Chemical Energetics

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Abstract:

Chemical energetics is a fundamental aspect of chemistry, governing energy transformations in chemical reactions. This paper provides an in-depth exploration of the principles and applications of chemical energetics. It discusses key concepts like enthalpy, entropy, Gibbs free energy, and Helmholtz free energy, highlighting their role in determining the spontaneity and feasibility of chemical processes. The thermodynamic laws governing these concepts are explained, laying the groundwork for a deeper understanding of chemical reactions. The paper also addresses applications in sustainability, chemical engineering, materials science, and biochemistry.

Introduction To Chemical Thermodynamics

What is Thermodynamics?

Thermodynamics is defined as the branch of science that deals with the relationship between heat and other forms of energy, such as work. It is frequently summarised as three laws that describe restrictions on how different forms of energy can be interconverted. There have been many attempts to build a device that violates the laws of thermodynamics. All have failed. Thermodynamics is one of the few areas of science in which there are no exceptions.

The Laws of Thermodynamics:

- **First law:** Energy is conserved; it can neither be created nor destroyed, but it can be changed from one form to another.
- **Second law:** Entropy in an isolated system always increases. Any isolated system spontaneously evolves towards thermal equilibrium—the state of maximum entropy of the system.
- **Third law:** The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K), ie. the entropy of a system approaches a constant value as the temperature approaches absolute zero.
- **Zeroth Law:** If two bodies are individually in equilibrium with a separate third body, then the first two bodies are also in thermal equilibrium with each other.

What is Chemical Thermodynamics?

It is the portion of thermodynamics that pertains to chemical reactions. It 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. It helps chemists identify whether a particular reaction is energetically possible in the direction in which it is written. It also gives the composition of the reaction system at equilibrium.

Basic Concepts of Chemical Thermodynamics

System and Surroundings:

One of the basic assumptions of thermodynamics is the idea that we can arbitrarily divide the universe into a system and its surroundings. Certain quantity of matter or the space which is under thermodynamic study or analysis is called the system. The system is covered by the boundary and the area beyond the boundary is called the surroundings.

The boundary of the system can be fixed or movable. The boundary between the system and its surroundings can be as real as the walls of a container that separates a solution from the rest of the universe (as in the figure A). Or it can be as imaginary as the set of points that divide the air just above the surface of a beaker from the rest of the atmosphere (as in the figure B). Between the system and surrounding the exchange of mass or energy or both can occur.

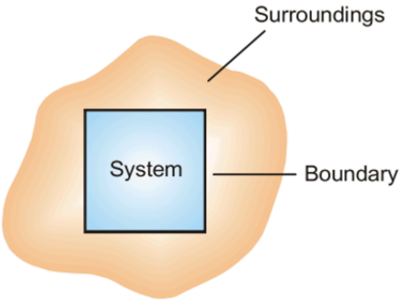


Figure A

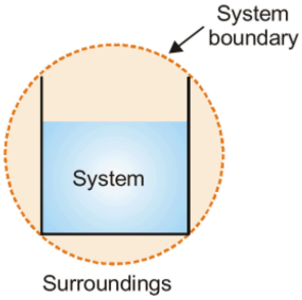
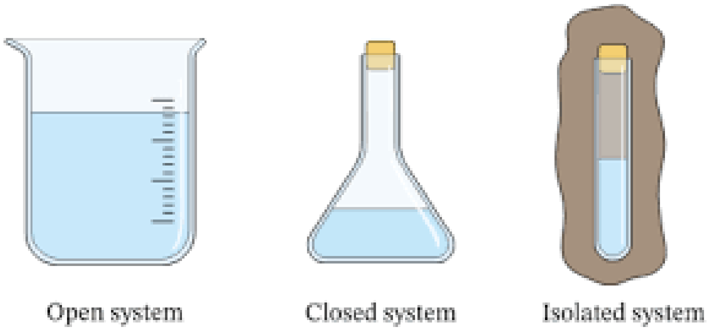


Figure B

Systems are generally of three main types:

1. **Open systems:** They are systems in which the transfer of mass as well as energy can take place across their boundaries.
2. **Closed systems:** They are systems in which the transfer of energy takes place across its boundary with the surrounding, but no transfer of mass takes place.
3. **Isolated systems:** They are systems in which neither the transfer of mass nor that of energy takes place across its boundary with the surroundings.



Thermodynamic Processes and Cycles:

A system undergoes a thermodynamic process when there is some energetic change within the system that is associated with changes in pressure, volume and internal energy.

There are four types of thermodynamic processes that have their unique properties, and they are:

- **Adiabatic Process:** A process where no heat transfer into or out of the system occurs.
- **Isochoric Process:** A process where no change in volume occurs and the system does no work.
- **Isobaric Process:** A process where no change in pressure occurs.
- **Isothermal Process:** A process where no change in temperature occurs.

A thermodynamic cycle is a process or a combination of processes conducted such that the initial and final states of the system are the same. This is also known as cyclic operation or cyclic processes.

Thermodynamic Equilibrium:

At a given state, all properties of a system have fixed values. Thus, if the value of even one property changes, the system's state changes to a different one. In a system that is in equilibrium, no changes in the value of properties occur when it is isolated from its surroundings.

- **Thermal Equilibrium:** It is when the temperature is the same throughout the entire system.
- **Mechanical Equilibrium:** It is when there is no change in pressure at any point of the system.
- **Chemical Equilibrium:** It is when the chemical composition of a system does not vary with time.
- **Phase equilibrium:** It is when in a two-phase system, the mass of each phase reaches an equilibrium level.
- **Thermodynamic Equilibrium:** It is when a thermodynamic system is in chemical equilibrium, mechanical equilibrium and thermal equilibrium and the relevant parameters cease to vary with time.

Internal Energy, Enthalpy and The First Law of Thermodynamics

Internal Energy:

One of the thermodynamic properties of a system is its internal energy, E, which is the sum of the kinetic and potential energies of the particles that form the system.

The internal energy of a system can be understood by examining the simplest possible system: an ideal gas. Since the particles in an ideal gas do not interact, this system has no potential energy and the internal energy of an ideal gas is, therefore, the sum of the kinetic energies of the particles in the gas.

And since the kinetic molecular theory assumes that the temperature of a gas is directly proportional to the average kinetic energy of its particles, the internal energy of an ideal gas is directly proportional to the temperature of the gas. This can be expressed as

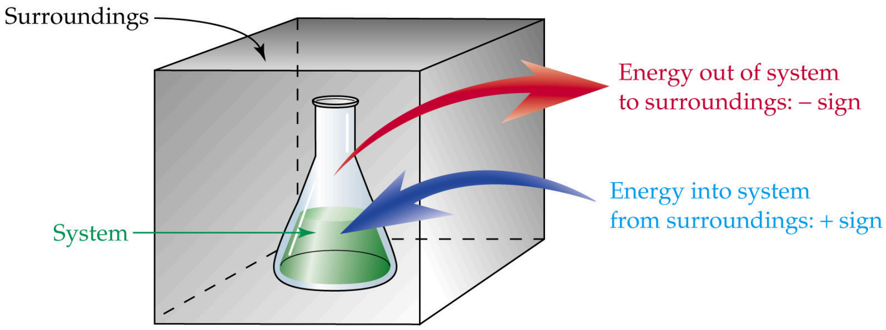
$$E_{sys} = {}^{3}/_{2}\, RT$$

where *R* is the ideal gas constant in joules per mole kelvin (J/mol-K) and *T* is the temperature in kelvin.

The internal energy of systems that are more complex than an ideal gas can't be measured directly. But the internal energy of the system is still proportional to its temperature. Therefore, changes in the internal energy of a system can be monitored by watching what happens to the temperature of the system. Whenever the temperature of the system increases we can conclude that the internal energy of the system has also increased.

Because the internal energy of the system is proportional to its temperature, which is a state function (ie. it depends only on the state of the system at any moment in time), internal energy is also a state function. And any change in the internal energy of the system is equal to the difference between its initial and final values:

$$\Delta E_{sys} = E_f - E_i$$



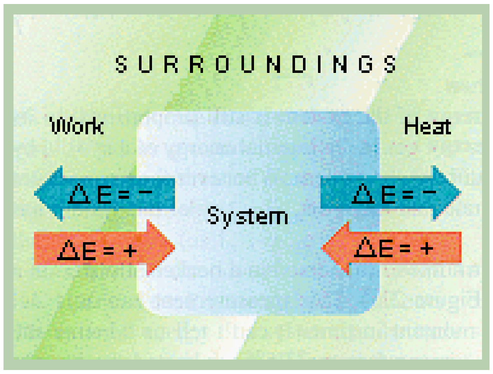
The First Law of Thermodynamics:

The system is usually defined as the chemical reaction and the boundary is the container in which the reaction is run. In the course of the reaction, heat is either given off or absorbed by the system. The system either does work on its surroundings or has work done on it by its surroundings. Either of these interactions can affect the internal energy of the system. This is given by the first law of thermodynamics.

The first law of thermodynamics states that the energy of the universe is constant. Therefore, energy can be transferred from the system to its surroundings, or vice versa, but it can't be created or destroyed: $\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$

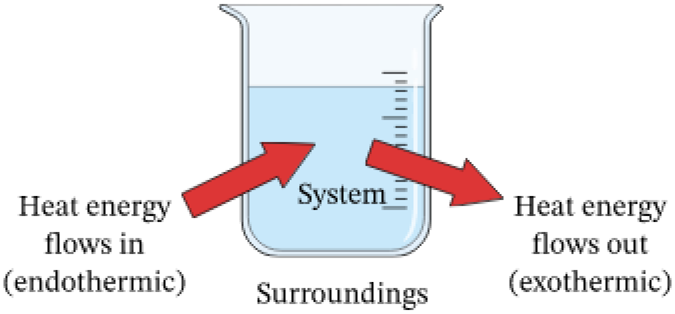
A more useful form of the first law describes how energy is conserved. It says that the change in the internal energy of a system is equal to the sum of the heat gained or lost by the system and the work done by or on the system: $\Delta E_{sys} = q + w$.

The sign convention for the relationship between the internal energy of a system and the heat gained or lost by the system can be understood by the figure below. The internal energy and temperature of a system decreases ($\Delta E < 0$) when the system either loses heat or does work on its surroundings. Conversely, the internal energy and temperature increase ($\Delta E > 0$) when the system gains heat from its surroundings or when the surroundings do work on the system.



Enthalpy:

Enthalpy is a central factor in thermodynamics. It is the heat content of a system. The measure of the heat that passes between a system and its surroundings at constant pressure during a reaction is the enthalpy change(ΔH). Whether the enthalpy of the system increases (i.e. when energy is added) or decreases (because energy is given off) is a crucial factor that determines whether a reaction can happen.



Sometimes, we call the energy of the molecules undergoing change the "internal enthalpy". Sometimes, we call it the "enthalpy of the system." These two phrases refer to the same thing. Similarly, the energy of the molecules that do not take part in the reaction is called the "external enthalpy" or the "enthalpy of the surroundings".

Changes in the internal energy ($\Delta U/\Delta E_{sys}$) are closely related to changes in the enthalpy (ΔH). This relationship between the change in the internal energy of the system during a chemical reaction and the enthalpy of reaction can be summarised as follows:

1. Since no work of expansion is possible at constant volume, the heat given off or absorbed when a reaction is run at constant volume is equal to the change in the internal energy of the system:

$$\Delta U = q_v$$

2. The heat given off or absorbed when a reaction is run at constant pressure is equal to the change in the enthalpy of the system.

$$\Delta H_{sys} = q_p$$

3. The change in the enthalpy of the system during a chemical reaction is equal to the change in the internal energy plus the change in the product of the pressure of the gas in the system and its volume.

$$\Delta H_{sys} = \Delta U + \Delta(PV)$$

4. The difference between ΔE and ΔH for the system is small for reactions that involve only liquids and solids because there is little if any change in the volume of the system during the reaction. The difference can be relatively large, however, for reactions that involve gases, if there is a change in the number of moles of gas in the course of the reaction.

The enthalpy change for a chemical reaction can be, generally, calculated using tabulated values of enthalpies of formation, ie. the enthalpy change that occurs when 1 mole of the substance is formed from its constituent elements in their standard states.

Spontaneity, Entropy and The Second Law of Thermodynamics

Spontaneous and Non-Spontaneous Processes:

The first law of thermodynamics suggests that we can't get something for nothing. It allows us to build an apparatus that does work, but it places important restrictions on that apparatus. It says that we have to be willing to pay a price in terms of a loss of either heat or internal energy for any work we ask the system to do. It also puts a limit on the amount of work we can get for a given investment of either heat or internal energy.

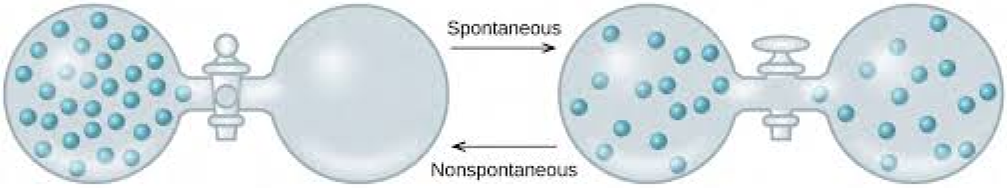
The first law allows us to convert heat into work, or work into heat. It also allows us to change the internal energy of a system by transferring either heat or work between the system and its surroundings. But it doesn't tell us whether one of these changes is more easy to achieve than another. Our experiences, however, tell us that processes have a natural tendency to occur in one direction under a given set of conditions.

We aren't surprised when a cup of coffee gradually loses heat to its surroundings as it cools, for example, or when the ice in a glass of lemonade absorbs heat as it melts. But we would be surprised if a cup of coffee suddenly grew hotter or the water in a glass of lemonade froze on a hot summer day, even though neither process violates the first law of thermodynamics.

Similarly, we aren't surprised to see a piece of zinc metal dissolve in a strong acid to give bubbles of hydrogen gas.

$$Zn(s) + 2H_2SO_4(aq) \text{-->} ZnSO_4(aq) + H_2(g)$$

But if we saw a video in which H_2 bubbles formed on the surface of a solution and then sank through the solution until they disappeared, while a strip of zinc metal formed in the middle of the solution, we would conclude that the video is being run backward.



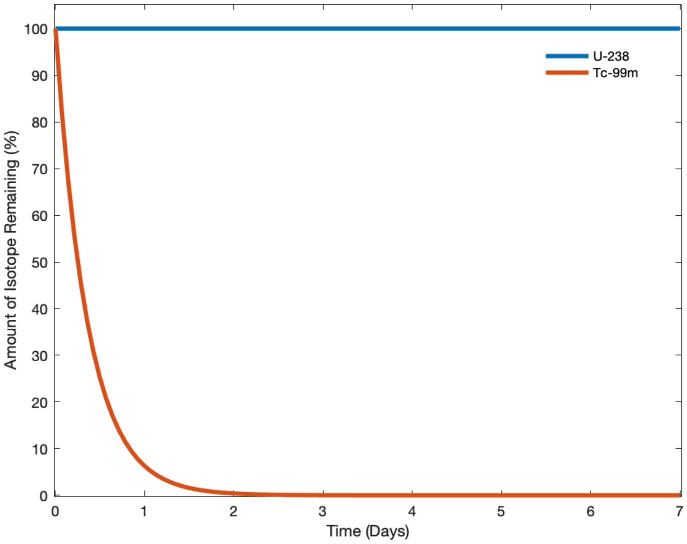
Many chemical and physical processes are reversible and yet tend to proceed in a direction in which they are said to be spontaneous. This raises an obvious question: What makes a reaction spontaneous? What drives the reaction in one direction and not the other?

A spontaneous process is one that occurs naturally under certain conditions. A non-spontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source.

A process that is spontaneous in one direction under a particular set of conditions is typically nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is not correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the rate of decay of the radioactive isotopes Technetium-99m and Uranium-238.

The former is a popular radioisotope used for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Whereas, the latter, which is the most abundant isotope of uranium, decays much more slowly, exhibiting a half-life of more than four billion years.



(Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axis represents the percentage of isotope remaining and the horizontal axis is the time that has elapsed in days. It is noted that both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.)

Predicting Spontaneity:

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, it is tempting to assume that one of the driving forces that determines whether a reaction is spontaneous is a tendency to give off energy.

In fact, observations of natural processes led a surprising number of chemists of the late 19th century (including Berthelot and Thomsen) to conclude that all spontaneous reactions must be exothermic since:

- Objects roll downhill spontaneously (i.e., energy is "lost" from the system)
- Objects do not roll uphill spontaneously (i.e., energy does not suddenly appear from nowhere)

If this were true all we would need to predict whether a reaction is spontaneous is the change of enthalpy. If ΔH were negative, the process should be able to occur by itself. If ΔH were positive, the reaction could not occur by itself.

Indeed, almost all exothermic reactions are spontaneous at standard thermodynamic conditions (1 atmosphere pressure) and 25°C, like:

$$2Al(s) + 3Br_2(l) \rightarrow 2AlBr_3(s) \quad \Delta H^\circ = -511 \text{ kJ/mol } AlBr_3$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H^\circ = -241.82 \text{ kJ/mol } H_2O$$

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \quad \Delta H^\circ = -2984 \text{ kJ/mol } P_4O_{10}$$

However a number of common processes which are both endothermic and spontaneous are known. The most obvious are simple phase changes, like ice melting at room temperature. Also, many solids dissolve in water and simultaneously absorb heat:

$$NH_4NO_3(s) \text{ –}H_2O\text{–> } NH^{4+}(aq) + NO^{3-}(aq) \quad \Delta H^\circ = 28.05 \text{ kJ/mol}$$

Thus, the tendency of a spontaneous reaction to give off energy can't be the only driving force behind a chemical reaction. There must be another factor that helps determine whether a reaction is spontaneous, but what is it?

In 1877, Ludwig Boltzmann provided a basis for answering this question when he introduced the concept of entropy.

Entropy:

Consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, such that $T_X > T_Y$. When these objects come into contact, heat spontaneously flows from the hotter object X to the colder one Y. This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a more uniform dispersal of energy.

Therefore, systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. This subtle property that matter possesses in terms of the way energy is dispersed in it is known as entropy.

Entropy is a measure of the degree of randomness or disorder of a system. It is the measure of the number of possible arrangements the atoms in a system can have. It is a thermodynamic property that is proportional to their degree of disorder ie. the physical state or condition of a system. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

For example, a liquid has higher entropy than a solid and a gas has a much higher entropy than a liquid. This is because a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; while molecules in a gas have even more freedom to move than those in a liquid. With each degree of motion, the number of available microstates increases, resulting in a higher entropy.

Thus, the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapour, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes must be accompanied by a decrease in the entropy of the system such that $\Delta S_{cond} < 0$.

When Ludwig Boltzmann introduced the concept of entropy, he proposed the following equation to describe the relationship between entropy and the amount of disorder in a system:

$$S = k \ln W$$

where *S* is the entropy of the system, *k* is a proportionality constant equal to the ideal gas constant divided by Avogadro's constant, *ln* represents a logarithm to the base e, and *W* is the number of equivalent ways of describing the state of the system.

Change in Entropy:

The change in entropy, denoted as ΔS, represents the change in randomness, or disorder of a system. At constant temperature, changes in entropy represent phase transitions. For example, liquid water will spontaneously turn to solid water at temperatures below water's freezing point.

Change in entropy (ΔS), at constant temperature is defined as:

$$\Delta S = \Delta QT$$

where *Q* is the heat exchanged between a system and its surroundings and *T* is the temperature in Kelvin.

Because entropy is a state function, the change in the entropy of the system that accompanies any process can be calculated by subtracting the initial value of the entropy of the system from the final value:

$$\Delta S_{sys} = S_f - S_i$$

ΔS for a chemical reaction is, therefore, equal to the difference between the sum of the entropies of the reactants and the products of the reaction.

$$\Delta S = \Sigma S_{(products)} - \Sigma S_{(reactants)}$$

When this difference is measured under standard-state conditions, the result is the standard-state entropy of reaction, ΔS^o:

$$\Delta S^o = \Sigma S^o_{(products)} - \Sigma S^o_{(reactants)}$$

By convention, the standard state for thermodynamic measurements is characterised by the following conditions:

- All solutions have concentrations of 1 M.
- All gases have partial pressures of 0.1 MPa (0.9869 atm)
- Although standard-state entropies can be measured at any temperature, they are often measured at 25°C.

Meanwhile, the total entropy change, what really matters, is calculated by the sum of the entropy changes of the system and the surroundings:

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$$

Where: $$\Delta S_{surroundings} = -\ \Delta H/T$$

Because:

$$q_{rev} \propto T$$
$$\Delta S \propto q_{rev}$$
$$q_{rev} = T\ \Delta S$$
$$\Delta S = q_{rev} / T$$

Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, *we can express change in internal energy during the process as:*

$$\Delta U\ = q_{rev} + w_{rev}$$
$$= T\Delta S - P\Delta V$$

According to the above equation, q_{rev} *must increase during expansion, that is, the system must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore* $\Delta S_{sys} = +\ q_{rev} / T$, *and the entropy change of the surroundings is* $\Delta S_{surr} = -\ q_{rev} / T$

And since this change is happening at constant pressure and at constant the heat given off or absorbed when a reaction is run at constant pressure is equal to the change in the enthalpy of the system ($\Delta H_{sys} = q_p$)*:*

$$\Delta S_{surr} = -\ H / T$$

The Second Law of Thermodynamics:

The second law of thermodynamics describes the relationship between entropy and the spontaneity of natural processes. It gives us the criterion we are seeking to decide whether a reaction will be spontaneous or not.

The law states that in an isolated system, natural processes are spontaneous when they lead to an increase in disorder, or entropy. According to it, any isolated system spontaneously evolves towards thermal equilibrium – the state of maximum entropy of the system.

In order to visualise this law, let's consider an already-existing untidy room. If the room is not tidied or cleaned, it invariably becomes more messy and disorderly with time. When the room is cleaned, its entropy decreases, but the effort to clean it has resulted in increased entropy outside the room exceeding the entropy lost.

Therefore, in a spontaneous process the entropy of the universe only increases and the second law of thermodynamics could be written in this way for a spontaneous process:

$$\Delta S_{sys} + \Delta S_{surr} > 0$$

We can apply this law to chemical reactions by noting that the entropy of a system is a state function that is directly proportional to the disorder of the system:

$S_{sys} > 0$ *implies that the system becomes more disordered during the reaction.*

$S_{sys} < 0$ *implies that the system becomes less disordered during the reaction.*

And that, for an isolated system, any process that leads to an increase in the disorder of the system will be spontaneous.

The following trends help decide when a chemical reaction leads to an increase in the disorder of the system:

- Solids have a much more regular structure than liquids. Liquids are therefore more disordered than solids.
- The particles in a gas are in a state of constant, random motion. Gases are therefore more disordered than the corresponding liquids.
- Any process that increases the number of particles in the system increases the amount of disorder.

Since ΔH and ΔS can determine the direction of reactions, it is therefore important to consider the effect of changes in both enthalpy and entropy that occur during the reaction to decide whether a reaction is spontaneous.

Gibbs Free Energy

Introduction:

We know that:

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$$

We also know how the entropy change of the surroundings is related to the enthalpy change of the reaction:

$$\Delta S_{surroundings} = - H / T$$

Putting these equations together, and rearranging them slightly by multiplying everything by T to get rid of the fraction gives:

$$\Delta S_{total} = -\frac{\Delta H}{T} + \Delta S_{system}$$

$$T\Delta S_{total} = -\Delta H + T\Delta S_{system}$$

$$-T\Delta S_{total} = \Delta H - T\Delta S_{system}$$

The term on the left-hand side is known as the Gibbs Free Energy, and is given the symbol G. That means that you can write the fairly simple looking equation for G as:

$$\Delta G = \Delta H - T\Delta S$$

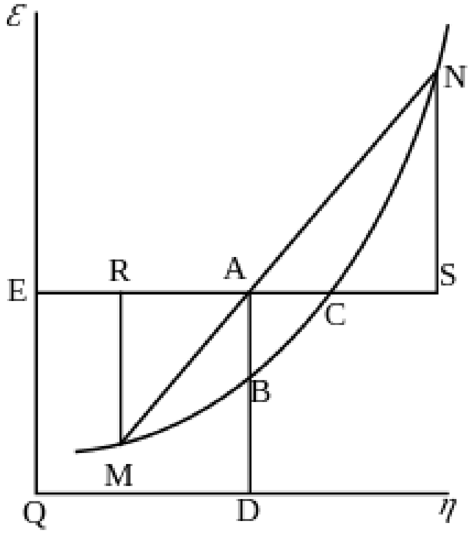
Josiah Willard Gibbs:

The Gibbs free energy (G), often called simply free energy, was named in honour of the American physicist Josiah Willard Gibbs (1838–1903), who first developed the concept in the 1870s and termed it as “available energy”.

His paper published in 1873, “Graphical Methods in the Thermodynamics of Fluids,” outlined how his equation could predict the behaviour of systems when they are combined. Gibbs described this “available energy” as ‘the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition.

The initial state of the body, according to Gibbs, is supposed to be such that "the body can be made to pass from it to states of dissipated energy by reversible processes". In his 1876 magnum opus 'On the Equilibrium of Heterogeneous Substances', a graphical analysis of multi-phase chemical systems, he engaged his thoughts on chemical-free energy in full.

Here is Willard Gibbs' 1873 available energy (Gibbs free energy) graph, which shows a plane perpendicular to the axis of v (volume) and passing through point A, which represents the initial state of the body. MN is the section of the surface of dissipated energy. $Q\varepsilon$ and $Q\eta$ are sections of the planes $\eta = 0$ and $\varepsilon = 0$, and therefore parallel to the axes of ε (internal energy) and η (entropy), respectively. AD and AE are the energy and entropy of the body in its initial state, AB and AC its available energy (Gibbs free energy) and its capacity for entropy (the amount by which the entropy of the body can be increased without changing the energy of the body or increasing its volume), respectively.



Definition of Gibbs Free Energy:

The Gibbs free energy of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system.

$$G = H - TS$$

It is a thermodynamic potential that can be used to calculate the maximum amount of work that may be performed by a thermodynamically closed system at constant temperature and pressure. Since it is defined in terms of three other state functions – enthalpy, temperature, and entropy – G is also a state function.

Change in Gibbs Free Energy:

The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temperature times the entropy of the system.

$$\Delta G = \Delta H - T\Delta S$$

where:

ΔG is change in Gibbs Free Energy
ΔH is change in enthalpy
T is temperature in Kelvin
ΔS is change in entropy

Standard-State Free-Energy Changes:

The standard-state free energy of formation is the change in free energy that occurs when 1 mole of a compound is formed from its elements in their most thermodynamically stable states at standard-state conditions (gases at 1 bar, solutions at 1 M concentration and at a constant temperature – usually 25°C). In other words, it is the difference between the free energy of a substance and the free energies of its constituent elements at standard-state conditions.

The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_{f}) and the standard entropy of formation (ΔS°_{f}) using the definition of free energy:

$$\Delta G^{o}_{f} = \Delta H^{o}_{f} - T\Delta S^{o}_{f}$$

Meanwhile, the standard-state free energy of a reaction (ΔG^{o}) is defined as the free energy of reaction at standard state conditions. It is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states.

The standard-state free energy change of a reaction ΔG^{o} (at which reactants are converted to products at 1 bar) can be calculated by:

1. Using the following version of the Gibbs equation if the standard enthalpy and entropy changes are known:

$$\Delta G^{o}_{r} = \Delta H^{o}_{r} - T\Delta S^{o}_{r}$$

2. Combining standard free energies of formation through the expression:

$$aA + bB \rightarrow cC + dD$$

$$\Delta G^{o}_{r} = c\,\Delta G^{o}_{f}(C) + d\,\Delta G^{o}_{f}(D) - a\,\Delta G^{o}_{f}(A) - b\,\Delta G^{o}_{f}(B)$$

$$\Delta G^{o}_{r} = \sum m\,\Delta G^{o}_{f}(\text{products}) - \sum n\,\Delta G^{o}_{f}(\text{reactants})$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation.

Gibbs Free Energy and Spontaneity:

Like we already established earlier, the effect of changes in both enthalpy and entropy that occur during the reaction need to be considered in order to decide whether a reaction is spontaneous. And since change in Gibbs Free Energy is expressed in terms of change in enthalpy and change in entropy, it is used to describe the spontaneity of a process.

ΔG can predict the direction of the chemical reaction under two conditions: 1. constant temperature and 2. constant pressure.

Since at constant temperature and pressure, for a spontaneous process' $S_{univ} > 0$ we obtain:

$$\begin{aligned} \Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} > 0 \\ &= \Delta S_{sys} - \Delta H_{sys} T > 0 \end{aligned}$$

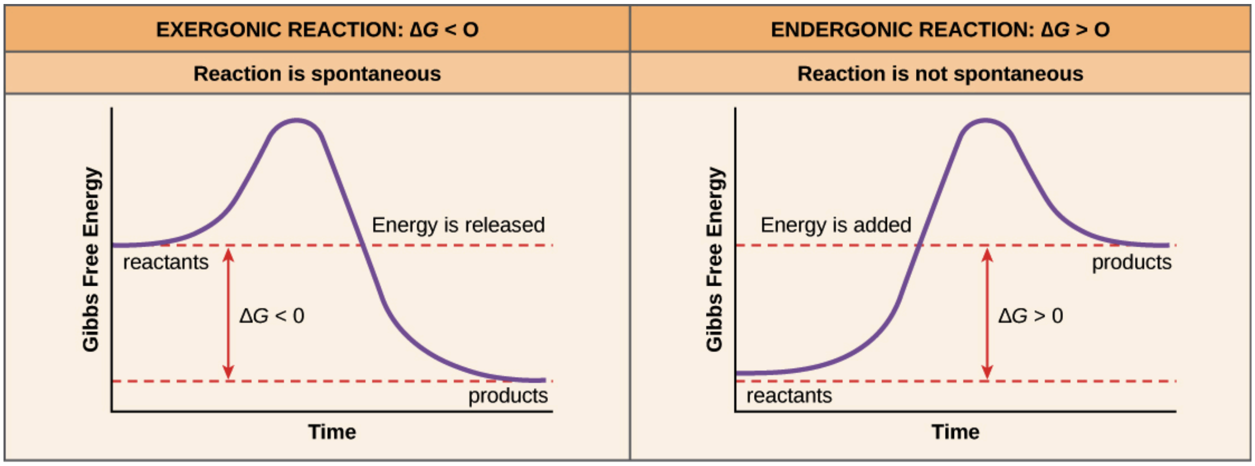
Multiplying both sides of the inequality by $-T$ reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0$$

which is equal to ΔG ie., $G < 0$.

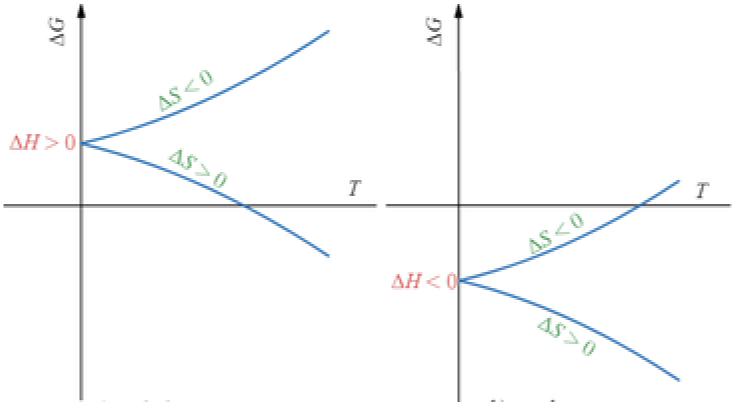
Therefore, for a process at constant temperature and pressure:

- If $\Delta G < 0$ ie., if ΔG is negative, the reaction is spontaneous in the direction written i.e., the reaction is exergonic.
- If $\Delta G = 0$, the system is at equilibrium and there is no net change either in forward or reverse direction.
- $\Delta G > 0$ ie., if ΔG is positive, the reaction is not spontaneous and the process proceeds spontaneously in the reserve direction. To drive such a reaction, we need to have input of free energy i.e., the reaction is endergonic.



In many cases, we can predict the sign from the signs of ΔH and ΔS. Here is the sign guide to predict spontaneity:

Enthalpy Change	**Entropy Change**	**Gibbs free energy**	**Spontaneity**
Positive	Positive	Depends on T, may be +ve or -ve	Yes, if the temperature is high enough
Positive	Negative	Always Positive	Never spontaneous
Negative	Positive	Always Negative	Always spontaneous
Negative	Negative	Depends on T, may be +ve or -ve	Yes, if the temperature is low enough



a) endothermic reaction *b) exothermic reaction*

Although G indicates whether a reaction will occur spontaneously or now, it necessarily does not indicate whether the reaction will occur rapidly ie. it does not indicate the speed or kinetics of a chemical reaction.

Gibbs Free Energy and Equilibrium Constant:

As we have noted, three criteria decide for whether a given reaction will occur spontaneously:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. The relative magnitude of the reaction quotient Q versus the equilibrium constant K is $Q < K$

Spontaneous	**Equilibrium**	**Non-Spontaneous (Spontaneous in the Other Direction)**
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$

$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$

[K *is the equilibrium constant which is a measure of the ratio of the concentrations of products to the concentrations of reactants. While* Q *is the reaction quotient which is a measure of the relative amounts of products and reactants present during a reaction at a particular point in time and it given by:*

$$Q_r(t) = \frac{\{R\}_t^{\rho}\,\{S\}_t^{\sigma}}{\{A\}_t^{\alpha}\,\{B\}_t^{\beta}}$$

Where Q_r = *reaction quotient,* α = *moles of a reactant* A, β = *moles of a reactant* B, ρ = *moles of a product* R, σ = *moles of a product* S, *and* t = *time.*]

Since both ΔG and K is a measure of how favourable a reaction is, they can be related:

1. A reaction with a negative ΔG, is very favourable, so it has a large K.
2. A reaction with a positive ΔG is not favourable, so it has a small K.
3. A reaction with ΔG = 0 is at equilibrium.

ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy as:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = V\Delta P - T\Delta S$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then,

$$\Delta G = V\Delta P$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. However, for reactions that involve gases, the effect of pressure on free energy is very important. Therefore, assuming ideal gas behaviour, we can replace the V by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (Pi and Pf , respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P$$

$$= nRT\frac{\Delta P}{P}$$

$$= nRT\ ln\left(\frac{P_f}{P_i}\right)$$

If the initial state is the standard state with $P_i = 1$ atm , then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^{o} = nRT\ln P$$

$$G = G^{o} + nRT\ln P$$

Let's now consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_{m} G_{\text{products}} - \sum_{n} G_{\text{reactants}}$$

$$= (cG_{C} + dG_{D}) - (aG_{A} + bG_{B})$$

Substituting $G = G^{o} + nRT\ln P$ for each term:

$$\Delta G = [(cG^{o}_{C} + cRT\ln P_{C}) + (dG^{o}_{D} + dRT\ln P_{D})] - [(aG^{o}_{A} + aRT\ln P_{A}) + (bG^{o}_{B} + bRT\ln P_{B})]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^{o} + RT\ln \left(\frac{P_{C}^{c} P_{D}^{d}}{P_{A}^{a} P_{B}^{b}} \right)$$

$$\Delta G = \Delta G^{o} + RT\ln Q$$

where ΔG^{o} indicates that all reactants and products are in their standard states. For gases at equilibrium, Q = Kp, and for a system at equilibrium, $\Delta G = 0$. Therefore, we can describe the relationship between ΔGo and Kp for gases as follows:

$$0 = \Delta G^{o} + RT\ln K_{p}$$

$$\Delta G^{o} = - RT\ln K_{p}$$

Although Kp is defined in terms of the partial pressures of the reactants and the products and the equilibrium constant K is defined in terms of the concentrations of the reactants and the products, the numerical magnitude of Kp and K are related:

$$K_{p} = K(RT)^{\Delta n}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant.

For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so Kp = K. For all such reactions and those that do not involve a change in the number of moles of gas present, the relationship in $\Delta G^{o} = - RT\ln K_{p}$ can be written as:

$$\Delta G^{o} = - RT\ln K$$

Gibbs Free Energy in Electrochemistry:

The value of ΔG for a reaction at any moment in time tells us not only what direction the reaction has to shift to reach equilibrium(sign) but also tells us how far the reaction is from equilibrium at that moment(magnitude). And since the potential of an electrochemical cell is a measure of how far an oxidation-reduction reaction is from equilibrium, we can relate ΔG and the cell potential (E):

During a reversible electrochemical reaction at constant temperature and pressure,

$$\Delta S = \frac{\Delta q}{T}$$

$$\Delta U = \Delta q + \Delta W_{\text{non-exp}} + \Delta W_{\text{exp}}$$

$$\begin{aligned} \Delta W_{\text{non-exp}} &= \Delta U - \Delta W_{\text{exp}} - \Delta q \\ &= \Delta U + p\Delta V - T\Delta S \qquad \text{(const. p and T)} \\ &= \Delta H - T\Delta S \\ &= \Delta G \end{aligned}$$

In an ideal chemical cell, if the potential difference between the electrodes is E, to move one mole electrons across the external circuit will be FE, which must be equal to the decrease in gibbs free energy of the system. Hence for n mole electrons transferred at the same potential,

$$W_{\text{non-exp}} = \Delta G = -\,nFE.$$

And since the Nernst equation describes the relationship between the cell potential at any moment in time and the standard-state cell potential, we can also derive it from this relation $\Delta G = -\,nFE$ by rearranging the equation with other equations that hold true during a reversible electrochemical reaction at constant temperature and pressure:

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

$$\Delta G^\circ = -\,RT \ln K$$

$$\Delta G^\circ = -\,nFE^\circ$$

$$\textit{into}$$

$$nFE^\circ = RT \ln K$$

$$nF\,E = nF\,E^\circ - RT \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

Where E = Cell Potential, E° = Standard Cell Potential, R = Gas Constant, T = Absolute Temperature, n = Number of moles of electrons transferred in the reaction, F = Faraday Constant (charge per mole of electrons) and ln Q = Natural Logarithm of the Reaction Quotient.

Helmholtz Free Energy

Introduction to Helmholtz Free Energy:

The Helmholtz free energy is deemed as a thermodynamic potential which calculates the "useful" work retrievable from a closed thermodynamic system at a constant temperature and volume. For such a system, the negative of the difference in the Helmholtz energy is equal to the maximum amount of work extractable from a thermodynamic process in which both temperature and volume are kept constant. In these conditions, it is minimized and held constant at equilibrium.

The Helmholtz free energy was originally developed by German physicist Hermann Helmholtz in 1882 and is generally denoted by the letter A, or the letter F. It is the thermodynamic potential found in a system of constant species with constant temperature and constant volume, given by the formula:

$$\Delta A = \Delta E - T\Delta S$$

A = Helmholtz Free Energy in Joule
E = Energy of the System in Joule
T = Absolute Temperature in KElvin
S = Entropy in Joule/Kelvin

The Helmholtz free energy is also the measure of an isothermal-isochoric closed system's ability to do work. If any external field is missing, the Helmholtz free energy formula becomes:

$$\Delta A = \Delta U - T\Delta S$$

A = Helmholtz Free Energy in Joule
U = Internal Energy in Joule
T = Absolute Temperature in Kelvin
S = Entropy in Joule/Kelvin

The Helmholtz free energy is also a measure of the sum of energy you have to put in to generate a system once the spontaneous energy transfer of the system from the environment is taken into account.

Relating Helmholtz Energy to Gibbs Energy:

The Helmholtz Energy is given by the equation:

$$A = U - TS$$

It is thus comparable to Gibbs Energy in this way:

$$G = A + PV$$

The Helmholtz Energy is used when having a constant pressure is not feasible.

Applications of the Chemical Energetics

Along with internal energy and enthalpy, the Helmholtz energy and Gibbs energy comprise the quartet of thermodynamic potentials, forming a cornerstone in the realm of chemical thermodynamics and energetics. Together, they offer a comprehensive and versatile toolkit for analysing and interpreting the energetics of chemical systems. Their significance extends beyond theoretical considerations to practical applications in fields as diverse as chemical engineering, materials science, and biochemistry.

In chemical engineering, these thermodynamic potentials serve as guiding principles for the design and optimization of chemical processes, facilitating the development of efficient and sustainable manufacturing techniques. Engineers leverage their understanding of thermodynamic potentials to maximise the yield of desired products while minimising energy consumption and waste generation.

Similarly, in materials science, the analysis of thermodynamic potentials plays a crucial role in understanding phase transitions, crystallisation processes, and the stability of materials under various conditions. By harnessing this knowledge, researchers can tailor the properties of materials to meet specific technological requirements, leading to advancements in areas such as electronics, nanotechnology, and renewable energy.

In biochemistry, thermodynamic potentials are indispensable for elucidating the energetics of biochemical reactions occurring within living organisms. They provide insights into the metabolic pathways responsible for energy production, cellular processes, and the regulation of biological systems. Understanding these thermodynamic principles is essential for drug discovery, enzyme engineering, and the development of therapies targeting metabolic disorders.

Moreover, the practical applications of thermodynamic potentials extend into environmental science and sustainability efforts. By analysing the energetics of chemical processes, researchers can assess the environmental impact of industrial activities, identify strategies for reducing greenhouse gas emissions, and optimise resource utilisation to mitigate environmental degradation.

In essence, the comprehensive understanding and application of thermodynamic potentials empower researchers and practitioners across diverse disciplines to address complex challenges and drive innovation in fields essential for human progress and well-being. From optimising industrial processes to advancing materials technology and fostering sustainable practices, these thermodynamic principles serve as invaluable tools for shaping the future of science and technology.

Conclusion

In conclusion, this paper provides a comprehensive exploration of chemical energetics, from its foundational principles to its wide-ranging applications. By delving into the intricate interplay of energy and matter in chemical systems, a deeper understanding of the fundamental processes governing our world is attained. As we continue to unravel the complexities of chemical energetics, its significance in driving scientific inquiry, technological advancement, and sustainable development remains paramount.

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