Module-2

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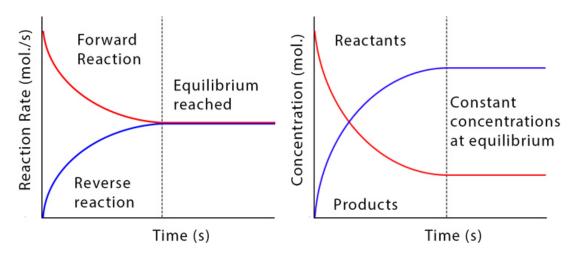
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What is Chemical Equilibrium?

- Chemical equilibrium refers to the state of a system in which the reactant and the products' concentration do not change with time.
- ✤ The system does not display any further change in properties.
- When the rate of the forward reaction is equal to the rate of the reverse reaction, the state of chemical equilibrium is achieved by the system.

Relationship b/w Rate of Reaction with Time and Concentration



<u>Types of Che. Eq</u>: I. Homogeneous Equilibrium, and

II. Heterogeneous Eq.

Type-I: In this type, the reactants and the products of che. Eq. are all in the same phase.

H₂ (g) + I₂ (g) \rightleftharpoons 2HI (g) N₂ (g) + O₂ (g) \rightleftharpoons 2NO (g) 2SO₂ (g) + O₂ (g) \rightleftharpoons 2SO₃ (g) COCl₂ (g) \rightleftharpoons CO (g) + Cl₂ (g)

Type-II:

In this type, the reactants and the products of chemical equilibrium are present in different phases.

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

$$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$$

Factors Affecting Chemical Equilibrium: Le-Chatelier's Principle

When a system under chemical equilibrium is subjected to any change in the factors affecting the equilibrium conditions, the system counteracts or nullifies the effect of the overall transformation.

- This principle applies to both chemical and physical equilibrium.
- Several factors such as temperature, pressure, and concentration of the system affect equilibrium.

i. Change in Concentration

When the concentration of reactants is lowered at equilibrium, the reaction proceeds in the backward direction so as to maintain equal concentration of reactants and products, and vice versa.

ii. Change in Pressure

Change in pressure happens due to the change in the volume. If there is a change in pressure, it can affect the gaseous reaction as the total number of gaseous reactants and products are now different.

According to Le-Chatelier's principle, in heterogeneous chemical equilibrium, the change of pressure in both liquids and solids can be ignored because the volume is independent of pressure.

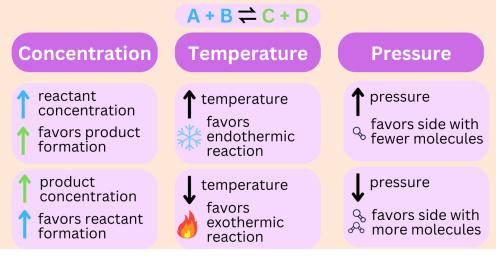
On the other hand, when pressure increases equilibrium shifts towards lesser volume (gaseous molecules).

iii. Change in Temperature

The effect of temperature on chemical equilibrium depends upon the sign of ΔH of the reaction. As temperature increases, the equilibrium constant of an exothermic reaction decreases whereas that of an endothermic reaction increases.

Le Chatelier's Principle

Disturbing a system at dynamic equilibrium shifts the equilibrium in the direction that counteracts the change.



iv. Effect of a Catalyst

A catalyst does not affect the chemical equilibrium; it only speeds up a reaction. In fact, the catalyst equally speeds up the forward as well as the reverse reaction. This results in the reaction reaching its equilibrium faster. The same amount of reactants and products will be present at equilibrium in a catalyzed or non-catalyzed reaction. The presence of a catalyst only facilitates the reaction to proceed through a lower-energy transition state of reactants to products.

v. Effect of Addition of an Inert Gas

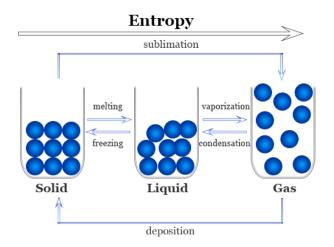
When an inert gas is added to a constant volume, it does not take part in the reaction, so the equilibrium remains undisturbed.

Importance of Chemical Equilibrium: It is useful in many industrial processes, like

- Preparation of Ammonia by Haber's process: In this process, nitrogen combines with hydrogen to form ammonia. The yield of ammonia is higher at low temperatures, high pressure, and in the presence of iron as a catalyst. N₂ (g) + 3H₂ (g) → 2NH₃ (g) + ▲H (-92 kJ/mol at 298 K, Exothermic rxn.).
- **Preparation of Fuming Sulfuric acid (Oleum, H₂S₂O₇) by Contact process:** In this process, the fundamental reaction is the oxidation of sulfur dioxide into sulfur trioxide. This involves chemical equilibrium.

Entropy (S): Classically, it is defined as the measure of randomness or disorder of a thermodynamic system. Qualitatively, entropy is simply a measure of how much the energy of atoms and molecules spreads out in a process. The SI unit of entropy is J.K⁻¹.mol⁻¹.

Example: A campfire is an example of entropy. The solid wood burns and becomes ash, smoke, and gases, all of which spread energy outwards more easily than the solid fuel.



Characteristics of entropy:

- The value of entropy is dependent upon the amount of substance present in the system. Entropy is therefore an extensive property.
- All spontaneous transformations in an isolated system proceed in the direction of increasing entropy. Entropy order: Gas > Liquid > Solids
- Ice melting, salt or sugar dissolving, and boiling water are processes with increasing entropy.
- In a chemical reaction if reactants break into more products, entropy is increased.
- A system at higher temperatures has greater randomness than a system at a lower temperature.

From the above discussion, it is clear that entropy increases with a decrease in regularity.

Determination of Entropy Change

Change in entropy is defined as the amount of heat emitted or absorbed isothermally and reversibly divided by the temperature. The entropy change during the isothermal reversible expansion of an ideal gas is given as follows:

$$\Delta S = \frac{q_{\rm rev,iso}}{T}$$

If we add the same quantity of heat at a higher temperature and a lower temperature, randomness will be maximum at a lower temperature. Hence, it suggests that temperature is inversely proportional to entropy.

> Total entropy change, $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

If the system loses an amount of heat q at a temperature T_1 , which is received by surroundings at a temperature T_2 .

$$\Delta S_{system} = -\frac{q}{T_1}$$
$$\Delta S_{surroundings} = \frac{q}{T_2}$$

$$\Delta S_{total} = -\frac{q}{T_1} + \frac{q}{T_2}$$

- If ΔS_{total} is positive, the process is spontaneous $(T_1 > T_2)$.
- If ΔS_{total} is negative, the process is non-spontaneous ($T_1 < T_2$).
- If ΔS_{total} is zero, the process is at equilibrium $(T_1 = T_2)$.
- Points to Remember: A spontaneous process is thermodynamically irreversible.
- For a given physical process, the entropy of the system and the environment will remain constant if the process can be reversed.

According to the first law of thermodynamics,

$$\Delta \boldsymbol{U} = \boldsymbol{q} - \boldsymbol{w}$$

Where ΔU is the change in internal energy, q is the heat added to the system and w is the work done by the system. In thermodynamics, the work done by a system is negative. This is because work done by a system uses energy and causes the system to lose energy.

For the isothermal expansion of an ideal gas, $\Delta U = 0$

$$\Rightarrow q_{rev} = -w_{rev} = nRTln(V_2/V_1)$$
$$\Rightarrow \Delta S = nRln(V_2/V_1)$$

Therefore,

Reversible isothermal expansion: At a constant temperature, the pressure decreases while the volume increases. The work done for an isothermal reversible expansion is

$$W = -nRT \ln(V2/V1)$$

Entropy Change During Reversible Adiabatic Expansion

For an adiabatic process, heat exchange will be zero (q = 0); therefore, reversible adiabatic expansion takes place at a constant entropy (**isentropic**),

Therefore,

However, the irreversible adiabatic expansion is not isentropic, i.e. $\Delta S \neq 0$.

Note:

- > Entropy increases when a solid changes to a liquid and a liquid changes into gases.
- Entropy also increases when the number of moles of gaseous products increases more than the reactants.

Some things are contrary to expectations about entropy.

A hard-boiled egg has greater entropy than an unboiled egg. It is due to the denaturation of the secondary structure of the protein (albumin). Protein changes from the helical structure into a randomly coiled form.

$$\Delta S = 0$$

If we stretch a rubber band, entropy decreases because macromolecules get uncoiled and arranged in a more ordered manner. Therefore, randomness will decrease.

Laws of thermodynamics

First Law of Thermodynamics: [Heat Transfer]

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

First Law of Thermodynamics: [Conservation of energy]

It states that heat is a form of energy. Thermodynamic processes therefore obey the principle of **conservation of energy**. This means that heat energy can be neither created nor destroyed. It can however be transferred from one place to another and converted to and from other forms of energy.

Second Law of Thermodynamics: [Concept of Entropy]

According to the concepts of entropy and spontaneity, the second law of thermodynamics has a number of definitions.

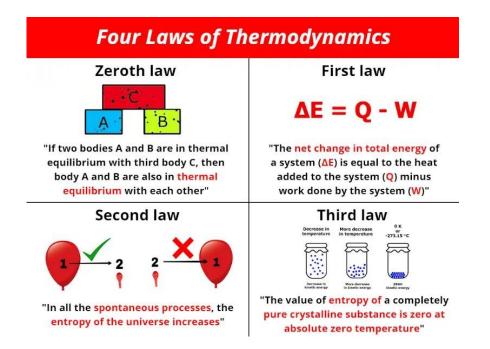
- > All naturally occurring spontaneous processes are thermodynamically irreversible.
- Complete transmission of heat into work is thermodynamically not feasible without the wastage of a certain amount of energy.
- > The entropy of the universe is continuously increasing.
- Total entropy change is always positive. The entropy of a system plus the entropy of its surroundings will be greater than zero.

$$\Delta S_{total} = (\Delta S_{system} + \Delta S_{surroundings}) > 0$$

Third Law of Thermodynamics: [Correlation b/w Crystallinity and Entropy]

The entropy of any crystalline solid approaches zero as the temperature approaches absolute temperature (0 K= -273.15 °C). It is because there is a perfect order in a crystal at absolute zero.

However, the limitation of this law is that many solids do not have zero entropy even at absolute zero. For example, a glassy solid and a solid containing a mixture of isotopes.



Entropy Changes During Phase Transition

Entropy of Fusion: It is the increase in entropy when a solid melts into a liquid. The entropy increases as the freedom of movement of molecules increases with phase change.

The entropy of fusion is equal to the enthalpy of fusion divided by the melting point (fusion temperature).

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{fus}}$$

A natural process (Spontaneous process) such as a phase transition (viz. fusion) will occur when the associated change in the Gibbs free energy is negative.

Entropy of Vaporization: The entropy of vaporization is a state when there is an increase in entropy as liquid changes into a vapour. This is due to an increase in molecular movement, which creates a randomness of motion.

The entropy of vaporization is equal to the enthalpy of vaporization divided by boiling point.

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}}$$

Standard Entropy of Formation of a Compound: It is the entropy change that takes place when one mole of a compound in the standard state is formed from the constituent elements in the standard state (1 bar, 298 K).

Criteria of Spontaneity Relating to Entropy of Chemical Equilibrium:

• Exothermic reactions are spontaneous because $\Delta S_{surrounding}$ is positive, which makes ΔS_{total} positive.

• Endothermic reactions are spontaneous because ΔS_{system} is positive and $\Delta S_{surrounding}$ is negative, but overall ΔS_{total} is positive.

• Free energy change criteria for predicting spontaneity is better than entropy change criteria because the former requires only free energy change of the system, whereas the latter needs entropy change of both system and surroundings.

Negentropy: It is the reverse of entropy. It means things becoming more in order. By 'order', it means organization, structure, and function. It is the opposite of randomness or chaos.

One example of negentropy is a star system such as a solar system.

Solved Questions

1. The entropy of an isolated system can never _____.

a) increase b) decrease c) be zero d) none of the mentioned

Explanation: The entropy of an isolated system always increases and remains constant only when the process is reversible.

2. Entropy may decrease locally in some regions within the isolated system. How can this statement be justified?

- a) This cannot be possible.
- b) This is possible because the entropy of an isolated system can decrease.
- c) It must be compensated by a greater increase of entropy somewhere within the system.

d) None of the above.

Explanation: The net effect of an irreversible process is an entropy increase in the whole system.

3. Clausius summarized the first and second laws of thermodynamics as _____.

a) The energy of the world is constant

b) The entropy of the world tends towards a maximum

c) Both of the above

d) None of the above

4. The entropy of an isolated system always _____ and becomes a _____ at the state of equilibrium.

a) decreases, minimum b) increases, maximum c) increases, minimum d) decreases, maximum

Entropy as Disorder

Even though there are many new and different interpretations of entropy, in general, it is defined as a measure of disorder and chaos. Chaos, as such, is the state of a physical or dynamic system wherein elements of all types are mixed evenly throughout the space, and so it becomes homogeneous.

Q1. Why is entropy constant at the triple point of water?

The triple point defines a situation of simultaneous equilibrium between the solid, liquid, and gas phases. The entropy of the gas phase is higher than the entropy of the liquid phase. Molecules in both the gas and liquids are less ordered than that of the ice state. Therefore, the extent of disorder caused by gases and liquids is compensated by the more ordered ice form resulting in no change in entropy of the system, three-phase equilibria.

Q2. Does freezing increase entropy?

Water has a greater entropy than ice, and so entropy favours melting. Freezing is an exothermic process; energy is lost from the water and dissipated to the surroundings. Therefore, as the surroundings get hotter, they gain more energy, and thus the entropy of the surroundings increases.

Q3. Can entropy ever decrease?

It just says that the total entropy of the universe can never decrease. Entropy can decrease somewhere, provided it increases somewhere else by at least as much. The entropy of a system decreases only when it interacts with some other system whose entropy increases in the process. That is the law.

Q4. Can entropy be infinite?

Since no finite system can have an infinite number of microstates, it is impossible for the entropy of the system to be infinite. In fact, entropy tends towards finite maximum values as a system approaches equilibrium.

Q5. What causes entropy?

Several factors affect the amount of entropy in a system. If you increase temperature, you increase entropy.

More energy put into a system excites the molecules and the amount of random activity.

As the gas expands in a system, entropy increases.

Gibb's Free Energy:

The Gibbs free energy change is the maximum amount of non-volume expansion work that can be extracted from a closed system at fixed temperature and pressure. This maximum can be attained only in a completely reversible process. Here, a close system means the system that can exchange heat and work with its surroundings, but not matter.

$$G(p,T) = U + pV - TS = H - TS$$
$$\Delta G = \Delta H - T\Delta S$$

Where p is pressure, T is the temperature, U is the internal energy, V is volume, H is the enthalpy, and S is the entropy.

If the reactants and products are all in their thermodynamic standard states, the defining equation is written as:

$$\Delta \boldsymbol{G}^{\circ} = \Delta \boldsymbol{H}^{\circ} - \boldsymbol{T} \Delta \boldsymbol{S}^{\circ}$$

	∆H <o< th=""><th>∠H > O</th></o<>	∠H > O
<u> </u>	spontaneous at all T (GG<0)	Spontaneous at high T (when TAS is large)
72×0	Spontaneous at low T (when TDS is small)	Non-spontaneous at all T (AG>O)

Gibbs-Helmholtz Equation: When temperature and pressure are the independent variables, the Gibbs free energy is the change criterion that takes the form:

$$dG = VdP - SdT$$

In chemical applications, temperature and pressure are often the most convenient choice of independent variables, making the Gibbs free energy a particularly useful function.

The Gibbs free energy of the system does not change when the system goes from one equilibrium state to another at the same temperature and pressure, $dG_{P,T} = 0$.

Consider a system that undergoes some arbitrary change from a state A, in which its Gibbs free energy is G_A to a second state B, in which its Gibbs free energy is G_B .

In general, $G_A \neq G_B$, since in the most general case, the pressures and temperatures of states A and B are different. (For example, state A might be a mole of ice at -10 °C and 0.5 bar, while state B is a mole of water at +10 °C and 2.0 bar.

Either of these states can be converted to the other; however, they are not at equilibrium with one another, and their Gibbs free energies are not equal.) Representing the pressures and temperatures as P_1 , T_1 , P_2 , T_2 , we can express the Gibbs free energies of these two states as $G_A = G_A(P_1, T_1)$ and $G_B = G_B(P_2, T_2)$, respectively. The difference is the change in the Gibbs free energy when the system passes from state A to state B:

$$\Delta G_{AB} = G_B(P_2, T_2) - G_A(P_1, T_1)$$

Similar considerations apply to expressing differences between the enthalpies and the entropies of two states that are available to a system. The Gibbs free energy is defined by

$$G = H - TS$$

When we are interested in a process that converts some state A to a second state B at constant pressure and temperature, $\Delta G = \Delta H - T\Delta S$, which relies on the context for the information about the pressure and temperature and the initial and final states. To explicitly denote that the change is one that occurs at a constant temperature, T0

, we can write

 $\Delta G(T0) = \Delta H(T0) - T0\Delta S(T0).$

Frequently we are interested in the way that ΔG

, ΔH

, and ΔS

vary with temperature at constant pressure. If we know how G

, H

, and S

vary with temperature for each of the two states of interest, we can find the temperature dependence of ΔG

, ΔH

, and ΔS

. The Gibbs-Helmholtz equation is a frequently useful expression of the temperature dependence of G

or ΔG

. Since it is a mathematical consequence of our thermodynamic relationships, we derive it here.

At constant pressure, the temperature derivative of the Gibbs free energy is

$$(\frac{\partial G}{\partial T})_P = -S$$

Using this result and the definition, G=H-TS, we obtain the temperature dependence of G as

$$(\partial G \partial T)P = G - HT$$

However, the Gibbs-Helmholtz equation can be expressed most compactly as the temperature derivative of G/T

. As a matter of calculus, we have

 $(\partial (G/T)\partial T)P = -GT2 + 1T(\partial G\partial T)P$

Using the relationships above, this becomes

 $(\partial (G/T)\partial T)P = -H + TST2 + ST = -HT2$

Since $\triangle ABG=GB+GA$

, we have

 $(\partial \Delta ABG/\partial T)P = -(SB+SA) = -\Delta ABS$

and

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(\partial(\Delta ABG/T)\partial T)P = (\partial(GB/T)\partial T)P + (\partial(GA/T)\partial T)P = -(HBT2 + HAT2) = -\Delta ABHT2 (The Gibbs-Helmholtz equation)
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If we know the temperature dependence of ΔS

or ΔH

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, we can find the temperature dependence of \Delta G
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by integrating the relationships above. That is, given ΔG

at T1

, we can find $\ \Delta G$

at T2

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. Thus, from (\partial G/\partial T)P=-S
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, we have

$$\int \Delta G(T2) \Delta G(T1) (\partial \Delta G \partial T) P dT = \Delta G(T2) - \Delta G(T1) = -\int T2T1 \Delta S dT$$

and from $(\partial (\Delta G/T)/\partial T)P = -\Delta H/T2$

, we have

$$\int \Delta G(T2)/T2\Delta G(T1)/T1(\partial (\Delta G/T)\partial T)PdT = \Delta G(T2)T2 - \Delta G(T1)T1 = -\int T2T1\Delta HT2dT$$

For small temperature differences, ΔH

is often approximately constant. Then, we can evaluate the change in ΔG from

$$\Delta G(T2)T2 - \Delta G(T1)T1 = \Delta H(1T2 + 1T1)$$

Another common application arises when we know ΔG

at several temperatures. A plot of $\Delta G/T$

versus 1/T

is then approximately linear with a slope that approximates the average value of ΔH

in the temperature interval.

Internal energy: This is the energy contained within a system due to the random motion of its particles. It includes the potential and kinetic energies of the molecules. The energy due to random motion includes Translational energy, Rotational energy, and Vibrational energy.

The value of internal energy depends on the state of the substance and not on the nature of the processes by which it attained that state. An increase in temperature for a material means an increase in its internal energy.

The internal energy formula for an ideal gas is: $U = C_v T$

$$\Delta U = C_v \Delta T$$

Where C_v is the specific heat at constant volume and ΔT is a change in temperature. Specific heat is the amount of heat required to raise the temperature of one gram of a substance by one degree Celsius (Joules.Gram⁻¹.Celsius⁻¹).

The main difference between enthalpy and internal energy is that enthalpy is the heat absorbed or evolved during chemical reactions that occur in a system whereas internal energy is the sum of potential and kinetic energy in a system.

Van't Hoff Equation: This concerns how the equilibrium constant (K_{eq}) changes with the change in temperature.

Derivation of Van't Hoff equation: Consider a chemical equilibrium, $aA + bB \Rightarrow cC + dD$

The derivation of the Van't Hoff equation starts from the following Gibbs-Helmholtz free energy relationship with Equilibrium constant:

$$\Rightarrow \Delta G^{\circ} = - RT \ln K \rightarrow (i)$$

 $\Rightarrow lnK = -\Delta G^{\circ}/RT \rightarrow (ii)$

Differentiating the equation (ii) with temperature, we get:

$$\Rightarrow dlnK/dT = - 1/R d((\Delta G^{\circ}/T)/dT)$$

It is rearranged into the following:

$$\Rightarrow d(\Delta G^{\circ}/T)/dT = -R\frac{dlnK}{dT} \rightarrow (iii)$$

Using the other expression of Gibbs free energy and enthalpy relationship, the Gibbs-Helmholtz equation, and rearranging, we get:

$$\Rightarrow \Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$
$$\Rightarrow \frac{\Delta G^{\circ}}{T} = \frac{\Delta H^{\circ}}{T} - \Delta S^{\circ} \rightarrow (iv)$$

Differentiating the equation (iv) with temperature, we get:

$$\Rightarrow d(\Delta G^{\circ}/T)/dT = -\Delta H^{\circ}/T^2 \rightarrow (v)$$

On combining Eqn. (iii) and (v), we get:

$$\Rightarrow R dlnK/dT = \Delta H^{\circ}/T^{2}$$

It rearranged into the following equation,

 $\Rightarrow d(lnK)/dT = \Delta H^{\circ}/T^{2}$

This Equation (vi) is known as the Van't Hoff Differential equation.

The integrated form of the Van't Hoff equation:

Van't Hoff Differential equation can be written in the following form:

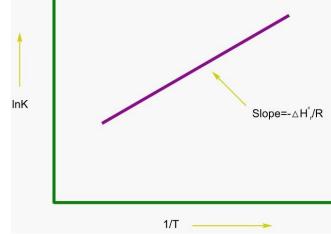
$$\Rightarrow dlnK = \Delta H^{\circ}/RT^{2} \times dT$$

By integrating the above equation w.r.t T, we get:

$$\Rightarrow lnK = -\Delta H^{\circ}/RT + I \quad \rightarrow \quad (vii)$$

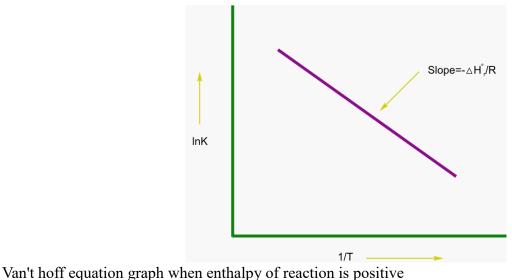
This Equation (vii) is known as the Van't Hoff Integrated equation. Where I, = constant of integration = Y-intercept, is obtained from the plot of lnK versus 1/T. Here, the slope is equal to $-\Delta H^{o}/R$. Based on the nature of a reaction whether endothermic or exothermic reaction, the enthalpy and therefore the nature of curve cum slope may change.

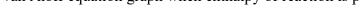
Case-I: The plot of lnK versus 1/T when ΔH° is negative.



Vant hoff equation graph when enthalpy of reaction is negative

Case-II: The plot of lnK versus 1/T when ΔH° is positive.





Application of the Van't Hoff equation:

- 1. For an endothermic reaction: For the endothermic reaction $\Delta H^{\circ} > 0$. Therefore, the righthand side of the equation is positive. Hence, 'lnK' increases with increasing temperature.
- 2. For exothermic reactions: For the exothermic reaction $\Delta H^{\circ} < 0$. Therefore, the right-hand side of the equation is negative. Therefore, lnK decreases with increasing temperature.

Is Van't Hoff factor always 1?

The Van't Hoff factor for the non-ionizing molecule is one. However, for the ionic compound, the value of Van't Hoff factor equals the number of ions that dissociate.

How do you determine Van't Hoff?

The Van'T Hoff factor can be determined by the values of calculated molar mass and experimentally observed molar mass,

What is Vant Hoff's rule of N?

The N is the number of ions produced by the complete dissociation of one mole of the substance.

What is meant by Van't Hoff's rule?

Van't Hoff's rule states that any change in temperature shifts the equilibrium in that direction which nullifies its effect.

Which has the highest Van t Hoff factor?

The aluminum sulfate $Al_2(SO_4)_3$ has the highest value of the Vant't Hoff factor.

What is the van 't Hoff factor of H₂O?

Although water undergoes self-ionization, but is dissociation is very weak. Therefore, it has a value of Van't Hoff factor one.

What is Van't Hoff isotherm?

According to Van't Hoff isotherm, at the constant temperature the osmotic pressure of the liquid is inversely proportional to the volume.