

Relation between Equilibrium constant and thermodynamic Properties:-

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The equilibrium constant of a chemical reaction is the value of its reaction quotient at chemical equilibrium, a state approached by a dynamic chemical system after sufficient time which its composition has no measurable tendency towards further change. For a given set of reaction conditions the equilibrium constant is independent of the initial analytical concentrations of the reactants and products species in the mixture. Thus given the initial composition of the system, known equilibrium constant values can be used to determine the composition of the system at equilibrium. However reaction parameters like temp., solvent and ionic strength may all influence the value of the equilibrium constant.

generally enthalpy will change with temperature: $\left(\frac{\partial H}{\partial T}\right)_p = C_p$

Where C_p is the heat capacity at constant pressure.

Pressure dependence:-

The pressure dependence of the equilibrium constant is usually weak in the range of pressures normally encountered in industry and therefore it is usually neglected in practice

Effect of isotopic substitution:-

Isotopic substitution can lead to change in the value of equilibrium constants especially if hydrogen is replaced of deuterium or tritium. This equilibrium isotope effect is analogous to the kinetic isotope effect on rate constants and is primarily due to the change in zero point vibrational energy of H-X bonds due to the change in mass upon isotopic substitution.

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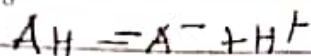
Rates are equal to each other.

water as both reactants and solvent —

For reaction in aqueous solution such as an acid dissociation reaction.



The concentration of water may be taken as being constant and formation of the hydronium ion is implicit.



water concentration is omitted from expressions defining equilibrium constants except when solutions are very concentrated.

$$K = \frac{[A][H]}{[AH]} \quad (K \text{ is defined as dissociation constant.})$$

Enthalpy and entropy, temperature dependence —

If both the equilibrium constant K and the standard enthalpy change ΔH° for a reaction have been determined, the standard entropy for the reaction is easily derived.

$$\text{Since } \Delta G = \Delta H - T\Delta S$$

$$\text{and } \Delta G = -RT \ln K$$

$$\Delta S^\circ = \frac{\Delta H^\circ + RT \ln K}{T}$$

Standard thermodynamic argument can be used to show that more

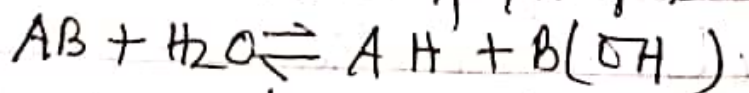
Thermodynamic equilibrium is characterised by the free energy for the whole (closed) system being a minimum. For a system at constant temperature and pressure the Gibbs free energy is minimum. The slope of the reaction free energy with respect to the reaction coordinate ξ is zero when the energy is at minimum value $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$

A general chemical equilibrium can be written as $\sum_j n_j \text{Reactant}_j \rightleftharpoons \sum_k m_k \text{Product}_k$

where n_j are the stoichiometric coefficient of the reactants in the equilibrium equation.

Equivalence of thermodynamic and kinetic expressions for equilibrium constants —

At equilibrium the rate of forward reaction is equal to the backward reaction rate. A simple reaction ~~such~~ such as ester hydrolysis



has reaction rates given by the expressions —

$$\text{Forward rate} = k_f [AB] [H_2O]$$

$$\text{Backward rate} = k_b [AH] [B(OH)]$$

According to Guldberg and Waage, equilibrium is attained when the forward and backward reaction