

We Hear From

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Uniqueness of Equilibrium: Nature's Choice as against Perpetual Motion

Our concept of equilibrium comes from the observed phenomenon that a system may sometime reach a stable static state (a balanced state of a body acted upon by several forces) or a stable dynamic state (for example, the dynamic equilibrium state in a chemical reaction where forward and backward rates are equal) that renders the system completely reluctant for any further change on its own, and remains invariant at this state with any further passage of time until the applied forces or other driving factors are changed. Various thermodynamic functions, usually Gibbs energy G and Helmholtz energy A have been successfully used to describe the equilibrium behaviour of a system. Theoretical analysis of gaseous reactions reveals that the equilibrium state is unique for an appropriately specified set of final restrictions on the system, and is independent of the path of attaining the equilibrium.

The equilibrium constant K of a chemical reaction depends only on temperature and is given by $\Delta_{\text{reaction}}G^\circ = -RT\ln K$. The equilibrium composition or state of a system with a known initial or intermediate composition depends on the constraints that prevail on the final state. The value of K can be determined from the activities or fugacities of the reactants and products of an equilibrium mixture at the concerned temperature. For ideal behaviour of gaseous systems, fugacities are equal to the partial

pressures of the respective species. At constant temperature and volume, let us consider a different state point, i.e. a point away from equilibrium. The mass balance requires that any increase or decrease in the values of the partial pressures of the products is accompanied by a calculable amount of decrease or increase of the partial pressures of the reactants. Hence the reaction quotient Q at any nonequilibrium point, defined as $Q = \prod(p_j)^{v_j} / \prod(p_i)^{v_i}$, will be different from K . Q corresponds to K at equilibrium. Π represents a multiplication of the partial pressures of the products or reactants, each raised to the power of stoichiometric coefficient of the concerned species. I and J represent the reactants and products respectively, p_i and p_j are partial pressures of I and J , and v_i and v_j are stoichiometric coefficients of I and J . K is a thermodynamically derived constant which precisely defines the point of equilibrium relevant to the prevailing situation. So, the point of equilibrium of a reaction at some specified conditions is unique, as Q differs from K at any other point.

To be more rigorous, we consider n identical systems, each follows a different path to its equilibrium state in a manner that some (presently two) of the state variables – pressure and temperature, temperature and volume, or pressure and volume – are same in all the equilibrium states. Notably, any set of these two variables forms a minimal basis for systems

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with constant composition or chemically inert systems. For a given initial composition of a reactive system, the variation of composition is a function of the extent of further reaction, and the value of equilibrium constant determines the ultimate extent of reaction. Also, equilibrium constant is a function of temperature only, then a most obvious statement for reactive systems is that the act of specifying the final temperature and another variable out of pressure and volume at equilibrium, does also take care of composition and the remaining variable – pressure or volume – at equilibrium. Equivalently, in the absence of any irreversible parallel reaction, the above observation amounts to the unequivocal acceptance of the path-independence of a chemical equilibrium.

On the contrary, if the equilibrium state would have depended on the method of preparing it, then what surprise (!) it could offer us? To decide it, we consider any two systems out of n systems in which composition and another variable – volume or pressure – are presumed to differ at equilibrium. One system, say the first one, is richer in products than in the second system. We know that attainment of equilibrium is a spontaneous process and can be reached from either direction (forward as well as backward), and allows us to perform some work whose maximum value equals the decrease in the concerned thermodynamic potential –

the Gibbs energy. Now we add a little portion of the first system to the second system. The resulting compositional imbalance in the second system will drive it to return back to its previous equilibrium, and at the same time it will allow us to perform some work. Now we return back an equivalent amount of the mixture from the second to the first system. It will now create a compositional imbalance in the first system, and restoring of its equilibrium will allow us to perform some more work. Repeating the cycle as many times as we like, the two-system device or machine will allow us to produce any amount of work we like without spending energy, or we would have created a perpetual motion machine of first kind! However such a thing never happens in nature and is thermodynamically forbidden. After all, the thermodynamic laws are based on observation of nature. So the assumption of two distinct equilibria for a chemical reaction is absurd. The uniqueness of a chemical equilibrium is essentially a choice of nature and does not depend anyway on the path of its attainment. Similar reasoning may also be extended to other systems. Thus the equilibrium state of a system subjected to a specified set of final restrictions is unique, otherwise it would be enough to violate conservation of energy, which never happens in nature nor is expected to happen in future.

Greek Alphabet

α alpha	η eta	ν nu	τ tau
β beta	θ theta	ξ xi	υ upsilon
γ gamma	ι iota	\omicron omicron	ϕ phi
δ delta	κ kappa	π pi	χ chi
ϵ epsilon	λ lambda	ρ rho	ψ psi
ζ zeta	μ mu	σ sigma	ω omega