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# Thermodynamic chemical energy transfer mechanisms of non-equilibrium, quasi-equilibrium, and equilibrium chemical reactions

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ABSTRACT

Chemical energy transfer mechanisms at finite temperature are explored by a chemical energy transfer theory which is capable of investigating various chemical mechanisms of non-equilibrium, quasi-equilibrium, and equilibrium. Gibbs energy fluxes are obtained as a function of chemical potential, time, and displacement. Diffusion, convection, internal convection, and internal equilibrium chemical energy fluxes are demonstrated. The theory reveals that there are chemical energy flux gaps and broken discrete symmetries at the activation chemical potential, time, and displacement. The statistical, thermodynamic theory is the unification of diffusion and internal convection chemical reactions which reduces to the non-equilibrium generalization beyond the quasi-equilibrium theories of migration and diffusion processes. The relationship between kinetic theories of chemical and electrochemical reactions is also explored. The theory is applied to explore non-equilibrium chemical reactions as an illustration. Three variable separation constants indicate particle number constants and play key roles in describing the distinct chemical reaction mechanisms. The kinetics of chemical energy transfer accounts for the four control mechanisms of chemical reactions such as activation, concentration, transition, and film chemical reactions.

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## 1. Introduction

Energy transfer is a central process in the evolution of the universe, and one distinctive form of energy transfer is chemical energy transfer. Thermodynamics dealing with energy transfer and chemical energy transfer dealing with chemical reactions have various application areas in science and engineering. The coupled mechanisms of thermodynamic and chemical reactions are definitely demanded in diverse fields including phase transition, chemistry, electrochemistry, corrosion, thermal devices, microscopic organisms, physics, mechanical engineering, biology, and energy.

Extensive research has been conducted for developing a thermodynamic theory to describe chemical reaction processes. Existing theories of chemical kinetics include the Arrhenius equation, collision theory, potential energy surfaces, Gibbs flux formalism, Lagrangian formalism, and transition state theory [1–26]. Nevertheless, chemical reaction mechanisms are so complicated that their entire understanding in terms of existing theories [27–29] is not possible yet. The kinetics based on the conservation of mass or concentration provides only the information about the rate of chemical reactions and the rate constant. Their nominal forms also depend on the orders of chemical reactions [27–29]. The concentration equation for mass (or particle number) transfer [33] is useful in investigating particle diffusion:

$$\partial C/\partial t + v_a \cdot \nabla C = D_0 \nabla^2 C + C_i'. \tag{1}$$

Eq. (1) is closely related to chemical reactions when the internal generation $C_i'$ is taken into account. However, the precise form of the internal convective energy generation is not exactly clarified so far. The other existing theories for chemical reactions are established under the assumption of chemical equilibrium, so they cannot predict non-equilibrium chemical processes. Otherwise, they describe chemical reactions under some limited situations. For example, transition state theory assumes intermediate reaction states which are described by a statistical formalism, and then they are combined with the reaction equation, but their detailed dynamic properties are not given explicitly [10–12,27]. Therefore, a robust theory of chemical reactions should provide essential dynamic and static information about chemical reactions under a

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certain fundamental principle. We are here interested in a chemical energy transfer theory which are simultaneously capable of integrating thermodynamic, spatial, and temporal properties as well as describing non-equilibrium, quasi-equilibrium, and equilibrium processes.

An internal energy transfer theory [30] for thermodynamic non-equilibrium, quasi-equilibrium, and equilibrium has been proposed. The systematically unified transport theory is capable of producing the three energy transfer mechanisms of thermodynamics so that it estimates parameters in thermodynamic equilibrium and non-equilibrium states and clarifies the characteristics of transport processes [30–36]. The kinetic theory is also applicable to understanding the chemical energy transfer mechanisms in various chemical phenomena in nature.

We have furthermore proposed the statistical thermodynamic theory for electrochemical reactions [31,32] which is vital to examine both diffusive and internal convective electrochemical reactions. It is a transport theory for electrochemical reactions leading to the integration of diffusion and internal convection, a generalization beyond quasi-equilibrium theories for migration and diffusion, and the unification of internal equilibrium and equilibrium. The Nernst equation is derived from the internal convective and equilibrium processes, the time rate of electrochemical reactions is obtained, and the spatial cross section is gained from the kinetic theory.

In these contexts, we propose a chemical energy transfer theory for non-equilibrium, quasi-equilibrium, and equilibrium chemical energy as a special case of the internal energy transfer theory [30]. The theory is analogous to the statistical thermodynamic theory for electrochemical reactions [31,32]. It is able to probe internal convective chemical energy transfer in chemical reactions since it is a generalization beyond chemical energy transfer in quasi-equilibrium. It is thus a non-equilibrium extension beyond chemical equilibrium and quasi-equilibrium. It is based on the conservation of energy rather than the rate of chemical reactions based on the conservation of mass which the existing theories [27–29] depend on. The chemical transfer theory provides the chemical potential and spatial dependence in addition to the temporal dependence of chemical reactions. The theory is likewise competent to explore both dissociation and synthesis chemical reactions regardless of the molecularity of a chemical reaction.

In the chemical energy transfer theory, the Gibbs energy fluxes are described as a function of chemical potential, time, and displacement simultaneously under a postulate that chemical potential, time, and displacement are independent and orthogonal variables in extended phase spaces. This is the first rigorous microscopic kinetic theory for internal convective chemical energy transfer.

External convective energy transfer is formulated in addition to internal convective energy transfer. Moreover, the thermodynamic behavior of the equilibrium chemical process is clarified through the theory. A connection between a rate equation and a reaction quotient is also proved through the chemical energy transfer theory since they are dependent on both concentration and temperature.

Fig. 1 sketches the hierarchy for energy transfer which consists of heat, work, and chemical energy transfer [30–36]. Each energy transfer possesses three modes of conduction (or diffusion), convection, and radiation in addition to equilibrium. Aside from radiation, this paper concentrates on internal convection, conduction, internal equilibrium, and convection of chemical energy transfer to explore chemical reactions. Moreover, the statistical thermodynamic theory of electrochemical reactions is reviewed as a branch of the chemical energy transfer.

The objective of this paper is hence to establish a chemical energy transfer theory for chemical reactions and to apply the chemical energy transfer theory to examine various chemical reactions to clarify their features. The theory is utilized to examine chemical energy transfer mechanisms in equilibrium, quasi-equilibrium, and non-equilibrium. The chemical energy transfer theory can be applied to internal convective chemical processes at a solid–liquid boundary as its demonstration. Chemical energy flux profiles are predicted as a function of chemical potential, time, and distance. The four control regimes are also anticipated as a function of chemical potential, time, and distance in analogy with electrochemical reaction regimes: activation, concentration, transition, and film chemical reaction regimes.

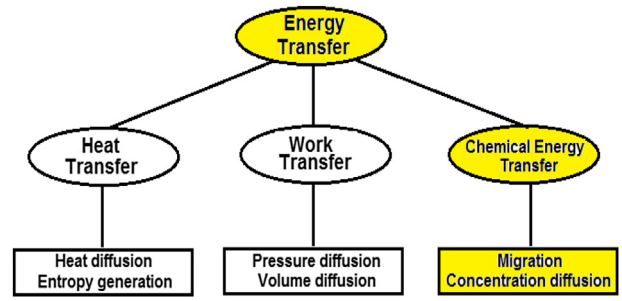


**Fig. 1.** Chemical energy transfer in the hierarchy for energy transfer mechanisms. Electrochemical energy transfer is considered as a branch of chemical energy transfer.

## 2. Internal energy transfer theory

The internal energy transfer theory [30] has been proposed for the transfer mechanisms of heat, work, and chemical energy. A total system containing reactants and products is thermodynamically isolated from its surroundings, and has thermodynamic energy transfer due to thermal, mechanical, and chemical non-equilibrium between reactants and products. The local thermodynamic non-equilibrium is characterized as the intensive variables of temperature, pressure, and chemical potential [37].

### 2.1. Motivation of internal energy transfer

Internal energy transfer theory is motivated from the thermodynamic point of view in which internal energy transfer depends on intensive state variables as well as extensive state variables. Internal energy transfer in a quasi-equilibrium (quasi-static) process is conventionally described only by extensive state variables, but internal energy in a non-equilibrium process can be stated by including intensive state variables. Here, the dependence of intensive state variables for internal energy transfer is discussed [30,31,33].

Euler's equation of thermodynamics for the internal energy is

$$U(T, S, P, V, \mu, N) = TS - PV + \mu N.$$

From Euler's equation, we have the first law of thermodynamics:

$$dU = \delta Q - \delta W + \delta G.$$

Rewriting the first law, we obtain

$$dU(T, S, P, V, \mu, N) = (TdS - PdV + \mu dN) + (SdT - VdP + Nd\mu) \quad (2)$$

where

$$\delta Q(T, S) = TdS + SdT,$$

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