



e-ISSN:2582 - 7219



# INTERNATIONAL JOURNAL OF MULTIDISCIPLINARY RESEARCH IN SCIENCE, ENGINEERING AND TECHNOLOGY

Volume 4, Issue 9, September 2021



INTERNATIONAL  
STANDARD  
SERIAL  
NUMBER  
INDIA

Impact Factor: 5.928



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# Chemical Thermodynamics-Interrelation of Heat and Work with Chemical Reactions

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**ABSTRACT:** Chemical thermodynamics is the study of the interrelation of heat and work with chemical reactions or with physical changes of state within the confines of the laws of thermodynamics. Chemical thermodynamics involves not only laboratory measurements of various thermodynamic properties, but also the application of mathematical methods to the study of chemical questions and the spontaneity of processes.

The structure of chemical thermodynamics is based on the first two laws of thermodynamics. Starting from the first and second laws of thermodynamics, four equations called the "fundamental equations of Gibbs" can be derived. From these four, a multitude of equations, relating the thermodynamic properties of the thermodynamic system can be derived using relatively simple mathematics. This outlines the mathematical framework of chemical thermodynamics.<sup>[1]</sup>

**KEYWORDS:** chemical thermodynamics, reactions, heat, laws, Gibbs", mathematics, spontaneity

## I. INTRODUCTION

In 1865, the German physicist Rudolf Clausius, in his Mechanical Theory of Heat, suggested that the principles of thermochemistry, e.g. the heat evolved in combustion reactions, could be applied to the principles of thermodynamics.<sup>[2]</sup> Building on the work of Clausius, between the years 1873-76 the American mathematical physicist Willard Gibbs published a series of three papers, the most famous one being the paper On the Equilibrium of Heterogeneous Substances. In these papers, Gibbs showed how the first two laws of thermodynamics could be measured graphically and mathematically to determine both the thermodynamic equilibrium of chemical reactions as well as their tendencies to occur or proceed. Gibbs' collection of papers provided the first unified body of thermodynamic theorems from the principles developed by others, such as Clausius and Sadi Carnot.<sup>1</sup>

During the early 20th century, two major publications successfully applied the principles developed by Gibbs to chemical processes and thus established the foundation of the science of chemical thermodynamics. The first was the 1923 textbook Thermodynamics and the Free Energy of Chemical Substances by Gilbert N. Lewis and Merle Randall. This book was responsible for supplanting the chemical affinity with the term free energy in the English-speaking world.<sup>2</sup> The second was the 1933 book Modern Thermodynamics by the methods of Willard Gibbs written by E. A. Guggenheim. In this manner, Lewis, Randall, and Guggenheim are considered as the founders of modern chemical thermodynamics because of the major contribution of these two books in unifying the application of thermodynamics to chemistry.<sup>[1]</sup>

The primary objective of chemical thermodynamics is the establishment of a criterion for determination of the feasibility or spontaneity of a given transformation.<sup>[3]</sup> In this manner, chemical thermodynamics is typically used to predict the energy exchanges that occur in the following processes:

1. Chemical reactions
2. Phase changes
3. The formation of solutions<sup>3</sup>

The following state functions are of primary concern in chemical thermodynamics:

- Internal energy (U)
- Enthalpy (H)
- Entropy (S)
- Gibbs free energy (G)



Most identities in chemical thermodynamics arise from application of the first and second laws of thermodynamics, particularly the law of conservation of energy, to these state functions.<sup>4</sup>

The 3 laws of thermodynamics (global, unspecific forms):

1. The energy of the universe is constant.
2. In any spontaneous process, there is always an increase in entropy of the universe.
3. The entropy of a perfect crystal (well ordered) at 0 Kelvin is zero.

Chemical energy is the energy that can be released when chemical substances undergo a transformation through a chemical reaction. Breaking and making chemical bonds involves energy release or uptake, often as heat that may be either absorbed by or evolved from the chemical system.<sup>5</sup>

Energy released (or absorbed) because of a reaction between chemical substances ("reactants") is equal to the difference between the energy content of the products and the reactants. This change in energy is called the change in internal energy of a chemical system.

The change in internal energy is equal to the heat change if it is measured under conditions of constant volume (at STP condition), as in a closed rigid container such as a bomb calorimeter. However, at constant pressure, as in reactions in vessels open to the atmosphere, the measured heat is usually not equal to the internal energy change, because pressure-volume work also releases or absorbs energy. (The heat change at constant pressure is called the enthalpy change; in this case the widely tabulated enthalpies of formation are used.)

A related term is the heat of combustion, which is the chemical energy released due to a combustion reaction and of interest in the study of fuels. Food is similar to hydrocarbon and carbohydrate fuels, and when it is oxidized, its energy release is similar (though assessed differently than for a hydrocarbon fuel — see food energy).<sup>6</sup>

In chemical thermodynamics, the term used for the chemical potential energy is chemical potential, and sometimes the Gibbs-Duhem equation is used.

In most cases of interest in chemical thermodynamics there are internal degrees of freedom and processes, such as chemical reactions and phase transitions, which create entropy in the universe unless they are at equilibrium or are maintained at a "running equilibrium" through "quasi-static" changes by being coupled to constraining devices, such as pistons or electrodes, to deliver and receive external work. Even for homogeneous "bulk" systems, the free-energy functions depend on the composition, as do all the extensive thermodynamic potentials, including the internal energy. If the quantities  $\{ N_i \}$ , the number of chemical species, are omitted from the formulae, it is impossible to describe compositional changes. While this formulation is mathematically defensible, it is not particularly transparent since one does not simply add or remove molecules from a system. There is always a process involved in changing the composition; e.g., a chemical reaction (or many), or movement of molecules from one phase (liquid) to another (gas or solid). We should find a notation which does not seem to imply that the amounts of the components ( $N_i$ ) can be changed independently. All real processes obey conservation of mass, and in addition, conservation of the numbers of atoms of each kind.<sup>7</sup>

In solution chemistry and biochemistry, the Gibbs free energy decrease ( $\partial G/\partial \xi$ , in molar units, denoted cryptically by  $\Delta G$ ) is commonly used as a surrogate for ( $-T$  times) the global entropy produced by spontaneous chemical reactions in situations where no work is being done; or at least no "useful" work; i.e., other than perhaps  $\pm P dV$ . The assertion that all spontaneous reactions have a negative  $\Delta G$  is merely a restatement of the second law of thermodynamics, giving it the physical dimensions of energy and somewhat obscuring its significance in terms of entropy. When no useful work is being done, it would be less misleading to use the Legendre transforms of the entropy appropriate for constant  $T$ , or for constant  $T$  and  $P$ , the Massieu functions  $-F/T$  and  $-G/T$ , respectively.<sup>8</sup>

## II. DISCUSSION

Generally the systems treated with the conventional chemical thermodynamics are either at equilibrium or near equilibrium. Ilya Prigogine developed the thermodynamic treatment of open systems that are far from equilibrium. In doing so he has discovered phenomena and structures of completely new and completely unexpected types. His generalized, nonlinear and irreversible thermodynamics has found surprising applications in a wide variety of fields.





The non-equilibrium thermodynamics has been applied for explaining how ordered structures e.g. the biological systems, can develop from disorder. Even if Onsager's relations are utilized, the classical principles of equilibrium in thermodynamics still show that linear systems close to equilibrium always develop into states of disorder which are stable to perturbations and cannot explain the occurrence of ordered structures.<sup>9</sup>

Prigogine called these systems dissipative systems, because they are formed and maintained by the dissipative processes which take place because of the exchange of energy between the system and its environment and because they disappear if that exchange ceases. They may be said to live in symbiosis with their environment.

The method which Prigogine used to study the stability of the dissipative structures to perturbations is of very great general interest. It makes it possible to study the most varied problems, such as city traffic problems, the stability of insect communities, the development of ordered biological structures and the growth of cancer cells to mention but a few examples.<sup>10</sup>

In this regard, it is crucial to understand the role of walls and other constraints, and the distinction between independent processes and coupling. Contrary to the clear implications of many reference sources, the previous analysis is not restricted to homogeneous, isotropic bulk systems which can deliver only PdV work to the outside world, but applies even to the most structured systems. There are complex systems with many chemical "reactions" going on at the same time, some of which are really only parts of the same, overall process. An independent process is one that could proceed even if all others were unaccountably stopped in their tracks. Understanding this is perhaps a "thought experiment" in chemical kinetics, but actual examples exist.

A gas-phase reaction at constant temperature and pressure which results in an increase in the number of molecules will lead to an increase in volume. Inside a cylinder closed with a piston, it can proceed only by doing work on the piston. The extent variable for the reaction can increase only if the piston moves out, and conversely if the piston is pushed inward, the reaction is driven backwards.<sup>11</sup>

Similarly, a redox reaction might occur in an electrochemical cell with the passage of current through a wire connecting the electrodes. The half-cell reactions at the electrodes are constrained if no current is allowed to flow. The current might be dissipated as Joule heating, or it might in turn run an electrical device like a motor doing mechanical work. An automobile lead-acid battery can be recharged, driving the chemical reaction backwards. In this case as well, the reaction is not an independent process. Some, perhaps most, of the Gibbs free energy of reaction may be delivered as external work.

The hydrolysis of ATP to ADP and phosphate can drive the force-times-distance work delivered by living muscles, and synthesis of ATP is in turn driven by a redox chain in mitochondria and chloroplasts, which involves the transport of ions across the membranes of these cellular organelles. The coupling of processes here, and in the previous examples, is often not complete. Gas can leak slowly past a piston, just as it can slowly leak out of a rubber balloon. Some reaction may occur in a battery even if no external current is flowing. There is usually a coupling coefficient, which may depend on relative rates, which determines what percentage of the driving free energy is turned into external work, or captured as "chemical work", a misnomer for the free energy of another chemical process.<sup>12</sup>

### III. RESULTS

Thermodynamic databases contain information about thermodynamic properties for substances, the most important being enthalpy, entropy, and Gibbs free energy. Numerical values of these thermodynamic properties are collected as tables or are calculated from thermodynamic datafiles. Data is expressed as temperature-dependent values for one mole of substance at the standard pressure of 101.325 kPa (1 atm), or 100 kPa (1 bar). Unfortunately, both of these definitions for the standard condition for pressure are in use. Thermodynamic data is usually presented as a table or chart of function values for one mole of a substance (or in the case of the steam tables, one kg). A thermodynamic datafile is a set of equation parameters from which the numerical data values can be calculated. Tables and datafiles are usually presented at a standard pressure of 1 bar or 1 atm, but in the case of steam and other industrially important gases, pressure may be included as a variable. Function values depend on the state of aggregation of the substance, which must be defined for the value to have any meaning. The state of aggregation for thermodynamic purposes is the standard state, sometimes called the reference state, and defined by specifying certain conditions. The normal standard state is commonly defined as the most stable physical form of the substance at the specified temperature and a pressure of 1 bar or 1 atm. However, since any non-normal condition could be chosen as a standard state, it must be defined in the context of use. A physical standard state is one that exists for a time sufficient to allow measurements of its properties. The most common physical standard state is one that is stable



thermodynamically (i.e., the normal one). It has no tendency to transform into any other physical state. If a substance can exist but is not thermodynamically stable (for example, a supercooled liquid), it is called a metastable state. A non-physical standard state is one whose properties are obtained by extrapolation from a physical state (for example, a solid superheated above the normal melting point, or an ideal gas at a condition where the real gas is non-ideal). Metastable liquids and solids are important because some substances can persist and be used in that state indefinitely. Thermodynamic functions that refer to conditions in the normal standard state are designated with a small superscript  $^{\circ}$ . The relationship between certain physical and thermodynamic properties may be described by an equation of state.<sup>13</sup>

It is very difficult to measure the absolute amount of any thermodynamic quantity involving the internal energy (e.g. enthalpy), since the internal energy of a substance can take many forms, each of which has its own typical temperature at which it begins to become important in thermodynamic reactions. It is therefore the change in these functions that is of most interest. The isobaric change in enthalpy  $H$  above the common reference temperature of 298.15 K (25  $^{\circ}\text{C}$ ) is called the high temperature heat content, the sensible heat, or the relative high-temperature enthalpy, and called henceforth the heat content. Different databases designate this term in different ways; for example  $H_T - H_{298}$ ,  $H^{\circ} - H^{\circ}_{298}$ ,  $H^{\circ}_T - H^{\circ}_{298}$  or  $H^{\circ} - H^{\circ}(T_r)$ , where  $T_r$  means the reference temperature (usually 298.15 K, but abbreviated in heat content symbols as 298). All of these terms mean the molar heat content for a substance in its normal standard state above a reference temperature of 298.15 K. Data for gases is for the hypothetical ideal gas at the designated standard pressure. The SI unit for enthalpy is J/mol, and is a positive number above the reference temperature. The heat content has been measured and tabulated for virtually all known substances, and is commonly expressed as a polynomial function of temperature. The heat content of an ideal gas is independent of pressure (or volume), but the heat content of real gases varies with pressure, hence the need to define the state for the gas (real or ideal) and the pressure. Note that for some thermodynamic databases such as for steam, the reference temperature is 273.15 K (0  $^{\circ}\text{C}$ ).<sup>14</sup>

When heat is added to a condensed-phase substance, its temperature increases until a phase change temperature is reached. With further addition of heat, the temperature remains constant while the phase transition takes place. The amount of substance that transforms is a function of the amount of heat added. After the transition is complete, adding more heat increases the temperature. In other words, the enthalpy of a substance changes isothermally as it undergoes a physical change. The enthalpy change resulting from a phase transition is designated  $\Delta H$ . There are four types of enthalpy changes resulting from a phase transition. To wit:

- Enthalpy of transformation. This applies to the transformations from one solid phase to another, such as the transformation from  $\alpha$ -Fe (bcc ferrite) to  $\gamma$ -Fe (fcc austenite). The transformation is designated  $\Delta H_{tr}$ .
- Enthalpy of fusion or melting. This applies to the transition of a solid to a liquid and is designated  $\Delta H_m$ .
- Enthalpy of vaporization. This applies to the transition of a liquid to a vapor and is designated  $\Delta H_v$ .
- Enthalpy of sublimation. This applies to the transition of a solid to a vapor and is designated  $\Delta H_s$ .

$C_p$  is infinite at phase transition temperatures because the enthalpy changes isothermally. At the Curie temperature,  $C_p$  shows a sharp discontinuity while the enthalpy has a change in slope.

Values of  $\Delta H$  are usually given for the transition at the normal standard state temperature for the two states, and if so, are designated with a superscript  $^{\circ}$ .  $\Delta H$  for a phase transition is a weak function of temperature. In some texts, the heats of phase transitions are called latent heats (for example, latent heat of fusion).<sup>15</sup>

#### IV. CONCLUSIONS

In a chemical reaction, chemical equilibrium is the state in which both the reactants and products are present in concentrations which have no further tendency to change with time,<sup>21</sup> so that there is no observable change in the properties of the system.<sup>20</sup> This state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero, but they are equal. Thus, there are no net changes in the concentrations of the reactants and products. Such a state is known as dynamic equilibrium.<sup>19</sup> At constant temperature and pressure, one must consider the Gibbs free energy,  $G$ , while at constant temperature and volume, one must consider the Helmholtz free energy,  $A$ , for the reaction; and at constant internal energy and volume, one must consider the entropy,  $S$ , for the reaction.



The constant volume case is important in geochemistry and atmospheric chemistry where pressure variations are significant<sup>18</sup>. Note that, if reactants and products were in standard state (completely pure), then there would be no reversibility and no equilibrium. Indeed, they would necessarily occupy disjoint volumes of space. The mixing of the products and reactants contributes a large entropy increase (known as entropy of mixing) to states containing equal mixture of products and reactants and gives rise to a distinctive minimum in the Gibbs energy as a function of the extent of reaction.<sup>17</sup> The standard Gibbs energy change, together with the Gibbs energy of mixing, determine the equilibrium state.<sup>16</sup>

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