0.039\right)(500 - 1) \; lit \; atm \; \text{mol}^{-1}$$

$$= -0.353 \times (2 / 0.083) \text{ cal mol}^{-1} = -8.51 \text{ cal mol}^{-1}$$

Problem (3)   Calculate $\left(\partial T / \partial P\right)_H$ for a vander Waals gas at 27°C and 1 atm. pressure and mention its significance. Given, C_P = 5 cal mol⁻¹ K⁻¹, a = 2 atm lit² mol⁻² and b = 30 cc mol⁻¹

[C U, 1999]

Solution: But, C_P = 5 cal mol⁻¹ K = 5 × 0.082 / 2 = 0.205 lit atm mol⁻¹ K⁻¹ and b = 30 cc mol⁻¹

= 0.03 lit mol⁻¹ we have the relation, $\mu_{JT} = \left(\partial T / \partial P\right)_H = \dfrac{1}{C_P}(\dfrac{2a}{RT} - b)$.

Hence, $\left(\partial T / \partial P\right)_H = \dfrac{1}{C_P}(\dfrac{2a}{RT} - b)$

$$= \frac{1}{0.205\, lit\, atm\, mol^{-1}\, K^{-1}} \left[\frac{2 \times 2\, atm\, lit^2\, mol^{-2}}{0.082\, lit\, atm\, mol^{-1}\, K^{-1} \times 300 K} - 0.03\, lit\, mol^{-1}\right]$$

= 0.634 K atm⁻¹

It signifies that the gas will be cooled down at 27°C and 1 atm. pressure by J T expansion and per atm pressure drop, the temperature drops by 0.634 K.

Problem (4)   Show that J T expansion is an isenthalpic process. What conclusion can be drawn from the sign of J T coefficient (μ_{JT})?

Derive an expression of μ_{JT} for a gas obeying the equation, P (V − b) = RT.

Comment on the result you obtain.   [CU' 90, Q 5(a), m = 2+2+4+2]

Solution: For answer of the 1st, 2nd and 3rd parts, see the text. Answer of 4th and 5th parts are

given here. From the equation, $V = \dfrac{RT}{P} + b$ or, $\left(\partial V / \partial T\right)_P = \dfrac{R}{P}$.

Or, $T\left(\partial V / \partial T\right)_P = \dfrac{RT}{P} = V - b$. Therefore, $\mu_{JT} = \dfrac{1}{C_P}\left[T\left(\dfrac{\partial V}{\partial T}\right)_P - V\right]$

$$= \frac{1}{C_P}[V - b - V] = -\frac{b}{C_P} = (-)ve\ always.$$

The result shows that the gas will be heated up always by the J T expansion and it has no T_i.

- **Nernst heat theorem :**

Introduction

In 1902, T. W. Richards studied the free energy change and enthalpy change of a number of chemical reactions in reversibly in electrochemical cell using the relations,

$$\Delta G = -\, nFE_{cell} \quad \text{and} \quad \Delta H = nF\left[T\left(\frac{\partial E_{cell}}{\partial T}\right)_P - E_{cell}\right].$$

Important deduction

The emf of the cell is determined by potentiometer at very low temperatures. He found that the value of ΔG and ΔH are approaching each other (i.e. $\Delta G \rightarrow \Delta H$) rapidly with lowering of temperature and at extremely low temperature (up to about -27^oC), ΔG becomes equal to ΔH (i.e. $\Delta G = \Delta H$)

Gibbs Helmholtz equation gives very interesting conclusions from the above experimental results.

The equation is, $\qquad \Delta G = \Delta H + T\left[\dfrac{\partial(\Delta G)}{\partial T}\right]_P$.

Since at $T \rightarrow 0K$, $\Delta G = \Delta H$, hence $T\left[\dfrac{\partial(\Delta G)}{\partial T}\right]_P = 0$. When $T = 0K$, $T\left[\dfrac{\partial(\Delta G)}{\partial T}\right]_P = 0$

whether, $\left[\dfrac{\partial(\Delta G)}{\partial T}\right]_P$ is zero or any finite value. But the equality, $T\left[\dfrac{\partial(\Delta G)}{\partial T}\right]_P = 0$

holds true for some range above and in the neighborhood of 0K.

Hence, $\left[\dfrac{\partial(\Delta G)}{\partial T}\right]_P = 0$, as $T \neq 0$. This is an important deduction from the experimental results.

Nernst postulate

In 1906, Nernst made bold postulate that for a process in condensed system

$\left[\dfrac{\partial(\Delta G)}{\partial T}\right]_P = 0$ in the vicinity of absolute zero temperature (up to about -27^oC).

The constancy P may be omitted, since the effect of P in the condensed system is very small.

Thus we may write, $\qquad$ Lt $T \rightarrow 0K$, $\dfrac{\partial(\Delta G)}{\partial T} = 0$.

That is, at extremely low temperature, ΔG would be constant and independent of T. Richard's experiment further shows that not only at $T \rightarrow 0$ K, $\Delta G = \Delta H$, but they approach equality for the processes at the neighbourhood of 0 K and some range above. This helps Nernst further to

suggest $\qquad \dfrac{\partial(\Delta H)}{\partial T} = 0$, Lt $T \rightarrow 0K$.

Thus, for condensed system, Nernst postulates are stated as,

$$\text{Lt } T \rightarrow 0K, \quad \frac{\partial(\Delta G)}{\partial T} \quad \text{and} \quad \text{Lt } T \rightarrow 0K, \quad \frac{\partial(\Delta H)}{\partial T} = 0,$$

These two postulates, we call Nernst Heat Theorem. This pair of simple relations has far-reaching implications in condensed phase of the system.
As we have seen, absolute zero temperature is unattainable so we shall use the limit $T \rightarrow 0$.
He remains a liquid as T goes to zero at one atm. All other elements are solids in this limit.

Change of ΔG and ΔH with T are opposite

It could be shown that when ΔG decreases with lowering of T, ΔH at the same time increases and vice-versa and when T is very low, $\Delta G \rightarrow \Delta H$.
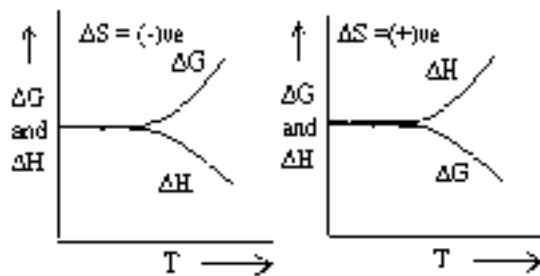To prove that we have, Gibbs Helmholtz equation,

$\Delta G = \Delta H + T \dfrac{\partial(\Delta G)}{\partial T}$. So the change with T, $\dfrac{\partial(\Delta G)}{\partial T} = \dfrac{\partial(\Delta H)}{\partial T} + \dfrac{\partial(\Delta G)}{\partial T} + T \dfrac{\partial^2(\Delta G)}{\partial T^2}$

or, $\dfrac{\partial(\Delta H)}{\partial T} = - T \dfrac{\partial^2(\Delta G)}{\partial T^2}$. Both terms have

opposite signs, and since ΔG is converging (tending to meet) to a limiting value, so slope and curvature have the same sign. That is,

$\dfrac{\partial(\Delta G)}{\partial T}$ and $\dfrac{\partial^2(\Delta G)}{\partial T^2}$ have the same sign.

This shows that $\dfrac{\partial(\Delta G)}{\partial T}$ and $\dfrac{\partial(\Delta H)}{\partial T}$ have opposite signs.

i.e. if ΔG decreases then ΔH increases with lowering of T and vice versa.

Another argument of justification

We have the relation, $\Delta G = \Delta H - T \Delta S$ or, $T \Delta S = \Delta H - \Delta G$.
For a finite T, we have in a process say, $\Delta S = (+)$ve i.e. $\Delta S \rangle 0$ then, $\Delta H \rangle \Delta G$ so with lowering of T, ΔH decreases and ΔG increases, and when Lt T $\to$ 0K, $\Delta G = \Delta H$.
Again for a process with $\Delta S = (-)$ve, i.e. $\Delta S \langle 0$ then, $\Delta H \langle \Delta G$ thus with lowering of T, ΔH increases and ΔG decreases, and when Lt T $\to$ 0K, $\Delta G = \Delta H$.
This concludes that variation of ΔG and ΔH as T is lowered will have opposite sign.

Implications of the theorem:
(1) $\Delta S = 0$ for processes near 0K:
   One of the basic equations is, $dG = - S\, dT + V\, dP$ but at constant P, $dG = - S\, dT$
   For the initial and final states of a system in a process, the forms are, $dG_1 = - S_1\, dT$ and
   $dG_2 = - S_2\, dT$ so, $dG_2 - dG_1 = - S_2\, dT + S_1\, dT$ or, $d(G_2 - G_1) = - (S_2 - S_1)\, dT$

$\Delta S = 0$ for processes near 0K

   or, $d(\Delta G) = - (\Delta S)\, dT$ or, $\dfrac{\partial(\Delta G)}{\partial T} = - \Delta S$. P is constant but omitted for simplicity.

   But Nernst theorem states Lt T $\to$ 0K, $\dfrac{\partial(\Delta G)}{\partial T} = 0$
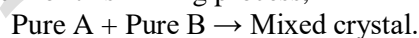
   hence, we can infer that Lt T $\to$ 0K, $\Delta S = 0$.
   Or, $S_2 = S_1$.
   It means that in the vicinity of absolute zero temperature, the processes occur without change of entropy. Thus in chemical reactions, reactants and products have the same entropy if it occurs near 0K (in condensed state).

Limitation of the theorem

Nernst heat theorem suffers some limitations.
(a) Let us imagine a mixed crystal which is to be formed from a pure crystal A and a pure crystal B at 0K, then for this mixing process,
   Pure A + Pure B $\to$ Mixed crystal.
   The entropy change of the process, $\Delta S_{mix.} = S$ (mixed crystal) $- S$ (pure A) $- S$ (pure B)
   $= - nR (x_A \ln x_A + x_B \ln x_B) = (+)$ve and not zero.

(b) Again, if a super cooled liquid is converting into crystalline solid at 0K, the entropy decreases and $\Delta S < 0$ since the randomness in super cooled liquid is greater than in the crystalline solid. But Nernst theorem states that Lt T $\to$ 0, $\Delta S = 0$, so there is limitation in the statement of the theorem.

Modified statement of the theorem

The above limitations of the theorem were removed by Simon and the Nernst-Simon statement is 'For any isothermal process that involves only pure substances and each in internal equilibrium, the entropy change goes to zero at T goes to zero.'

An example of this type of processes is the reversible phase transition involving pure crystalline solid, such as, $S_\alpha \to S_\beta$ at the transition temperature and pressure.
Mixed crystals are not pure substances or super cooled liquids are not in their internal equilibrium. So the Nernst heat theorem is not applicable.
(2) $\Delta C_P = 0$ for processes at near 0K:

The constant pressure molar heat capacity is defined in thermodynamics as, $C_P = \left(\dfrac{\partial H}{\partial T}\right)_P$.

$\Delta C_P = 0$ for processes at near 0K

The change in the properties of a system in a process is, $\Delta C_P = \left(\dfrac{\partial (\Delta H)}{\partial T}\right)_P$.

ΔC_P and ΔH are the change of constant pressure molar heat capacity and enthalpy of final state and initial state of the system for the process respectively.

But Nernst theorem states that, $\mathrm{Lt}\ T \to 0K, \dfrac{\partial (\Delta H)}{\partial T} = 0,$ hence $\mathrm{Lt}\ T \to 0K,\ \Delta C_P = 0.$

It implies that heat capacities of the initial substance (reactant) and final substance (product) for a process are same when it occurs at near 0K.

Application: Calculation of ΔG of a process from thermal data:

Expression of ΔC_P of a process at near 0K

C_P of a substance can be expressed in the form of power series of T.
$$C_P = a + bT + cT^2 + ------$$
where a, b, c, etc are virial coefficients of the substance in the condensed state.
Hence, $\Delta C_P = C_{P_2} - C_{P_1} = (a_2 - a_1) + (b_2 - b_1)T + (c_2 - c_1)T^2 + ----$
or, $\Delta C_P = \alpha = \alpha + \beta\ T + \gamma\ T^2 + ----$ where α, β, γ etc. depend on the nature of the initial state and final state of the system for the process.
But at T = 0K, $\Delta C_P = 0$ so, putting this we get, $\alpha = 0$.
Hence, the expression of C_P of a process near 0K is, $\Delta C_P = \beta\ T + \gamma\ T^2 + ----$

Expression of ΔS of a process near 0K

We may recall one basic equation, $dH = TdS + VdP$.
Or, $C_P\ dT = TdS + VdP$
but at constant pressure, $dS = (C_P/T)\ dT$.

Considering the change for two states of the system, $\dfrac{\partial(\Delta S)}{\partial T} = \dfrac{\Delta C_P}{T}$. Constancy P is omitted.

Separating the variables and integrating, $\int d(\Delta S) = \int \dfrac{\Delta C_P}{T}dT$,

or $\Delta S = \int \dfrac{\Delta C_P}{T}dT + \Delta S_o$ (integration constant).

But at 0K, $\Delta S = 0$, and $\Delta C_P = 0$, hence, $\Delta S_o = 0$. Thus, $\Delta S = \int \dfrac{\Delta C_P}{T}dT$.

Putting $\Delta C_P = \beta\ T + \gamma\ T^2 + ---$, $\Delta S = \int \left(\dfrac{\beta T + \gamma T^2 + ----}{T}\right)dT$.

Values of β and γ are determined from the equation, $\Delta C_P = \beta\ T + \gamma\ T^2 + ----$ by measuring ΔC_P values of the system for the process thermally at two temperatures.
Therefore, ΔS can also be calculated from the values of β and γ for the system by using the

expression, $\Delta S = \beta T + \dfrac{\gamma}{2}T^2 + ---$

Again, $\left(\dfrac{\partial(\Delta H)}{\partial T}\right)_P = \Delta C_P.$ Using the expression of ΔC_P and integrating,

Expression of ΔH of a process near 0K

we get,
$$\int_1^2 d(\Delta H) = \int_0^T \left(\beta T + \gamma T^2 + ---\right)dT$$

or, $\Delta H_T = \Delta H_0 + \dfrac{\beta}{2}T^2 + \dfrac{\gamma}{3}T^3 + --.$

ΔH_0 of the process can be obtained from the ΔH_T and β, γ values of the process.

Expression of ΔG of a process near 0K

Now, we may proceed to find expression of ΔG so that it can be calculated from the thermal data of the system for the process.

We have relation, $\Delta G = \Delta H - T\,\Delta S$. Now inserting the expression of ΔS and ΔH of the process from above,
$$\Delta G = (\Delta H_0 + \dfrac{\beta}{2}T^2 + \dfrac{\gamma}{3}T^3 + ---) - T(\beta T + \dfrac{\gamma}{2}T^2 + ---).$$

Or,
$$\Delta G = \Delta H_0 - \dfrac{1}{2}\beta T^2 - \dfrac{1}{6}\gamma T^3 - ----------.$$

This equation is utilized to calculate ΔG of a process from the thermal data β, γ, and ΔH_0 etc. (by thermal data we mean measurement of properties like ΔH, heat capacities).

Example: Calculation of transition temperature of sulphur:

For the process of transition, $S_\alpha \to S_\beta$, we can write $\Delta C_P = \beta T$.

Measuring heat capacity of the two forms of sulphur at a known temperature, β can be obtained. The value of β is found for the process, $\beta = 2.30 \times 10^{-5}$ cal mol^{-1}K^{-2}.

Again ΔH is determined for the process at any temperature and thus ΔH_0 (enthalpy-change at 0K) can be evaluated from the relation, $\Delta H = \Delta H_0 + \dfrac{\beta}{2}T^2$ and $\Delta H_0 = 1.57$ cal mol^{-1}.

Worked out: Now , $\quad \Delta G = \Delta H_0 - \dfrac{\beta}{2}T^2.$

But at the transition point, $T = T_t$ and $\Delta G_t = 0$, since the two forms of sulphur are in equilibrium. Hence, $\quad 0 = \Delta H_0 - \dfrac{\beta}{2}T_t^2$

or, $T_t = \sqrt{\dfrac{2\Delta H_0}{\beta}} = \sqrt{\dfrac{2 \times 1.57\, cal\, mol^{-1}}{2.30 \times 10^{-5}\, cal\, mol^{-1}\, K^{-2}}}$ or, $T_t = 369.5$ K,

The experimental value is 368.4 K, so the matching is excellent and this verifies Nernst heat theorem.

Nernst heat theorem is a precursor of third law of thermodynamics

From Nernst heat theorem, we have Lt $T \to 0K$, $\Delta C_P = 0$ i.e. heat capacities of all substances (reactants or products) at 0 K temperature must be same.

$\Delta C_P = C_P \text{(product)} - C_P \text{(reactant)} = 0$ or, $C_P \text{(product)} = C_P \text{(reactant)}$, at 0K temp.

This must hold good what ever may be the chemical nature of the products and reactants. This suggests that C_P of any substance itself may be zero at 0K.

This also finds justification from the quantal principle. At this very low temperature, heat energy of a solid consists of only vibrational energy and vibrational energy levels have energy gap so high that there is insufficient energy to provide even for change of one vibrational level. So solids can be heated near 0K without absorbing appreciable amount of energy.

In other words, Lt $T \to 0K$, $C_P = 0$. [đq = C_V dT, but C_V is very small and so small heat supplied (đq) can raise T to an appreciable amount.

From the expression of C_V ($\approx C_P$) $= 3R \dfrac{x^2 e^x}{(e^x - 1)^2} \approx 3R\ x^2\ e^{-x}$ at low T where, $x = \dfrac{h\nu_0}{kT}$

This shows that C_P decrease rapidly with decrease of T as the exponential term becomes zero much ahead than x gets infinite value and C_P is equal to zero when T approaches to zero. That is, $C_P = 0$ at $T \rightarrow 0K$.

- **Planck Formulation of the Third Law of Thermodynamics:**

Let us take the basic thermodynamic equation, dH = TdS + VdP

but,   dH = C_PdT,

putting we get, C_PdT = TdS + VdP.

Again at constant P, C_PdT = TdS, or, $dS = \dfrac{C_P}{T} dT$.

From Einstein approach of C_P, we infer that $\dfrac{C_P}{T}$ is zero or a finite positive quantity, as $T \rightarrow 0K$.

Therefore, integration of the entropy term we get, $\displaystyle\int_{S_o}^{S_T} dS = \int_0^T \dfrac{C_P}{T} dT$

or, $S_T - S_o = \displaystyle\int_0^T \dfrac{C_P}{T} dT$,

where, S_T and S_o are the entropy of the system at temperature T K and 0 K respectively.

Since C_P is positive or zero, hence $\displaystyle\int_0^T \dfrac{C_P}{T} dT$ = (+)ve or 0.

hence, $S_T - S_o$ = positive or zero.

This refers that $S_T \rangle S_o$,

i.e. entropy of a substance at any temperature, T must be greater than its entropy at 0 K.

Thus at 0 K, the entropy has its smallest possible algebraic value S_0, the entropy at any higher temperature is greater than S_0.

Max Planck in 1913 made a striking proposal and stated third law as ,

Plank statement of third law

          'The entropy of a solid or liquid is zero at absolute zero temperature'

Thus for condensed system,   (i) Nernst theorem states,   Lt $T \rightarrow 0$ K, $\Delta S = 0$

and,   (ii) Planck law states,   Lt $T \rightarrow 0$ K, $S = 0$.

It is obvious that the third law does not contradict the heat theorem rather it supports and makes the later quantitative. At 0K, solid reactant or solid product each has zero entropy and hence entropy change (ΔS) is zero.

Planck's generalization may be true for solids but not for liquids. Since statistical mechanics shows that entropy becomes least when the substance is present in a perfectly arranged crystalline state, the Planck's relation is,

                    S = k lnW,   W is the thermodynamic probability.

           For S = 0, W must be 1 only when there is one arrangement of the molecules.

This is possible only when the system is pure and perfectly crystalline state. In the case of super cooled liquid or in case of solid solution or mixture, even at 0K, W $\rangle$ 1 and entropy (S) will be some what greater than zero.

          Thus for pure and perfectly crystalline substances (W = 1), S = 0 at T = 0.

Lewis and Randall Statement of the Third Law

Lewis and Randall stated the law more precise way as under:

"Every system has finite positive entropy but at the absolute zero of temperature the entropy may become zero and does so become in the case of a pure crystalline substance."

Application of the Law : Determination of Absolute Entropy of a Substance

The above expression of entropy is $S_T - S_0 = \int_0^T \dfrac{C_P}{T} dT$

where S_T is the entropy of the solid at temperature T and pressure P atm. When P = 1 atm, it is called standard entropy of the solid at temperature T and denoted by S_T^0.

S_0 is the entropy at 0 K and it is equal to zero according to the third law of thermodynamics.

Therefore, $\qquad\qquad\qquad S_T . = \int_0^T \dfrac{C_P}{T} dT \quad$ or, $\; S_T = \int_0^T C_P \, d\ln T$.

S_T is determined graphically by plotting $\dfrac{C_P}{T}$ against T

or C_P against lnT and finding the area enclosed between the two temperatures 0 to T K
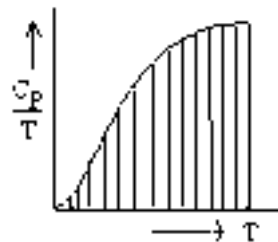
Since the change in the state of aggregation (melting or vaporization) involves an increase in entropy, this contribution is to be included in the calculation of the entropy of a liquid or of a gas.

Thus, for the entropy of a liquid above the melting point of a substance,

$$S_T = \int_0^{T_m} \frac{C_P(s)}{T} dT + \frac{\Delta H_{fusion}}{T_m} + \int_{T_m}^{T} \frac{C_P(l)}{T} dT$$

Similarly, for a gas above the BP of the substance,

$$S_T = \int_0^{T_m} \frac{C_P(s)}{T} dT + \frac{\Delta H_{fusion}}{T_m} + \int_{T_m}^{T} \frac{C_P(l)}{T} dT + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} \frac{C_P(g)}{T} dT$$

$$= \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

To calculate the entropy, the heat capacity of the substance in its various states of aggregation must be measured accurately over the range of temperature. The values of the heats of transition and the transition temperature must also be measured. All these measurements can be done calorimetrically.

Measurements of the heat capacity of some solids have been made at temperature as low as a few hundredths of a degree above 0K. However, ordinarily, measurements of C_P are made down to a low temperature which frequently lies in the range from 10 K to 15 K. At such temperature, C_P follows Debye T- cubed law accurately.

$C_V = A \left(\dfrac{T}{\theta_D} \right)^3$, where A is universal constant

$\qquad\qquad = 464.5$ cal mol^{-1} K^{-1},

and θ_D is called Debye temperature, a characteristic constant of the solid.

Determination of C_V at any appreciably higher temperature T gives the value of θ_D. Substituting this value of θ_D of the substance in the above equation it is possible to calculate C_V in the vicinity of 0 K.

At the extremely low temperature, the difference of C_P and C_V is negligible and so these values can be taken for C_P as well.

The hike of the curve at T_m and at T_b is due to $C_P(l) > C_P(s) > C_P(g)$.
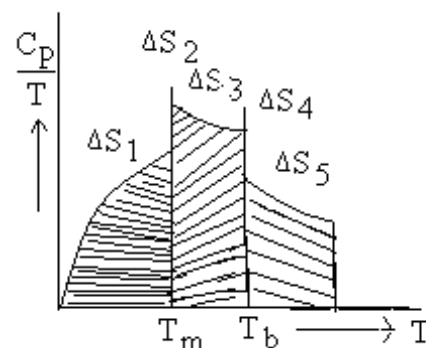
Example: Evaluation of S_T of a substance in the gaseous state at 25°C.

The evaluation of S_T at 25°C is done by adding the ΔS values keeping in mind that $S_0 = 0$.

(1) ΔS of the solid from 0K to 10K and to the melting point of the solid,

$$\Delta S_1 = S_{T_m}(s) - S_{0K}(s) = \int_{0K}^{10K} \frac{C_P(s)}{T} dT + \int_{10K}^{T_m} \frac{C_P(s)}{T} dT .$$

1st C_P is calculated by using Debye T^3 relation and 2nd C_P is determined by actual experiment.

(2) ΔS for the fusion of the solid at T_m temperature is given as,

$$\Delta S_2 = S_{T_m}(l) - S_{T_m}(s) = \frac{\Delta H_{fusion}}{T_m} = \frac{\overline{L_f}}{T_m} .$$

This is done by simple calculation of molar latent heat of fusion ($\overline{L_f}$) and the melting point (T_m) of the solid.

(3) ΔS for raising the temperature of the liquid from T_m to T_b of the substance,

$$\Delta S_3 = \Delta S_3 = S_{T_b}(l) - S_{T_m}(l) = \int_{T_m}^{T_b} \frac{C_P(l)}{T} dT .$$

Where $C_P(l)$ is the molar heat capacity of the liquid

(4) ΔS for the vaporization of the liquid at its T_b,

$$\Delta S_4 = \Delta S_4 = S_{T_b}(g) - S_{T_b}(l) = \frac{\Delta H_{vap}}{T_b} = \frac{\overline{L_v}}{T_b} .$$

Where $\overline{L_v}$ is the molar latent heat of vaporization of the liquid.

(5) ΔS for raising the temperature of the gaseous substance from T_b to 298 K,

$$\Delta S_5 = \Delta S_5 = S_{298K}(g) - S_{T_b}(g) = \int_{T_b}^{298K} \frac{C_P(g)}{T} dT .$$

Where $C_P(g)$ is the molar heat capacity of the substance in the gaseous phase.

Adding all these ΔS values, we get the entropy (S_{298K}) of the substance at 25°C.

If the solid exists in different allotropic forms,

$$\Delta S = \frac{\Delta H_{transition}}{T_{trans}}$$ is to be added to the ΔS_T values,

To compare the S_T values of different substances, it is better to express the molar entropy at 1 atm pressure (standard state). This gives standard molar entropy (S_T^0) of the substance at T temperature.

Problems: Calculate the entropy of ethylene gas at 25°C. Given the following data:

(i) 0K — 15K (by extrapolation with Debye T^3 law), $\Delta S = 0.24$ cal mol^{-1} K^{-1}

(ii) 15K — 104K (graphically, using $C_P(s)$ vs. T plot), $\Delta S = 12.25$,,

(iii) Fusion at 104K (= T_m), $\Delta S = \left(\dfrac{\overline{L_V}}{T_B} = \dfrac{3237}{169.4} \right)$ or $\Delta S = 7.70$,,

(iv) 104K — 169.4K (graphically, using $C_P(l)$ vs. T plot), $\Delta S = 7.90$,,

(v) Vaporization at 169.4K (= T_b), $\Delta S = \left(\dfrac{\overline{L_V}}{T_B} = \dfrac{3237}{169.4} \right)$ or $\Delta S = 19.10$,,

(vi) 169.4K — 298K (graphically, using $C_P(g)$ vs. T plot), $\Delta S = 5.12$,,

Thus molar entropy of ethylene gas at 25°C = 0.24 + 12.25 + 7.70 + 7.90 + 19.10 + 5.12

Or, S_{298K} (ethylene, g) = 52.31 cal mol^{-1} K^{-1}.

Test of the third law of thermodynamics:

(1) The third law of thermodynamics predicts that in the neighborhood of 0K,
the heat capacity (C_P) and coefficient of thermal expansion (α) would vanish.
These have been confirmed experimentally in many instances.

$[\ \alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$,*but Maxwell relation states that* $\left(\dfrac{\partial V}{\partial T}\right)_P = -\left(\dfrac{\partial S}{\partial P}\right)_T$.

But third law states that at 0K temperature, S = 0 for any perfectly crystalline solid whatever

may be the pressure. Therefore, $\left(\dfrac{\partial S}{\partial P}\right)_T = 0$ and so $\alpha = 0$.]

(2) The third law may be used to calculate the change of entropy in the transformation of one
form of a substance to another form.

The calculated value corresponds to the experimental results.

Let us consider the change of one crystalline form (X) to another crystalline form (Y) at the
transition temperature (T_t), $X \rightarrow Y$. Since $\Delta G = 0$ for the process,

hence in the equation, $\quad \Delta G = \Delta H - T\Delta S$, $\quad$ or $\quad \Delta S = \dfrac{\Delta H_t}{T_t}$,

where, ΔH_t = enthalpy of transition, i.e. $\quad S_Y - S_X = \dfrac{\Delta H_t}{T_t}$.

$S_Y - S_X$ can be determined from the enthalpy of the transition and the transition temperature.
The third law states that the entropy value at 0K is zero for both X and Y,

so, $\qquad S_Y - S_X = \int\limits_0^{T_t} \dfrac{C_P(Y)}{T} dT - \int\limits_0^{T_t} \dfrac{C_P(X)}{T} dT$.

Thus, at the transition temperature (T_t), both S_X and S_Y can be determined using the third law.
These two values of ΔS are found to be same.

Example: White tin $\rightarrow$ Grey tin at 298 K. The third law entropy of white tin and grey tin are
11.17 and 9.23 in cal mol^{-1} K^{-1} respectively.

Solution: Thus, $\qquad \Delta S = S_{\text{Grey tin}} - S_{\text{White tin}} = 11.17 - 9.23 = 1.94$ cal mol^{-1} K^{-1}
The value of ΔS is obtained from measured enthalpy of transition and free energy
of transition. The value of ΔS at 298 K is found to be 1.87 cal mol^{-1} K^{-1}.
The result is quite satisfactory with the third law value.

**Residual entropy — Apparent deviation of third law:**

In most cases, entropies determined by heat capacities agree well with those
determined by statistical method. In few cases, there appear discrepancies; the third law entropies
(obtained from heat capacity) are being slightly less than the statistical entropies.
That these substances have actually residual entropies at 0 K.
It appears that the substances which appears to deviate from the third law, are not pure and
perfectly crystalline in the Lewis-Randall sense of the term. Some of such cases are given here,

(1) Super cooled liquids: Glass, glossy materials, plastics etc have residual entropies.
For example, glossy glycerine has residual entropy of 5.6 cal mol^{-1} K^{-1}.

(2) Solid solutions: Different atoms and molecules are distributed in random way and
so they have residual entropy. Such as AgCl-AgBr.

(3) Mixture of isotopes: It is same as above. Cl_2 at 0K consists of solid solution of $Cl^{35}-Cl^{35}$, $Cl^{35}-Cl^{37}$ and $Cl^{37}-Cl^{37}$ molecules. We ignore in chemical reactions as the products also have residual entropy like the reactants.

(4) Nuclear spins: Hydrogen is a typical example. Hydrogen is a mixture of ortho-form (nuclear spin parallel) and para-form (nuclear spin anti parallel).
At ordinary temperature, the two forms remain in equilibrium.
But near 0K, hydrogen should remain completely in the para form (lowest energy form).
In practice, as the temperature is lowered, the shift towards the para form is sluggish.
Even near 0K, hydrogen still is a mixture of the two forms and it has nuclear spin entropy.

(5) *Geometrical arrangements or orientations:* Examples belonging to this type are CO, N_2O, NO and $COCl_2$ where the sizes of the atoms are comparable. Let us take the CO molecules. They can arrange in solid as CO and OC.

$$\text{CO} \quad \text{OC} \quad \text{CO} \quad \text{OC}$$
$$\text{OC} \quad \text{CO} \quad \text{OC} \quad \text{etc.}$$
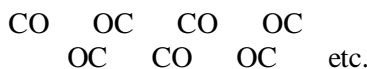
The dipole moment of CO is very small (0.1D) so the energy difference between the two arrangements is small. Due to free rotation, one arrangement can easily pass into other.
The Boltzmann distribution of population in the two different energy levels corresponding to the two orientations of the molecule is given by

$$\frac{n_1}{n_2} = e^{-(\epsilon_1-\epsilon_2)/kT} = e^{(\epsilon_2-\epsilon_1)/kT} = e^{\Delta\epsilon/kT}.$$

At the normal freezing temperature (66 K), when the crystal of the substance is formed,

$\Delta\epsilon/kT$ is very small and $\frac{n_1}{n_2} = e^{\Delta\epsilon/kT} \to e^0 \to 1$. The crystal is formed with approximately

equal number of carbon monoxide molecules in two different orientations.

But as $T \to 0$ K, $\Delta\epsilon/kT$ becomes significant. At 0 K, $e^{\Delta\epsilon/kT} \to e^\infty \to \infty$.

That is, if thermodynamic equilibria were maintained, all the CO molecules would adopt the same orientation of lower energy. How ever, to have incorrectly oriented CO molecules rotate $180°$ in the crystal requires substantial activation energy which is not available to the molecule at low temperature. The CO molecules remains locked into their nearly random orientations as T is lowered. That is, the rotations are frozen.

If the randomization were equal in the arrangements, then the entropy of 1 mole of the substance would be, $S = k \ln W$, where W is the number of ways by which Avogadro number of molecules can take the orientations with equal proportion and it is 2^{N_A} i.e., $W = 2^{N_A}$.

So the entropy, $S = k \ln W = k \ln 2^{N_A} = k \times N_A \ln 2 = R \ln 2 = $ **1.386 cal mol^{-1} K^{-1}.**

But experimental value of the residual entropy of CO is **1.0 cal mol^{-1} K^{-1}.** This suggests that one orientation prevails over the other and complete randomization does not occur.

(6) Unsymmetrical hydrogen bindings:
Examples are ice, KH_2PO_4 etc. Ice had residual entropy of 0.82 cal mol^{-1}K^{-1} at 0K and this is due to different ways of orientation of water molecules. In ice, each O-atom is tetrahedrally surrounded by four H-atoms ─ of these two are covalently bonded and other two are hydrogen bonded. Thus each O-atom has two H-atoms are near and two other H-atoms are relatively far located.
Two ways of arrangements are shown.
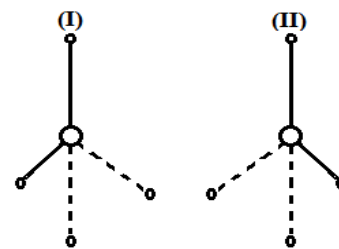
O: Oxygen atom, o: hydrogen atom
─ : covalent bond, ---- : H-bond.

It could be shown that thermodynamic probability for the two the orientations at 0K is 1.5.

The entropy, $S = R \ln W = 2\ln 1.5 = 0.81 \, cal K^{-1} mol^{-1}$.

Thus it appears that for the application of third law, the substance must be in perfectly crystalline state and should be in a single quantum state.

Unattainability of absolute zero:

The third law has also been stated in an elegant fashion as:

"It is impossible to attain absolute zero temperature in a finite number of operations."

That is, we can not, by any process occurring in finite dimensions, cool a body to absolute zero temperature.

By considering the functions of a reversible refrigerator, we can easily arrive at the above statement. Let us suppose a substance at a low temperature (T' K) is being cooled further by withdrawing heat (Q') from it.
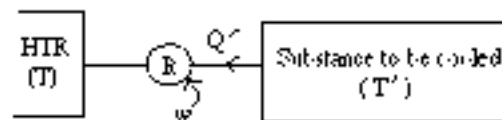
We can use a reversible refrigerator working between TK and T' K (T $\rangle$ T').

The minimum amount of work (w) needed to extract Q' heat from the cold substance is given as:

The efficiency of the refrigerator,

$$\Psi = \frac{Q'}{w} = \frac{T'}{T-T'} \quad \text{or,} \quad w = Q' \times \frac{T-T'}{T'}$$

Now as the temperature T' is lowered, more and more work would be needed to extract the same amount of heat Q', since as T' is decreasing, $\frac{(T-T')}{T'}$ increases rapidly.

If the temperature of the substance (which is to be cooled) is lowered to 0K (i.e. $T' = 0K$), then infinite amount of work would be required. That is, any finite amount of work would not be sufficient to cool the body to 0K. Hence, absolute zero of temperature can not be attained.

Problem(1): Write down the Lewis-Randall statement of third law of thermodynamics and justify it from the concept of thermodynamic probability.　(4)　　　　　　　　[BU '92]

Ans　For statement, see the Text, page

This statement finds justification from the concept of thermodynamic probability. When a pure substance remains in a perfectly crystalline state, all the lattice points are in perfectly ordered form. At 0K temperature, the lattice points are all in the lowest energy level, so, the thermodynamic probability,

$$W = \frac{\lfloor N_0}{\lfloor N_0 \rfloor 0 \rfloor 0} = 1. \text{ the Planck relation, } S = k \ln W = k \ln 1 = 0$$

i.e. the entropy of a pure and perfectly crystalline substance at 0K is zero which is also the statement of Lewis-Randall.

Problem (2): T^3 law predicts that Lt.T→0, $C_V = 0$. Justify this also from the third law of thermodynamics. (2)

[BU '92]

Ans　The T^3 law is , $C_V = A\left(\dfrac{T}{\theta_D}\right)^3$, where A is Universal constant = 464.5 cal mol^{-1}K^{-1}

and θ_D is Debye temperature which is a characteristic of the substance.

The third law also states that the entropy of a pure substance is zero at the absolute zero temperature. Hence $S_T = \int_0^T \dfrac{C_P}{T} dT$, thus when T = 0, S_T = 0, and this can happen only when

$$C_P = 0. \text{ At this 0K temperature, } C_P = C_V .$$

Thus T^3 law justifies the Planck's statement of the third law of thermodynamics.

Problem(3): At 25°C, the third law entropy of water is about 82 JK^{-1}mol^{-1} less than that of bromine at the same temperature. What does this signify? (2) [BU '92]

Ans Since both are liquids and at the same temperature, hence the data given signify that liquid water is in more ordered state than liquid bromine. This is due to the H-bonding in the liquid water that forms the water molecules in intermolecular association resulting more ordered state than liquid bromine.

Problem(4): Calculate the entropy change accompanying the mixing of 1 mole of a substance A with 1 mole of another substance B, the process being carried out at T = 0. Does the result go against or in favor of the Nernst heat theorem? Explain. (2½) [BU '92]

Ans The entropy change, ΔS = 2.772 cal K^{-1}. See the Text, page,
This goes against the Nernst heat theorem as the theorem states that at T = 0, the process will occur without entropy change.

Problem(5): Write the expression for the Standard entropy (S_T^0) of a gas above its boiling point. (2) [BU '93]

Ans See the Text, page $\quad S_T^0 = \int_0^{T_m} \dfrac{C_P^0(s)}{T} dT + \dfrac{\Delta H_{fusion}^0}{T_m} + \int_{T_m}^{T_b} \dfrac{C_P^0(l)}{T} dT + \dfrac{\Delta H_{vap}^0}{T_b} + \int_{T_b}^{T} \dfrac{C_P^0(g)}{T} dT$.

Problem(6): Show that heat capacity remains unchanged in any transformation in the vicinity of absolute zero.
(2) [BU '93]

Ans We know that $\left(\dfrac{\partial (\Delta H)}{\partial T} \right)_P = \Delta C_P$. But Nernst law states that $\left(\dfrac{\partial (\Delta H)}{\partial T} \right)_P = 0$ when T → 0

thus, as T → 0, ΔC_P = 0 or C_P(product) − C_P(reactant) = 0 or C_P(product) = C_P(reactant).
This means that heat capacity remains unchanged in any transformation in the vicinity of absolute zero.

Problem(7): Is there any need for a third law of thermodynamics? Discuss the Nernst heat theorem and point out its significance. (4) [BU '98]

Ans 2nd law of thermodynamics provide the calculation of ΔS of a process.
For reversible phase transition, X → Y, we can only calculate ΔS of the process using the

relation, $\qquad \Delta S = \dfrac{\Delta H_t}{T_t} \qquad$ but, $\qquad \Delta S = S_Y − S_X$,

thus, the individual absolute value of S_X and S_Y cannot be determined by the use of the 2nd law.
Only 3rd law can provide method to determine the absolute value of entropy of a substance
i.e. absolute values of S_X and S_Y are known only from the 3rd law.
(See the test of 3rd law, page,).
2nd part; State the Nernst heat theorem.
The significance of the theorem is that at extremely low temperature, ΔG and ΔH would be constant with change of T. Two values tends to equality as T→0.
This instantly leads to ΔS = 0 as t = 0K.

Problem(8):   Justify / criticize: Entropy of a solid is zero at zero Kelvin temperature.   (3)   [BU '99]

Ans   The statement is not fully correct. Only when the solid is pure and perfectly crystalline state and it remains in one quantum state (W = 1), the entropy of the substance is zero at zero Kelvin temperature.
When the solid is in mixed state (alloy), its entropy is not zero but has (+)ve value.
If the solid is not in one quantum state, the solid has some residual entropy.
(see the residual entropy).

MULTI-COMPONENT OPEN SYSTEM WITH VARIABLE COMPOSITIONS

Open system and extensive properties

In open system, both mass and energy are exchanged with the surrounding. So, the extensive properties of the open system depend, besides the other variables, on the mole numbers of the components present in the system.

Concept of chemical potential (μ)

Let us consider a multi-component open system which contains n_1 moles of component A_1, n_2 moles of component A_2, n_3 moles of component A_3 etc. at constant T and P.

The volume (V) is an extensive property and hence $V = f(T, P, n_1, n_2, ---- n_i)$
On partial differentiation, we get,

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n_j} dP + \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_{j\neq 1}} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_{j\neq 2}} dn_2 + -----$$

$$---------- + \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i.$$

But, $\left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_{j\neq 1}} = \overline{V_1}$, called partial molar volume.

The free energy (G) is also an extensive property like volume (V).

So, $G = f(T, P, n_1, n_2, n_3, -------).$

So, $dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_j} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_{j\neq i}} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_{j\neq 2}} dn_2 + ----$

$$-------- + \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i.$$

But, $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \overline{G_1}$, called partial molar free energy and it is called chemical potential of the 1st component (μ_1).

Thus, $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ = chemical potential of the ith component (μ_i).

Expression of dG in multi-component open system

Therefore, $dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_j} dP + \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + -----+ \mu_i dn_i.$

But, $\left(\frac{\partial G}{\partial T}\right)_{P,n_j} = -S$ and $\left(\frac{\partial G}{\partial P}\right)_{T,n_j} = V$.

So the expression of dG for the multi-component open system is,

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + ------+ \mu_i dn_i.$$

or, $$dG = -SdT + VdP + \sum \mu_j\, dn_j.$$

Definition of chemical potential

Chemical potential is an intensive property of the system and defined as change of free energy of the component when 1 mole is added to infinitely large system so to keep the composition of the system fixed. It may also be defined as the change of free energy when infinitesimal amount, dn_i of the ith component is added to a finite system and then calculated per mole,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}.$$

Physical meaning of chemical potential

It is the actual free energy per mole of the component in the system. Its unit is energy /mole and so Joule/mole or cal/mole. Its dimension is $M\,L^2\,T^{-2}\,mole^{-1}$.

Chemical potential of a component is a measure of escaping tendency of the component from

the state where it exists to another available state. Thus, a component (i) moves spontaneously from its phase (α) to phase (β) if $\mu_i^\alpha \rangle \mu_i^\beta$. Flow of the component stops and attains equilibrium when $\mu_i^\alpha = \mu_i^\beta$. This leads to the conclusion that when a substance remains in different phases at equilibrium, the chemical potential of the substance will be same in every phase.

This idea plays vital role in formulating the thermodynamics in general phase equilibrium.

Molar quantity and partial molar quantity.

Let us take the volume as the quantity as for explanation. The molar volume is denoted by $\overline{V}_i^0$ and partial molar volume by $\overline{V}_i$ of the ith component.

(a) Molar volume ($\overline{V}_i^0$) is the volume of 1 mole of the ith component when it is in pure state while partial molar volume ($\overline{V}_i$) is the actual volume of 1 mole of the component that occupies in a multi-component system at a given composition.

(b) In case of ideal systems, where either there exists no interaction between the constituents (ideal gas) or all interactions are of same magnitude (ideal solution), the two volumes are same

i. e. $\overline{V}_i = \overline{V}_i^0$.

In non ideal systems, due to intermolecular interactions, the partial volume ($\overline{V}_i$) is not equal to the molar volume ($\overline{V}_i^0$). The extent of interaction depends on the nature of the components presents and their relative amounts (composition). Since $\overline{V}_i$ is not same in all compositions thus for non-ideal system, $\overline{V}_i^0 \neq \overline{V}_i$ at given T and P of the system.

Gibbs-Duhem equation

Gibbs –Duhem equation:

The free energy change for open system at constant temperature (T) and pressure (P)

is given by $\quad dG_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_i dn_i = \sum \mu_j dn_j$.

Now, if the addition of each component is of same proportion (Δx) of initial moles, then free energy change will also be the same proportion of its initial value. That is,

if $\quad dn_1 = n_1 \Delta x, dn_2 = n_2 \Delta x, dn_i = n_i \Delta x, \ then, dG_1 = G_1 \Delta x.$ Therefore,

$G_{T,P}\, \Delta x = \mu_1 \times n_1 \Delta x + \mu_2 \times n_2 \Delta x + \cdots + \mu_i \times n_i \Delta x + \ or,\ G_{T,P} = \mu_1 n_1 + \mu_2 n_2 + \cdots + \mu_i n_i + \cdots$ (1)

$$G_{T,P} = \sum \mu_j n_j.$$

On complete differentiation, we get,

$$dG_{T,P} = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \cdots + \mu_i dn_i + n_i d\mu_i + \cdots$$

Subtracting equation (1) from the above, we have $0 = n_1 d\mu_1 + n_2 d\mu_2 + \cdots + n_i d\mu_i + \cdots$.

$$or,\ 0 = \sum n_j d\mu_j$$

This equation is called Gibbs-Duhem equation.

Effect of T and P on chemical potential

We have, $\quad \mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ so, $\quad \left(\dfrac{\partial \mu_i}{\partial T}\right)_{T,P,n_{j\neq i}} = \dfrac{\partial^2 G}{\partial T\, \partial n_i}$

Again, $\quad dG = -S\, dT + V\, dP + \sum \mu_j\, dn_j \quad$ or, $\quad \left(\dfrac{\partial G}{\partial T}\right)_{P,n_j} = -S$

or, $\dfrac{\partial^2 G}{\partial n_i\, \partial T} = -\left(\dfrac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} = -\overline{S_i}$, called partial molar entropy of the ith component.

As G is perfectly differential quantity, it obeys Euler's theorem i.e. $\dfrac{\partial^2 G}{\partial T\, \partial n_i} = \dfrac{\partial^2 G}{\partial n_i\, \partial T}$

Hence we have the effect of T on μ_i as, $\left(\dfrac{\partial \mu_i}{\partial T}\right)_{P,n_j} = -\overline{S_i}$. By similar way,

we can formulate $\left(\dfrac{\partial \mu_i}{\partial P}\right)_{T,n_j} = \overline{V_i}$ where, $\overline{V_i}$ = partial molar volume of the ith component.

These two expressions signify that chemical potential of a component decreases with rising temperature and increases with increase of pressure since $\overline{S_i}$ and $\overline{V_i}$ are always positive.

For open system, the terms containing the change in mole numbers of the components are included in the basic thermodynamic equations. So the equations are:

Basic equations for multi-component open system

$$(1)\ dG = -SdT + VdP + \sum \mu_j\, dn_j \ \ \text{and}\ \ \mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$(2)\ dA = -SdT - PdV + \sum \mu_j\, dn_j \ \ \text{and}\ \ \mu_i = \left(\dfrac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}}$$

$$(3)\ dH = TdS + VdP + \sum \mu_j\, dn_j \ \ \text{and}\ \ \mu_i = \left(\dfrac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}}$$

$$(4)\ dU = TdS - PdV + \sum \mu_j\, dn_j \ \ \text{and}\ \ \mu_i = \left(\dfrac{\partial V}{\partial n_i}\right)_{S,V,n_{j\neq i}}$$

Expression of chemical potential (μ_i) in ideal system:

(1) For pure ideal gas: $\left(\dfrac{\partial \mu}{\partial P}\right)_{T_j} = \overline{V}$. But, $\overline{V} = \dfrac{RT}{P}$,

 substituting and integrating, we get,
$$\mu\,(T, P) = \mu^\circ\,(T) + RT \ln P,$$
 where, $\mu^\circ\,(T)$ is standard chemical potential of the substance at temperature T, and
 $\mu\,(T, P)$ is its chemical potential at T and pressure P.

(2) For an ideal gas mixture: The expression is, $\mu_i\,(T, P) = \mu_i^0\,(T) + RT \ln p_i$,
 where, p_i = partial pressure of the ith component in the ideal gas mixture and
 $\mu_i^0\,(T)$ = standard chemical potential of the ith component at temperature T i.e.,
 it is the chemical potential of the pure ith component at temperature T and 1 atm pressure.

(3) Chemical potential in terms of mole fraction (x_i):

 We have, $\qquad\qquad\qquad\qquad p_i = x_i \times P.$

When partial pressure, p_i is replaced by mole fraction, x_i, the expression of chemical potential

is $\qquad\qquad\qquad \mu_i\,(T, P) = \mu_i^0\,(T) + RT \ln (x_i \times P)$

$$= [\, \mu_i^0\,(T) + RT \ln P\,] + RT \ln x_i$$

or, $\qquad\qquad\qquad (T, P) = \mu_i^0 (T, P) + RT \ln x_i$,

where, $\mu_i^0 (T, P) = \mu_i^0 (T) + RT \ln P$, called chemical potential of the ith component in pure state at T and pressure P.

Since, $x_i \langle 1$, so, $\ln x_i \langle 0$. Thus $\mu_i (T, P) \langle \mu_i^0 (T, P)$. That is, chemical potential of a component in a mixture is less than that in pure state under the same T and P.

Explanation of osmosis

Osmosis can be explained on the basis of the above concept. Chemical potential of the solvent in solution is lower than that in pure state.

Thus solvent will flow spontaneously from the higher chemical potential to the lower chemical potential, i.e. from the solvent side to the solution side through the semi permeable membrane. It is osmosis.
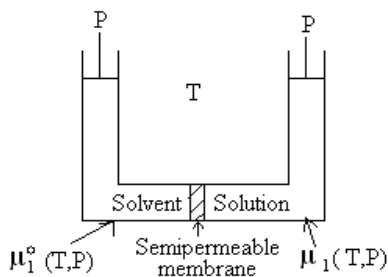
Expression of $\Delta G_{mix.}$, ΔS_{mix} and ΔH_{mix}

This expression of μ can be utilized to calculate the free energy change due to mixing of two ideal gases at constant T and P.
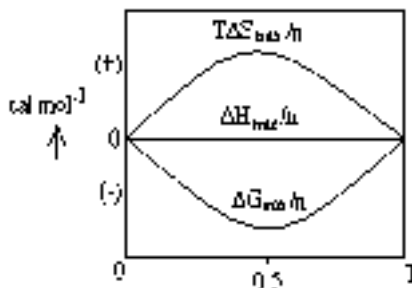
$$\Delta G_{mix.} = G_{mix.} - G_{pure} = (n_1 \mu_1 + n_2 \mu_2) - (n_1 \mu_1^0 + n_2 \mu_2^0)$$

$$= n_1 (\mu_1^0 + RT \ln x_1) + n_2 (\mu_2^0 + RT \ln x_2) - (n_1 \mu_1^0 + n_2 \mu_2^0)$$

$$= n_1 RT \ln x_1 + n_2 RT \ln x_2 = nRT (x_1 \ln x_1 + x_2 \ln x_2).$$

Or, $\Delta G_{mix.} = nRT \sum x_i \ln x_i$. Since, $x_i \langle 1$, $\ln x_i \langle 0$. Therefore, $\Delta G_{mix.} \langle 0$.

Again, $\Delta S_{mix.} = - \left[\dfrac{\partial(\Delta G_{mix.})}{\partial T} \right]_P$, $\qquad$ or, $\qquad \Delta S_{mix.} = - nR \sum x_i \ln x_i \rangle 0$.

So, $\qquad \Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix} = 0$.

Greatest decrease of G and increase of S in the mixture

The greatest decrease of free energy and greatest increase of entropy occur when equal number of moles of the components are mixed up. This can be shown as follows.

$\Delta G_{mix.} = nRT (x_1 \ln x_1 + x_2 \ln x_2)$. But $x_2 = 1 - x_1$

so, $\Delta G_{mix.} = nRT [x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1)]$.

Differentiating ΔG_{mix} with respect to x_1 at constant T and P we get,

$$\left[\dfrac{\partial(\Delta G_{mix.})}{\partial x_1} \right]_{T,P} = nRT [\ln x_1 + x_1 \times \dfrac{1}{x_1} + (-1)\ln(1 - x_1) + (1 - x_1) \times \dfrac{1}{(1 - x_1)}(-1)]$$

$$= nRT [\ln x_1 - \ln (1 - x_1)] = nRT \ln \left(\dfrac{x_1}{1 - x_1} \right) = 0$$

Thus, for ΔG_{mix} attains minimum, $\quad \ln \left(\dfrac{x_1}{1 - x_1} \right) = 0, \quad$ or, $\quad \left(\dfrac{x_1}{1 - x_1} \right) = 1$,

or, $\qquad\qquad\qquad x_1 = 0.5 \qquad$ and $\qquad x_2 = 1 - x_1 = 1 - 0.5 = 0.5$.

Likewise, it can be shown that for the ideal mixture, ΔS_{mix} attains maximum when equal number of moles of the components are mixed up i.e., $x_1 = x_2 = 0.5$

Problem	Show that in a binary system, the decrease in free energy of mixing is maximum if $x_1 = x_2 = 0.5$

(where x_1 and x_2 are the mole fraction of the 1st and 2nd components respectively)

[IIT, KGP '1999]

Chemical potential of a substance in condensed phase

Since, the solid or liquid state remains under equilibrium with its vapor, chemical potential of the substance in condensed phase is also given by:

$$\mu_i\,(T, P) = \mu_i^0\,(T) + RT \ln P,$$

where, P is the vapor pressure over the condensed phase of the substance.

When the substance remains in a mixture, it is, $\quad \mu_i\,(T, P) = \mu_i^0\,(T) + RT \ln p_i.$

where, p_i is the partial vapor pressure of the substance in condensed state.

We can write in terms of x_i, $\mu_i\,(T, P) = \mu_i^0\,(T, P) + RT \ln x_i$.

Since molar conc. (c_i) is directly related to mole fraction (x_i),

hence, $\qquad \mu_i\,(T, P) = \mu_i^0\,(T, P) + RT \ln c_i$,

where, c_i = molar conc. of the component in the condensed mixture.

Chemical potential in real system:

We have, $\qquad \left(\dfrac{\partial \mu}{\partial P}\right)_T = \overline{V}.$

But for real system, $\overline{V}$ is to be replaced in terms of T and P using real gas equation but it is not very easy mathematically. To remove such difficulty and to retain the same functional form as in ideal system, G.N.Lewis expressed the form for real gaseous system as,

$$\mu = \mu^0(T) + RT \ln f$$

where, f is the fugacity (fictitious pressure) of the real gas as called by G.N.Lewis.

Fugacity and chemical potential

Fugacity (f) measures the chemical potential of a real gas in the same way as the pressure measures it in ideal gas. Thus, it has the same role as pressure but not exactly equal to pressure. It is rather called corrected pressure in real system.

Fugacity is related with the pressure by the relation, $(f / P) = \gamma$, called fugacity coefficient.

Fugacity and pressure of a real gas

When, $\gamma = 1$, $f = P$, and the system is ideal. When $\gamma \neq 1$, $f \neq P$, the gas is not ideal.

Departure of the value of γ from unity measures the extent of non-ideality of the gas.

Fugacity of a gas is measured by the relation $\ln \gamma = \dfrac{BP}{RT}$

where, B is the 2nd virial coefficient of the gas.

For vander Waals gas, $B = \dfrac{1}{RT}\left(b - \dfrac{a}{RT}\right)$. Thus, $\gamma = e^{BP/RT} \quad$ or, $\quad f = P\,e^{BP/RT}$.

For mixture, the ith component will have $\quad \mu_i = \mu_i^0 + RT \ln f_i.$

Chemical potential in real condensed system (such as in solution)

The expression of chemical potential in the real condensed system is given as,

$$\mu_i\,(T, P) = \mu_i^0\,(T, P) + RT \ln a_i,$$

where, a_i = activity of the ith component in the mixture,

and, $a_i = x_i\,\gamma_i$ where, γ_i = activity coefficient of the ith component.

When, $\gamma_i = 1$, $a_i = x_i$, solution is ideal and when $\gamma_i \neq x_i$, solution is non-ideal.

$\mu_i^0\,(T, P)$ = standard chemical potential of the ith component

i.e. chemical potential of the pure ith component , i.e. $x_i \to 1$

Standard states in thermodynamics: For all states of aggregation (solid, liquid and gas), standard state is defined as the state of unit activity (a = 1).

For ideal gas, standard state is the state of unit pressure (1 atm, now 1 bar) at a specified temperature.

For real gas, it is the state of unit fugacity (f = 1) at a given temperature.

For liquid, standard state is the pure liquid at unit pressure at a given T.

For solid, it is the state of pure solid at unit pressure at the given T.

For ideal solution, the solvent's standard state is the pure solvent ($x_{solvsent} = 1$) at unit pressure (1 atm) at the given T and solute's standard state is at unit molar concentration.

For non-ideal solution, activity = 1 is taken the standard state at a given temperature.

Statement of the law	This law is derived from experience and states that
	
	    'Two systems that are each found to be in thermal equilibrium with third system will be found to be in thermal equilibrium with each other.'
	Or, in other words, it is,
	
	    'If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then A is also in thermal equilibrium with C'

Concept of temperature	Like as, systems in mechanical equilibrium have a common pressure, it seems possible that there is some thermodynamic property common to systems in thermal equilibrium.
	    This property, we call temperature (T).
	    Thus, two systems in thermal equilibrium have a common temperature.
	    But, when the systems are not in thermal equilibrium, they have different temperatures.
	Thus the zeroth law of thermodynamics can be illustrated in terms of temperature.
	Since A and B are each in thermal equilibrium with C, hence $T_A = T_C$ and $T_B = T_C$.
	Then T_A must be equal to T_B, and A and B are in thermal equilibrium. This means that if A and B are brought in contact to each other via conducting wire, there will be no flow of heat.
	    This law is formulated after the 1st and 2nd law of thermodynamics.
	Moreover, a statement of the zeroth law logically precedes the other three, hence it is the zeroth law.
	This law allows us to define the concept of temperature as a thermodynamic state function.

Measurement of temperature	To measure temperature of a system, we use commonly liquid mercury thermometer that is kept in contact with the system. The volume change of the mercury is noted when it becomes in equilibrium with the system. This volume change gives the reading of temperature from the scale of the thermometer.
Set-up of temperature scale	To set up a temperature scale, we need a reference system (r) which, we call thermometer. We choose the reference system to be homogeneous with fixed composition and a fixed pressure. Further we require that the substance inside the thermometer (called thermometric substance) must always expand when heated. This requirement ensures that at a fixed pressure, volume always increases with temperature (say linearly). This is why, liquid water is not suitable since it contracts at temperature below 4°C and expand above 4°C when heated at one atmosphere pressure.
Formulation of the scale	We can thus define temperature as $T = Q\,V_r + R$, where V_r is the volume of fixed amount of liquid mercury at 1 atm and Q, R are constants, with P being (+)ve. Once Q and R are specified, a measurement of volume (V_r) can give temperature T.
Description of the thermometer	The mercury in thermometer is kept in a glass container that consists of a bulb and narrow capillary tube. Let the area of cross section of the tube is 'a', then, $$T = Q\,V_r + R = Q\,(V_{bulb} + al) + R = (Q\,a)\,l + (Q\,V_{bulb} + R)\ \ \text{or},\ T = S\,l + A$$ where, S and A are constants for the thermometer. To fix S and A, we define temperature of equilibrium between pure ice and air saturated liquid water at 1 atm pressure as 0°C and we define temperature of equilibrium between pure liquid water and water vapor at 1 atm pressure as 100°C. These points are called ice point and steam point. Since our scale is linear with the length of the mercury column, we mark off 100 equal intervals between 0°C and 100°C. We can extend the marks above and below these temperatures.
Reading of temperature in the thermometer	Now having this thermometer with us, we can determine the temperature of any system B. To do so, we put system B in contact with the thermometer through a thermally conducting wall, wait until thermal equilibrium is reached and then read the thermometer's temperature from the

graduated scale. Since B is in thermal equilibrium with thermometer, B's temperature equals that of thermometer.

Arbitrary way of formulating the temperature scale	It is to be noted that how the arbitrary way the thermometer scale is defined. This scale depends on the expansion of mercury liquid. If we take ethanol as thermometric substance, then expansion of ethanol can be taken to measure the temperature. But these two thermometers would show little bit different temperature when used to record the temperature of the substance. Further, apart from simplicity, there is no other reason to choose linear relationship T and l. Since temperature is a fundamental concept so it should be less arbitrary. This can be obtained when ideal gas is proposed in absolute scale.
Common points of using different thermometric substances	If the systems A and B have same temperature ($T_A = T_B$), i.e. they are in thermal equilibrium and B and C have different temperatures ($T_B \neq T_C$), then although the numerical values of the temperature in the two thermometers, based on liquid mercury and liquid ethanol, may be different yet A and B have same temperature and B and C have different temperatures in both the thermometer. Other properties utilized in measuring temperature: Electrical resistance, light emission of hot bodies can be used to measure the temperature of a system.

Mathematical interlude:

Some simple calculi are often used in thermodynamical treatments. A prior familiarity with these would be helpful.

(1) Partial derivatives: Let a quantity z is a function of two independent variables of x and y. That is , z = f (x, y). If the coordinates x, y change by very small amounts dx and dy, then the

change in the value of z is given by $dz = \left(\dfrac{\partial z}{\partial x}\right)_y dx + \left(\dfrac{\partial z}{\partial y}\right)_x dy$ ---------- (1)

where, $\left(\dfrac{\partial z}{\partial x}\right)_y$ is the change of z for unit change of x at constant y. Similarly, $\left(\dfrac{\partial z}{\partial y}\right)_x$ is the

change of z for unit change of y when x remains constant. The subscript x and y indicate the constancy during the change of the others.

Let us suppose the three quantities x , y and z are related as f (x , y, z) = 0, then we have $x = \psi$ (y, z) and y = φ (z, x), then we can write,

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \text{ ------- (2)}$$

and $dy = \left(\dfrac{\partial y}{\partial z}\right)_x dz + \left(\dfrac{\partial y}{\partial x}\right)_z dx$ ------------- (3). Substituting equation (3) in (2) we get,

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial y}{\partial x}\right)_z dx\right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Or, $dx = \left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial x}\right)_z dx + \left[\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x + \left(\dfrac{\partial x}{\partial z}\right)_y\right] dz$ ------- (4)

Now the equation (4) is generally true for all values of x , y and z
Let us consider x and y as independent variables so that dx and dz may have any value.

(a) Let us suppose dz = 0 but d$x \neq 0$,

Two important deductions

then, $dx = \left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial x}\right)_z dx$ or, $\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial x}\right)_z = 1$ or, $\left(\dfrac{\partial x}{\partial y}\right)_z = \dfrac{1}{\left(\dfrac{\partial y}{\partial x}\right)_z}$ ------------- (5)

(b) Let us take dz $\neq$ 0 but dx = 0, then $\left[\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x + \left(\dfrac{\partial x}{\partial z}\right)_y\right] = 0$

or, $\left[\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x = -\left(\dfrac{\partial x}{\partial z}\right)_y\right]$. But, $\left(\dfrac{\partial x}{\partial z}\right)_y = \dfrac{1}{\left(\dfrac{\partial z}{\partial x}\right)_y}$,

hence $\left[\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x \left(\dfrac{\partial z}{\partial x}\right)_y\right] = -1$ --------- (6)

One proof of the equation

The ideal gas equation PV = RT may be used to prove the relation.

Here, f (P, V, T) = 0 and $\left(\dfrac{\partial P}{\partial V}\right)_T = -\dfrac{RT}{V^2}$, $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P}$ and $\left(\dfrac{\partial T}{\partial P}\right)_V = \dfrac{V}{R}$. Thus,

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = \left(-\frac{RT}{V^2}\right)\left(\frac{R}{P}\right)\left(\frac{V}{R}\right) = -\frac{RT}{PV} = -1 \, .$$

So,
$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

This is called cyclic rule.

Perfect differentials:

Let us consider a quantity z whose value is determined solely by two other variables x and y at any moment in any given state. That is, if x and y are given a particular value, the value if z is thereby fixed. If x and y vary, then z will also vary. Thus x and y are called independent variables while z is dependent variable. Thus z is also a single-valued quantity. dz is called perfect or complete or exact differential. Mathematically, we say, z = f (x, y)

The change in z can be estimated provided the derivative of the function z with respect to x and y are known. The derivative is the rate of change of dependent variable (z) with the independent variable (x or y). Thus,

$\left(\dfrac{\partial z}{\partial x}\right)_y$ = Rate of change of z with x at const. y and $\left(\dfrac{\partial z}{\partial y}\right)_x$ = Rate of change of z with y at

constant, x

Therefore, the change of z for change of x at constant y is equal to the rate of change of z with

x at constant y multiplied by dx i.e. dz = $\left(\dfrac{\partial z}{\partial x}\right)_y$ dx and dz = $\left(\dfrac{\partial z}{\partial y}\right)_x$ dy.

But if both x and y are changed simultaneously, then the total change

dz = $\left(\dfrac{\partial z}{\partial x}\right)_y$ dx + $\left(\dfrac{\partial z}{\partial y}\right)_x$ dy.

This is called total differential of the function z. To make the meaning of the exact differential clear, let us represent graphically the variables x and y along two axes right angles.

At point P, the value of z is z_1 and it is determined by the variables x and y.

At the point Q, the magnitude of z is z_2 and it is determined by (x' and y').

Then, dz = z_2 - z_1 will always have the same value determined by x, y, x' and y'.

dz is perfect differential and dz is independent of the path of transformation. It is obvious that if a change from P to Q is brought about by the path (I) and reverse change is effected by path (II),the magnitude of z will come back to the same value, defined by x and y at P. Hence for a complete cyclic process of change reverting to the original state

$\sum \Delta z = 0$ or, $\oint dz = 0$. In another way, it is possible to show that if dz is perfectly

differential, then, $\dfrac{\partial^2 z}{\partial x \partial y} = \dfrac{\partial^2 z}{\partial y \partial x}$.

This is called Euler's reciprocal theorem.