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Thermodynamic Equilibrium

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Abstract: The arguments in this paper lead to a new definition of thermodynamic equilibrium that remedies the deficiencies of the current forms. This definition relates thermodynamic equilibrium to its physical causes and accounts for all factors that determine it for all types of equilibrium. Standard definitions of thermodynamic equilibrium are incomplete. They do not take account of all factors that determine such equilibriums, discuss the impediments which may prevent them being reached or relate the properties that define equilibriums to the physical reasons that determine them when impediments are present. The laws of thermodynamics determine the requirements for equilibrium. These laws arise from the physical behaviour of the molecules in molecular systems and are consequences of the conservation of energy, the energies of molecules, statistics, Newton's laws of motion, and the equi-partition of energy. The standard definition of thermodynamic equilibrium correctly defines equilibrium whenever impediments are not factors. The discussion demonstrates how impediments arise, accounts for their role in defining equilibrium and how they relate to the energies of molecules at the conditions of the system. The new definition applies to all types of equilibrium.

Key words: Thermodynamics, equilibrium, statistical mechanics.

1. Introduction

The definition of thermodynamic equilibrium is a basic concept in chemistry for all theories and measurements. Yet there is no single definition of it which is applicable to all equilibriums [1-3]. The two current definitions cannot account for all factors determining equilibrium nor do they relate thermodynamic equilibrium to the physical reasons that determine it.

The arguments in this paper show there is a single definition of thermodynamic equilibrium applicable to all molecular systems that takes account of all factors determining equilibrium. They explain why the standard definition, in terms of the minimum in the Gibbs function and constant conditions of temperature, pressure and composition, is incomplete and accounts for the additional factors that often determine equilibrium that are ignored. It also relates those properties to the molecular behaviour that gives rise to them.

The arguments presented here are suitable only for more advanced courses as they involve the Gibbs function. Lack of space precludes discussion of how they can be simplified for elementary courses.

2. The Laws of Thermodynamics and Equilibrium

The thermodynamic properties of a system at equilibrium, containing a mole of molecules, are determined by its temperature, pressure and composition. The molecules are distributed over a range of energy states described by the MBD (Maxwell Boltzmann distribution) [1]. The average values calculated from the MBD for the temperature and pressure have precise values because their standard deviations, σ, calculated from the MBD have small values ca. 10^{-10}. Hill [4] showed values of σ for the average energy vary with the inverse square of Avogadro's number, $N^{-0.5}$; the large value of N, 6 × 10^{23}, explains why the value of σ is so small.

The absolute temperature is defined in terms of the kinetic energy of helium molecules and measured by the pressure generated by that kinetic energy.

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Consequently all molecules have kinetic energy at temperatures above 0° K.

It is easy to show that the temperature and pressure of a system must be equal to those of the surroundings. At equilibrium there is no nett transfer of energy and the average kinetic energy of the system and the surroundings, and hence the temperatures, must be equal. Similarly the pressures must be equal and opposite to satisfy Newton's third law.

All other properties involve the conservation of energy in interchanges of work and energy. They are determined by the laws of thermodynamics which govern the conditions for equilibrium. These laws arise as the result of five factors: the energies of molecules, the conservation of energy, which governs the conversion of work and energy, statistics, Newton's laws of motion, and the equi-partition of energy as the discussion below demonstrates.

The first and second laws are complex because they involve kinetic energy and other forms of energy. The third law is easiest to define because molecular systems have no kinetic energy at 0° K.

The third law is: At 0° K the molecules of a system are at their rest positions in a crystalline state which maximise their mutual interactions, the system cannot do work and the entropy is zero.

That the entropy is zero at 0° K follows from the definition of entropy [1], $\sum p_i \log(p_i)$, in terms of p_i, the probabilities of the molecules with energies u_i. At 0° K the values of p_i are one at the rest positions of the molecules and zero elsewhere; hence all the products $p_i \log(p_i)$, and the entropy, are zero.

The first law states that heat supplied to a system produces a change in energy and work is done. From the definition of work, as a force times distance, a system in a cylinder with a moveable piston (area A) at constant pressure will do work given by PΔV; the force is the pressure times A which moves the piston a distance l and Al is the increase in volume, ΔV. The pressure arises from Newton's second law applied to the momentum of each individual molecule but it requires the statistical behaviour of the system to convert these collisions into a force that does work.

This leads to the definition of H, the enthalpy [1].

$$H = U + PV \qquad (1)$$

The differences, ΔH, for changes at constant pressure include the work term PΔV automatically, so ΔH is the heat supplied to the system at constant pressure. For molecules to produce a force that does work, the molecules must move which is why the kinetic energy is the prime means by which systems do work. The relationship between P, V and T for a system determines the amount of work. The actual work done depends on the pressure of the surroundings during a change and is a maximum for a reversible change, where the pressure of the surroundings is infinitesimally less than that of the system as it changes between states.

Molecules have three basic forms of energy. Electrons in molecules interact with electrons in other molecules to produce attractive and repulsive forces between them that depend on the distance between them. The electrons have electronic energy levels in the molecules and can absorb or emit energy through changing their energy states in the molecule or in reactions that transfer or share electrons in new bonds. The third form of energy is kinetic energy due to their motion which is the major way in which energy is converted into work.

The energy levels for kinetic energy are so closely spaced that they can be treated as continuous. The number of molecules with energy u_i is n_i. Nothing prevents the changes in n_i occurring which are needed to adjust to new conditions, and with momenta of all molecules contributing to pressure, they occur quickly. Hence the pressure responds quickly to changes, even with non-uniform temperatures, as a system changes between states. That systems always do work in a change at constant pressure explains the first law.

The second law must be stated using the conservation of energy, relating work and energy. Its restatement leads directly to the definition of the

Gibbs function, G. The minimum of G at equilibrium follows from the third law defined above. The second law always involves the conversion of energy into work so must be discussed using the enthalpy as that includes a term that reflects the conversion of energy into work at constant pressure. The alternative definition of molar energy, U, defined at constant volume, excludes conversion of energy into work.

As the kinetic energies of ideal gases define the international temperature scale, all substances have kinetic energies above 0° K. For gases, kinetic energy takes the form of motion via the velocity plus rotational and vibrational energies. Liquids and solids are restricted to vibrational and rotational motion, which limits the work done by these systems. Equipartition of energy ensures each mode of motion has same amount of energy.

The second law is:

$$\text{Enthalpy} = \text{Enthalpy convertible to work} + \text{Enthalpy not convertible to work} \quad (2)$$

Re-arranging, leads to G as the enthalpy convertible to work:

$$\text{G} = \text{Enthalpy} - \text{Enthalpy not convertible to Work} \quad (3)$$

The MBD, where n_i molecules have energy u_i, determines the behaviour of molecular systems. It was Boltzmann's insight that the log of the most probable distribution of energies defines the entropy, S:

$$\text{S}/k = \log(\text{W}) \quad (4)$$

W is the number of ways of arranging molecules n_i in energy levels u_i and k is Boltzmann's constant. Finding the maximum value of W in Eq. (4) when the system has an energy U leads to the MBD. The percentage of molecules in the MBD is unknown and the values of properties obtained from it are estimates from a representative sample of the total system. The central limit theorem shows that for any percentage in the MBD between 1% and 50% the values of obtained from the MBD represent the entire system within the precision of the corresponding MBD standard deviation [5].

Algebraic manipulation of Eq. (4) and the addition of the PV term leads to the Gibbs function, G:

$$\text{G} = \text{H} - \text{TS} \quad (5)$$

G is the enthalpy convertible to work and is the maximum amount of work that the system could do if returned reversibly to 0° K. This is the physical reason G is a minimum at equilibrium. For equilibrium at temperature, T, U is the minimum energy that is consistent with the kinetic energy that the system has at that temperature. TS is the energy not convertible to work.

That G is a minimum at fixed temperature and pressure is a necessary but not a sufficient condition for equilibrium. The requirements that temperatures and pressure must be uniform and the amount of energy convertible to work must be a maximum is the physical reason that the Gibbs function is a minimum. When the maximum amount of a chemical reaction has occurred also this ensures the resulting state is a global minimum. Otherwise, depending on the extent of the reaction a local minimum in the Gibb function results.

3. The Means of Attaining Equilibrium

Molecular systems change between equilibrium states by a series of steps where they are not at equilibrium unless the path is reversible. For all other pathways the energy distributions of the molecules are unknown. The changes in molecular systems that occur are caused by molecules with appropriate energies and momentums able to contribute to them. All changes occur at a molecular level by collisions between molecules involving transfers of energy via either elastic collisions or with transfer or exchange of electrons in chemical reactions. The number of molecules that contribute to the transfers determines the rates of changes of energies between molecules. The maximum rate is when all the molecules contribute; when an insufficient number of molecules contribute the change ceases or does not occur.

For chemical reactions the process of reaction by which they occur is called "mechanism". This term covers the collisions of the reacting molecules and the transfers or exchange of electrons which occur in the reactions. Elastic collisions are the corresponding process for physical processes for changes in the equilibrium of a molecular system without any reaction. These types of collision are the means by energy changes occur.

It seems easier to redefine the meaning of "mechanism" by its effect rather than its cause, including all processes that transfer energies for both chemical reactions and physical changes. The term "mechanism" is defined as any process by which a molecular system can reach a thermodynamic equilibrium where the molecules have an MBD and the Gibbs function is a minimum. It includes all experimental methods designed to promote equilibrium.

Mechanisms can be divided into molecular mechanisms and macroscopic changes. Molecular mechanisms operate at the molecular level via collisions. Macroscopic processes enable a large number of molecules to take part in molecular processes so that the molecular system may reach an MBD of energies. This category includes all experimental techniques promoting equilibrium and any process that enables large number of molecules to exchange energies such as stirring or convection currents.

It remains to identify which molecules can contribute to changes between equilibrium states and what impediments may prevent the changes occurring successfully.

4. Active Molecules and Impediments

Collisions of molecules are always involved in transfers of energy. In the absence of an energy barrier preventing a change, all molecular systems with a fixed temperature pressure and composition, will always reach the minimum of the Gibbs function at those conditions. When there is an energy barrier present it will form part of the definition of equilibrium if there insufficient molecules with energies greater than that of the barrier. Where there are enough molecules with energies greater than that of the barrier the change will occur at a lower rate.

Energy barriers that impede energy transfers arise within and between molecules. For chemical reactions activation energies, due to mutual repulsions of electrons, are the cause. For physical interactions there are no barriers to collisions if the mean free paths of molecules in the system are greater than the diameter of the largest molecule involved. Where the mean free path is less the diameter of the largest molecule taking part in the change there will be an energy barrier due to the physical presence and interactions of the molecules impeding the change. Both these types of barriers are non thermodynamic and unmeasured.

The contributing molecules depend not just on the energy barrier and the MBD but also the numbers of each type of molecule involved in the change. The discussion in the preceding paper [6] of flammability limits makes this clear and so involves the composition of the mixture in the definition of equilibrium. Only experimental measurements can show whether, at given conditions, there are enough molecules with energies contributing to a change for it to occur.

The molecules contributing to a change, in general, have kinetic energies greater than the average kinetic energy at the temperature of the system and there have to be enough of them for it to occur. The mathematics of the MBD governs the distribution of kinetic energies of the molecules about u_a, the average molecular energy, which is 1.5 kT for an ideal gas. The value of σ for the MBD of an ideal gas is also u_a and, using the central limit theorem and the ND (normal distribution), this shows ~ 2.5% molecules have energies $> 2\,u_a$. It is not possible to say what percentage molecules is enough for a change to occur but the discussion in Ref. [5] suggests it is of the order of 1-3%. It is clear that all reactions cease when a flammability limit, or its equivalent, is reached.

The presence of multiple energy barriers inhibiting systems from reaching either a global or a local minimum also explains why painstaking experimental methods are needed to measure accurately the equilibrium properties of molecular systems.

5. A New Definition of Thermodynamic Equilibrium

This discussion leads to a new definition of thermodynamic equilibrium which restates that given in Ref. [5]: A molecular system at equilibrium has constant and uniform temperature, pressure composition and MBD, the Gibbs function is a minimum, and mechanisms for reaching and maintaining that equilibrium.

The possible outcomes are:

Option 1: Enough molecules with sufficient energy for a change to proceed

Option 2: Insufficient molecules with enough energy for a change to proceed and it ceases or does not start.

The equilibrium is not fully defined until the option which applies to the system at the current conditions is specified. Standard definitions assume Option 1 applies to all equilibriums and omit Option 2. The third option in Ref. [5] establishes the basic model for equilibrium but is not needed to define equilibrium.

This definition differs from that in Ref. [5] in the meaning of "mechanisms". Here it means any process that assists in reaching equilibrium; previously it referred to chemical reactions. No general statement can be made as to which option applies to the state of a molecular system at a particular temperature pressure and composition. This is because defining the state of the system in terms of the minimum of the Gibbs function, temperature pressure and composition does not specify all the factors determining all equilibriums.

6. Conclusions

This new definition applies to all types of thermodynamic equilibrium. It explains the following aspects of equilibrium that standard definitions cannot account for:

(1) It explains how and why changes occur and why they may not occur.

(2) It correctly predicts outcomes for all reactions.

(3) It predicts only thermodynamic equilibrium states that can be reached.

(4) It caters for the sustainability of reactions.

(5) It accounts for all factors that determine equilibrium.

(6) It takes account of the surroundings in determining the equilibrium.

(7) It explains the connection between the standard definitions of thermodynamic equilibrium.

For systems at a global minimum in the Gibbs function the standard definition is correct because they are fully defined. For other systems further information is needed to decide which option applies at each condition before thermodynamic equilibrium is fully specified. Reactions in closed molecular systems generally terminate in a state defined by Option 2.

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