Review on Chemical equilibrium as a balance of thermodynamics forces

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ABSTRACT:

This study is done to justify how Chemical Equilibrium is acting as a balance of Thermodynamic forces and for that various parameters related to equilibrium and thermodynamics have been discussed which are concepts of chemical transformations , Le- Chatilier's Principle , linear equations of irreversible thermodynamics, internal and external thermodynamics forces , concepts of non-equilibrium, basics of stoichiometry and De Donder's definition of thermodynamic forces. The relations between all these parameters have been carried out step by step in this article. Also some of the basic concepts related to some thermodynamic forces have been used here. In this article we are checking how different concepts of the field of science are having their impact on the thermodynamic forces.

INTRODUCTION:

We deal with many scientific phenomena in our day to day life and it is the matter of fact that how our each and every action is having impact on something and due to that many changes occur in our life and we may admire those changes. Same is the fact with the chemical engineering, each and every fact that we are studying are not only theoretical but having their own significances in the physical world also. Every single second some reaction is going on in the nature that we are unaware of. Some internal and external forces are working simultaneously. When these forces work then they are not only creating or absorbing energies but they are creating a balance in nature. When we talk about balance then only one thing comes to in our mind as a chemical scholar is chemical equilibrium. We are familiar with this term from our school days itself. In this article we are dealing with the same things. We are trying to study that how different-different concept are having their impacts on the internal and external forces of the systems whether it is closed or open and how we are going to find the proper values.

These concepts or u can say phenomena are something which cannot be neglected as a scholar but every single thing is causing some big transformations. And again these chemical transformation leads to drastic changes. That is why it is necessity to be familiar to understand all these to understand the deep core chemistry which will open a new world of science.

DEFINITIONS:

CHEMICAL EQUILIBRIUM:

The state at which the rate of forward reaction becomes equal to the rate of backward reactions. Chemical equilibrium is considered as an equilibrium in motion i.e. it is dynamic in nature. The reason behind this nature is that doesn't matter if the process seems to be still or static but the backward and forward reactions will take place inside it.
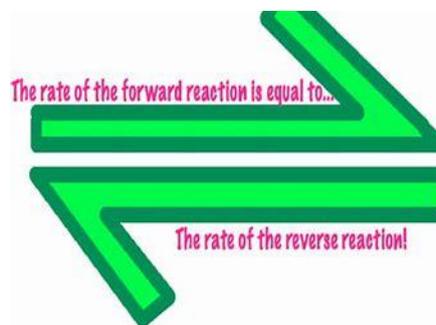
THERMODYNAMIC FORCES:

Also called as thermodynamic driving forces. These kinds of forces occur due to potential differences and its direction is the maximal decrease in μi.

i= flow component cause by X (where X may be any thermodynamic parameter).

LINEAR EQUATIONS OF IRREVERSIBLE THERMODYNAMICS:

These are conservation equations. We are studying macroscopic evolution of densities of conserved variables such as mass, energy and momentum. The macroscopic equations of motion for the conserved quantities are called as the Navier Stokes equation. This concept can be understood by this simple mass conservation derivation:

$$M = \int_v dr\rho(r,t)$$

$\rho(r,t)$ is the mass density at position r and time t

$$\frac{dm}{dt} = -\int_s ds.\rho(r,t).u(r,t)$$

$$= -\int_v dr\, \nabla[\rho(r,t)u(r,t)]$$

∇= spatial gradient vector operator

$$\frac{dM}{dt} = \int_v \frac{dr\partial\rho(r,t)}{dt}$$

LE CHATILIER'S PRINCIPLE:

It is also known as the equilibrium law and it states that:

"*When a system at equilibrium is subjected to a change in temperature, volume, concentration or pressure, the system readjusts to partially counter the effect of the change, resulting in new equilibrium*"

ENERGY CHARACTERISTICS OF CHEMICAL TRANSFORMATIONS:

When new substances are formed after certain chemical reaction then either there is a release of energy or absorption of energy.

INTERNAL AND EXTERNAL ENERGY OF THERMODYNAMIC FORCES:

As the headline reads it is the internal energy of the system and it is represented by U and it has certain relation with the thermodynamic parameters which are Q and W

Q=Heat transferred to the system;

W=Work done by the system or on the system

And these parameters can be written in an equation as:

$$\Delta U = Q \pm W$$

Where ΔU=change in internal energy of the system.

Work done is referred as the external energy of the system.

NON-EQUILIBRIUM:

Where we counter lack of balance in the system then that state is referred to as the non-equilibrium state.
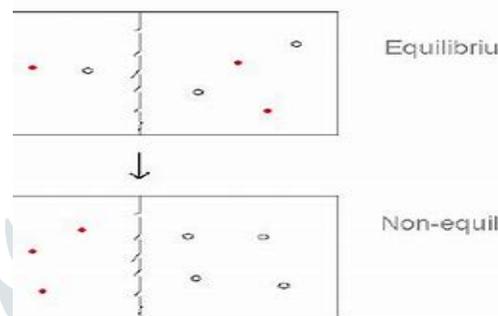
LAW OF STOICHIOMETRY:

We are already familiar with the basics of molarity and we are going to apply this concept know different parameters and one of which is the affinities.

$$\Delta n_a/v_a = \Delta n_b/v_b = \Delta n_c/v_c$$

$$n_{j=} \Delta n_{kj}/v_{kj}$$

Where n_j= homogenous equivalent of transformation.

Following these concepts De Donder introduced the reaction coordinate ξ_D in differential form.

$$d\xi_{D=} dn_{kj}/v_{kj}$$

we can rewrite this equation by using different reaction coordinate:

$$d\xi_{z=} dn_{kj}/v_{kj}$$

$\Delta \xi_z$= difference between running and initial values of the reaction coordinate and initially $\Delta \xi_z$ =0 and at thermodynamic equilibrium $\Delta \xi_z$=0

From the above concept we can jot them down in an equation as follows:

$$\delta \xi_z = 1 - \Delta \xi_z$$

Where δ is defined as the shift from equilibrium in finite decreases.

Shift sign is positive when the reaction does not reach TDE (Thermodynamic equilibrium) and the shift is negative if shifted beyond TDE initially $\delta\xi_z = 1$ and at TDE $\delta\xi_z = 0$

And we can further write the different reaction coordinates as follows:

$$\Delta\xi_z = {}^{\Delta\xi_D}/n_j$$

Thermodynamic force (TDF) as a moving power of chemical transformation was introduced by De Donder and he defined it as thermodynamic affinity

$$Aj = - (\Phi j/\xi j)x,y$$

Where Φj = enthalpy

x,y = any thermodynamic parameters

Aj = internal affinity/ eugenaffinity

And this affinity that we have derived the basic cause of chemical reactions. Affinity works as a force which is considered as the thermodynamic force itself that is why we need to be familiar with the concept of affinity.

PROPOSITION AND BASICS OF THE THEORY:

1. First we have to study the relation between the linear equations of non-equilibrium and affinities:
   For that we have certain equations to know the concept;
   $$v_j = a_{ji}A_{ji} + \sum a_{je}A_{je}$$
   Where A_{ji} = for internal thermodynamic force
       A_{je} = for external thermodynamic force
       j = system
       v_j = speed of chemical reaction
       a_{ji}, a_{je} = Onsager coefficients
   Where Onsager reciprocal relation is a relation that is not necessary for fulfilling the requirements of thermodynamics and completely out of thermodynamics.

   Where v_j=0 implies equilibrium is achieved i.e. equilibrium is maintained between the internal and external thermodynamic forces.
   So, we can rewrite the above equation as;
   $$A_{ji} + \sum a_{je}A_{je} = 0$$
2. To understand Le chatilier's principle we have to understand the relation between the reaction shift from TDE and external thermodynamic force (TDF)

$$\delta_j = -({}^1/\alpha_j)F_{je}$$

α_j = Proportionality coefficient, its SI unit is joules same as the energy

$-$ = decrease in the external TDF (F_{je})

F_{je} = its SI unit will be joules (J)

δ_j = it is dimensionless quantity and it is called as the shift

When the shift from TDE becomes equal to TDF i.e. at the state of equilibrium. This relation can be represented mathematically as:

$$\alpha_j \delta\xi_j^* = o_j A_{je}^*,$$

substituting this in the chemical equilibrium equation

$$A_{ji}^* = \left(\frac{\Delta \Phi_j}{\Delta_j}\right)^* x, y$$

*= it is just showing that the system is just in equilibrium

Multiplying both the sided by Δ_j we will get:

$$-\Delta \Phi_j^* (n_j, \delta_j^*) x, y - \alpha_j \delta_j^* \Delta_j^* = 0 \text{(basis for EOS at const. pressure and temperature)}$$

UNDERSTANDING THE CONCEPT OF EQUATION OF STATE AT CONSTANT PRESSURE AND TEMPERATURE:

For this we have to keep in mind the concept of Gibb's energy and for that also we have certain set of equation:

$$-\Delta G_j^* (n_j, \delta_j^*) x, y - \alpha_j \delta_j^* (1 - \delta_j^*) = 0$$

(this equation have been derived from the above equation itself)

And we have the standard mathematical representation for Gibb's energy as follows:

$$\Delta G = \Delta G^0 + RT \ln Q$$

Where ΔG = it is the free energy at any moment

$\quad \Delta G^0$ = standard free energy

$\quad$ R= molar constant and it values to 8.314 J/mol-K

Some conditions:

When $\delta_j^* = 0$, then $\Delta G^* = 0$

We can derive various other relation by either dividing or multiplying some of the parameters to ease our calculations.

THE DOMAIN STATES OF THE CHEMICAL SYSTEM:

Getting familiar with the terms that are we using is necessary:

τ_j = it is factor to control the evolution from total extinction and chaos and it is referred to as the reduced chaotic temperature.

The plot between the reduced the reduced chaotic temperature and the solution to equation, expressed in terms of δ_j^* is known as the bifurcation diagram and its value varies from 0 to 1, Also, we know that chemical equilibrium shows the shifts towards reactants or products and $\delta_j < 0$. To justify this statement the researchers have given a two-way bifurcation diagram as follows:
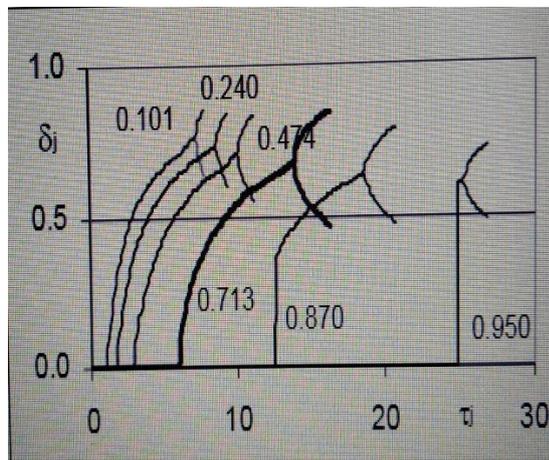
This figure shows the system domain of states, when $\delta_j^* = 0$ that means the equilibrium is maintained and when $\delta_j^* \neq 0$ that means at that condition only one solution exists and it is the state of open equilibrium.

Another concept is when the system is unstable the we obtained such kind of plot as follows:
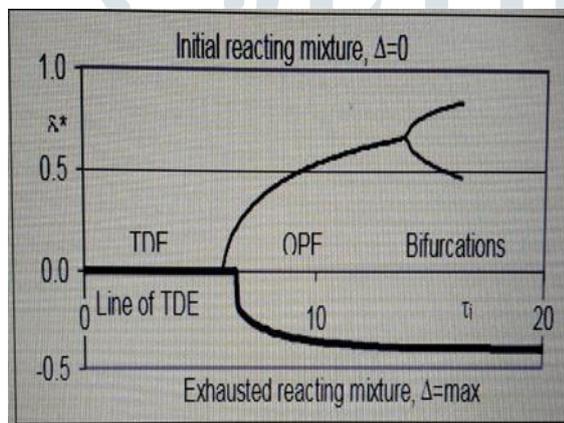
Two way bifurcation diagram of states, reaction at 373.15K

When the solution becomes unstable then we will have multiple values of the bifurcation region

To make our task less tedious we take some range i.e. the limits to get the approximate values an for this two way bifurcation diagram we are taking area limits from τ_{TDE}, τ_{OPE} & τ_{B2}

And value for this τ_{TDE} is 1 when n_j tends to 0.

These all are experimented by the researchers.

Result of the above theory:

The TDE area is not only a particular point but it is a stretched out region towards the open systems with $\tau_j > 1$, up to a certain critical value of the reduced chaotic temperature.
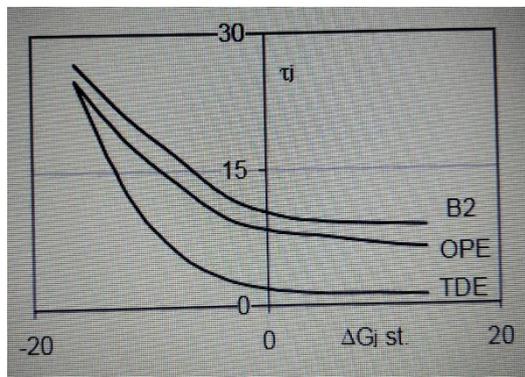
The area limits that we are taking to find out the regions.

THE PROOF OF THE THEORY PROPOSITION:

The reaction affinity reflects the external TDF (thermodynamic force) and this is proved by three different reactions just to show how it is actually behaving:

| A | B | C |
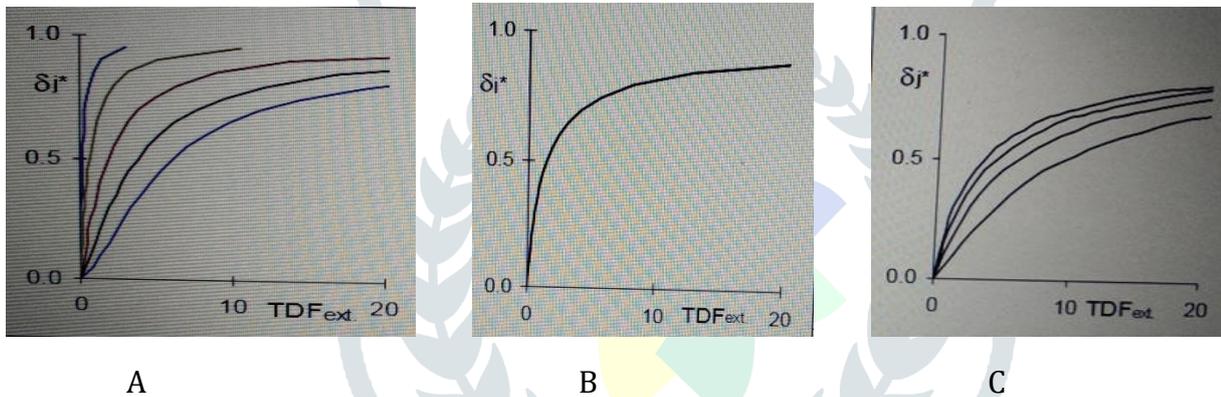
Shift of some simple chemical reactions from true equilibrium δ_j vs. dimensionless shifting force.

What each of them are for:

A= A+B=AB

B= A+2B=AB2

C= 2A+2B=A2B2
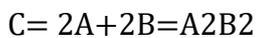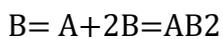
These different reactions will show different curve for TDF as $\tau_j \delta_j^*$ by varying n_j and δ_j and using the following equation:

$$F_{je}/_{RT} = \ln[k_j(n_j, 0)/k_j(n_j, \delta_j^*)]/\Delta_j^*$$

AREA LIMITS AND CHARACTERISTIC REDUCED CHAOTIC TEMPERATURE:

Area limits depends on from where the process has been initialized and up to what extent it has been carried out and here it in the theory it is governed by the initial composition and thermodynamic parameters and can be found by direct computer simulation.

But time consumption is more in doing simulation , so we prefer to avoid it and for that we should keep in mind the concepts of mathematical functions, logarithmic and parabolic equations because the

curves obtained by these have a great significance in the area or range related fields and after joining those curves we will find put a trivial solution (a point where all the three parameters meet.)

The curve should at least cut at two points so that number of roots obtained can be more than one because it will help us to verify the process properly whether it going correct or not.

When there is no intersection then the equation turns out to be

$$d(\tau\delta\Delta)/d\delta < d[\ln(k'/k^*]/d\delta$$

This condition leads to a universal formula to calculate TDE limit as

$$\tau_{TDE} = 1 + \eta_j \sum[\left.^{v_{kj}}\middle/(n_{kj}^0 - v_{kj}\eta_j)\right.$$

where n_{kj}^0 = initial amount and

v_{kj} = stoichiometric coefficient of k-participant in j-system

To find the limits let us take a simple reaction:

$$A+B=C$$

Each of the component is having 1,1 and 0 moles each then τ_{TDE} can be written as:

$$\tau_{TDE} = (1+\eta_i) / (1-\eta_j)$$

Where τ_{TDE} is obtained by iterative process which further depends on η_j

And we can write shift as a function depending on moles as follows:

$$\delta_{j(n-1)}^* = f(\delta_{jn}^*)$$

The value of limits of open equilibrium varies from -1 to +1 and its value can be derived by iterative calculations.

GIBB'S FREE ENERGY OF THE SYSTEM:

We will write the Gibb's free energy as a differential equation:

$$\frac{dG_j^*}{RT} = \frac{dG_{rj}}{RT} - \tau_j\delta_j d\Delta_j$$

Gibb's free energy is basically a thermodynamic potential which helps us to calculate the work done in the system and the work done may be on the system or by the system and by calculating the work done we can also calculate the force required to do that work which is further referred to as thermodynamic force.

In the above equation replace G/RT by G and $d\Delta_j$ by δ_j then we will get:

$$G^* = G_{rj}^* - \tau_j(\delta_j *)^{\wedge}2/2$$

Now we got the above equation behaving in the chemical equilibrium further if we want to reduced the Gibb's free energy than we can reduce it by RT also.

CONCLUSION:

from the above proofs and propositions, we conclude that chemical equilibrium is considered that chemical equilibrium is considered to be as a system where different reactions are taking place simultaneously which depends on the internal and external thermodynamic forces which we have discussed above. Here we used concepts of logarithmic, functions and parabolic equations. Also, we

discussed about quantities behaving simply as energies like affinity. We came to know about how we are finding the area limits using different plots like bifurcation diagram that we mentioned in different conditions i.e. stable and unstable equilibrium. We also related the concepts of the stoichiometry i.e. the concepts of moles and Gibb's free energy for that we have gone through many mathematical equations. We studied about the concept of non-equilibrium, took basis pf Le chatilier's principle and we also mentioned about the reduced chaotic temperature. Also , we discussed about the difference between the open equilibrium and closed equilibrium and how the reaction differs when there is a shifts due to chemical transformations.

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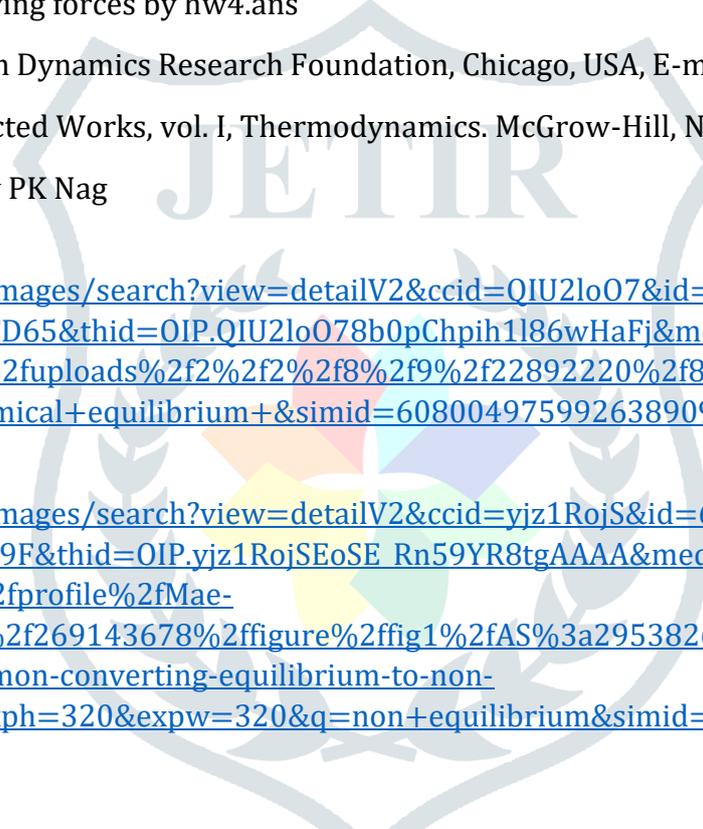
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