



Lecture 3

Thermodynamics

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Introduction

Thermodynamics is derived from two words: '*Thermo*' which means 'Heat' and '*Dynamics*' which means 'Power'

Thermodynamics is the study of the relationships between heat and other forms of energy (such as mechanical, electrical, or chemical energy).

The main forms of energy of interest in thermodynamics are heat (Q) and work (W)

Energy

Potential energy

Potential energy is the energy of interaction between particles, it is due to the position of a body or the configuration of its part(s).

Examples:

Potential energy of a body is higher when it is high in the air than when it is on the surface of the earth. Energy is required to throw the body into the air against the force of gravity.

Potential energy of two separate nitrogen atoms is higher than of a diatomic nitrogen molecules. Energy is required to separate the N_2 molecules into N atoms.

Energy

Kinetic energy

Kinetic energy is the energy of motion of a body (e.g. a molecule)

$$E_k = \frac{1}{2}mv^2 \quad \text{m: mass, v: velocity}$$

SI unit for energy is *Joule*

$$\text{J} = \text{Kg m}^2 \text{ s}^{-2} = \text{N m} = 10^7 \text{ erg}$$

Non-SI unit for energy is *Calorie* (widely used in chemistry and biology).

$$1 \text{ cal} = 4.184 \text{ J}$$

Energy

Internal energy

Internal (total) energy of a body is the sum of its kinetic and potential energies

$$U = \sum E_K + \sum E_p$$

Thermodynamics deals with changes in the energy ΔU of a system as the system passes from one state to another state

The internal energy is the difference (ΔU) between the energies in the two states:

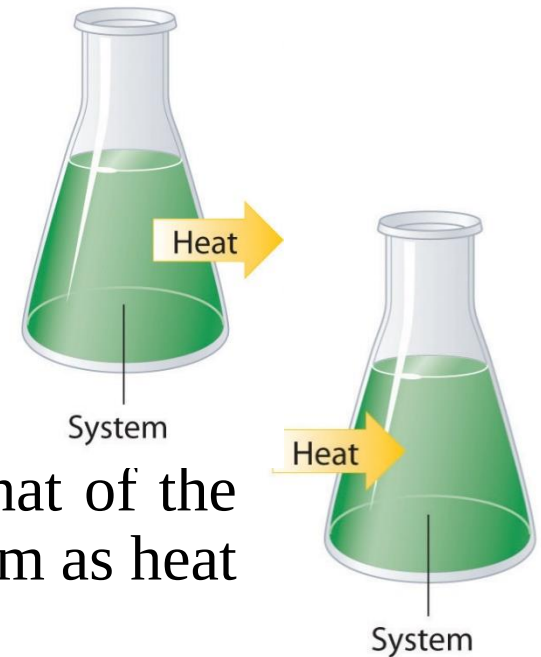
$$\Delta U = U_{Final} - U_{Initial}$$

Energy

Heat

Heat (Q) is a form of energy that is transferred as the result of a temperature difference between a system and its surroundings

If the temperature of the system is more than that of the surrounding, then energy flows out of the system as heat and Q is negative (the system is exothermic)



If the temperature of the system is less than that of the surrounding, then energy flows into the system as heat and Q is positive (the system is endothermic)

Heat is expressed in joules (J) or calories (cal). Heat is not “degree of hotness,” which is measured by temperature

NOTE: - The differences between heat and temperature can be summarised in points as follows:

Heat	Temperature
Heat is the form of energy that flows from the system to its surroundings.	Temperature is the result of heat
Mass of the body affects the total heat.	Mass of body does not effect on temperature but depends on the molecular vibration of the body.
Heat is measured in joules or calories. $4.2 \text{ Joules} = 1 \text{ calorie}$	Temperature is measured in degree Celsius or degree Fahrenheit or Kelvin Scale.
Heat is measured by using a Calorimeter.	Temperature is measured using the thermometer.

Energy

Work

Work (W) is the transfer of energy by any process other than heat. There are many forms of work including mechanical, electrical, and gravitational work.

For our purposes, we are concerned with thermal work which is the work done in an enclosed chemical system. In this type of system, work is defined as the change in the volume (V) within the system (in liters) multiplied by a pressure (P).

Energy

Work

$\therefore W = - P \Delta V$ (work of compression)

$W = P \Delta V$ (work of expansion)

If the work is done by the system then W is negative

If the work is done on the system then W is positive

Like heat, the unit measurement for work is joules.

Thermodynamic system

Definition

System is the sample for which the energy is studied (e.g. chemical reaction)

Surrounding is everything outside the system (e.g. the surrounding of a chemical reaction is the water bath in which it is immersed).

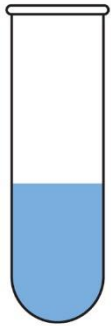
Boundary is the barrier that separate the system from its surrounding (e.g. the wall of the flask).

Universe is the system and its surroundings.

Thermodynamic system

Types of thermodynamic systems

Three types of systems are frequently used to describe thermodynamic properties:



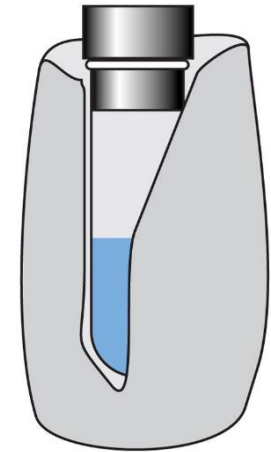
Open system

Energy and matter can be exchanged with the surroundings



Closed system

there is no exchange of matter with the surroundings, but the energy can be transferred by *work* or *heat* through the *closed* system's boundaries.



Isolated system

neither matter nor energy can be exchanged with the surroundings.

Thermodynamic processes

Process is the change of a system from one equilibrium state to another.

Isothermal process is a process in which the **temperature** of the system is kept **constant**.

e.g. Placing the system in a constant-temperature bath so that heat is exchanged without affecting the temperature.

Isobaric process is a process in which **pressure** of the system remains **constant**.

Isochoric process is a process in which **volume** of the system remains **constant**

Adiabatic process is a process in which **no heat** is exchanged with the surroundings

Thermodynamic state

State function

Thermodynamic state means the condition of the system that is identified by values of a set of parameters known as *state functions or state variables*.

State function is a property with a unique value that depends only on the **current state** of the system and is **independent** of the manner in which the state was reached (i.e. **the path**) e.g. temperature, pressure and volume...etc.

Thermodynamic state

Path function

Path function or *process function* is a quantity whose value depends on **the path** of a transition between equilibrium states of a thermodynamic system

Both Q and W depend on the manner in which the state of the system is reached (depend on the path).

Q and W are *Path functions*

E.g. The amount of heat that is produced if a box is dragged on a rough surface for a certain distance is more than that produced if the surface was smooth, due to frictional resistance.

Thermodynamic state

Extensive and intensive variables

Extensive variables are variables that depend on the **size** of the system; e.g. **mass and volume**

Intensive variables are variables that **do not depend on size**; e.g. **pressure and temperature**

The first law of thermodynamics

Conservation of energy

Enthalpy change

Heat capacity

Conservation of energy

The first law of thermodynamics states that ***energy can be transformed from one form to another, but cannot be created or destroyed.*** Put in another way : The total energy of an isolated system cannot change during any operation.

If an amount of heat (Q) is supplied to a system, a part of it may increase the internal energy (ΔU) while the remaining may be used as work (W) done by the system.

$$\Delta U = Q + W$$

Change in
internal energy

Heat gained
by the system

Work lost by
the system

Conservation of energy

Q and W are **positive** if the **energy is gained** by the system (i.e. the heat is taken up by the system or the work is done on the system).

Q and W are **negative** if the **energy is lost** by the system (i.e. the heat is released by the system or the work is done by the system).

The absolute value for the internal energy is extremely difficult to attain in practice. Therefore, change of internal energy ΔU rather than absolute energy value is the concern of thermodynamics.

Enthalpy change

Definition

The *enthalpy change* is the amount of heat gained or lost in a process at constant pressure. ($\Delta H = Q_p$)

ΔH does not depend on the path between the states of the system (ΔH is a state function)

Since enthalpy is an energy, it is measured in the usual energy units e.g. joule.

Only changes in enthalpy (ΔH) can be measured in practice (as with all energy quantities), (It is difficult to measure the absolute value of H).

Enthalpy change

Equation

Most chemical studies are conducted at constant pressure.
(The reaction is open to the atmosphere, and $P = 1 \text{ atm}$).

From the first law:

$$\Delta U = Q_P + W_P$$

$$Q_P = \Delta U - W_P, \text{ and since } W = -P\Delta V$$

$$\text{Then } Q_P = \Delta U + P\Delta V$$

By defining a new state function ΔH , the *enthalpy change* which is equal to Q_P , the equation become:

$$\Delta H = \Delta U + P\Delta V$$

Enthalpy change

Enthalpy of phase transitions

Specific symbols and names are used to identify H with particular physical changes. $\Delta H = H_{\text{final}} - H_{\text{initial}}$:

The **enthalpy of fusion** (ΔH_{fusion} or ΔH_{mel}) is the heat absorbed by a 1 mole of solid on melting

$$\Delta H_{\text{fusion}} = H_{\text{liquid}} - H_{\text{solid}}$$

The **enthalpy of vaporization** (ΔH_{vap}) is the heat absorbed by a 1 mole of liquid on vaporization.

$$\Delta H_{\text{vap}} = H_{\text{gas}} - H_{\text{liquid}}$$

The **enthalpy of sublimation** (ΔH_{sub}) is the heat absorbed by a 1 mole of solid on sublimation.

$$\Delta H_{\text{sub}} = H_{\text{gas}} - H_{\text{solid}}$$

These are molar properties. E.g. ΔH_{vap} (water, 25 °C) = 44 KJ/mol.

Enthalpy change

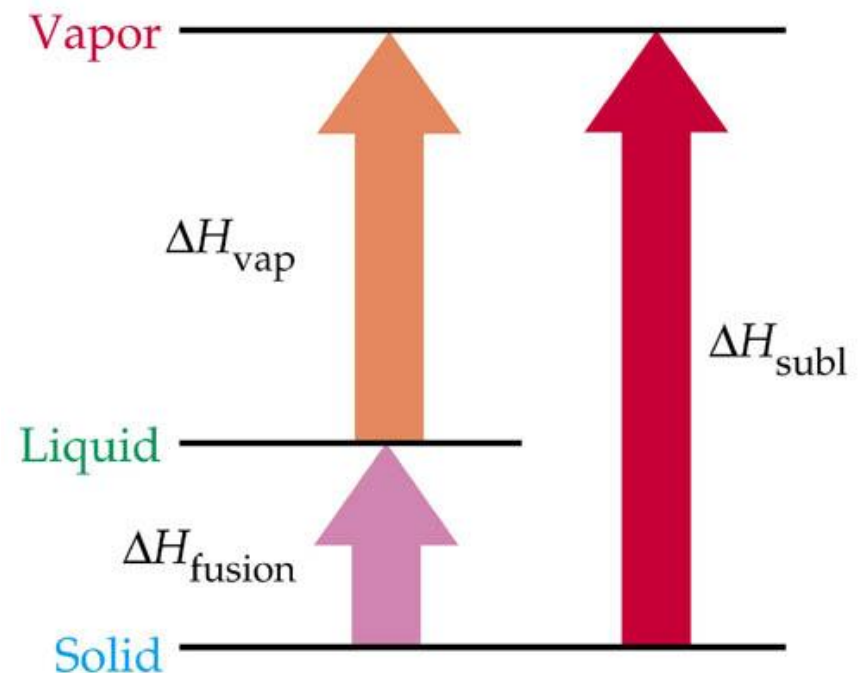
Enthalpy of phase transitions

ΔH (forward change) = - ΔH (reverse change)

ΔH is positive for physical change from a more condensed to a less condensed phase (melting, vaporization, and sublimation). (energy is required to break the intermolecular forces in a more condensed phase).

ΔH is negative for physical change from a less condensed to a more condensed phase (freezing, condensation, and deposition). (energy is released when intermolecular forces is formed in a less condensed phase).

The stronger is the interaction, the greater is ΔH



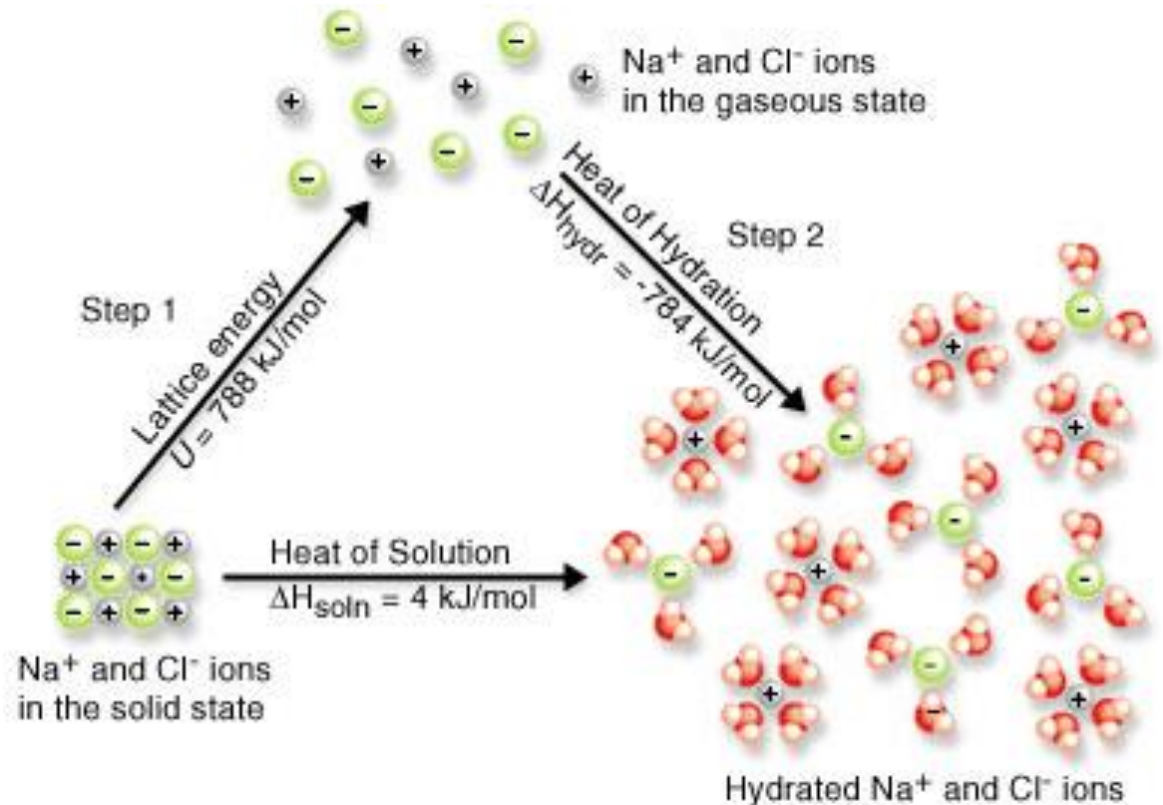
Enthalpy change

Enthalpy of solution

The *enthalpy of solution* (ΔH_{sol}) is the **heat absorbed or released** when a 1 mole of solute dissolves in a solvent.

The breaking of bonds in a crystal lattice is an endothermic process ($\Delta H_{lattice}$ is positive).

The formation of bonds between solute and solvent molecules (i.e. solvation) is an exothermic process (ΔH_{solv} is negative).



Enthalpy change

Enthalpy of solution

$$\Delta H_{\text{sol}} = \Delta H_{\text{lattice}} + \Delta H_{\text{solv}}$$

If $\Delta H_{\text{lattice}} > \Delta H_{\text{solv}}$

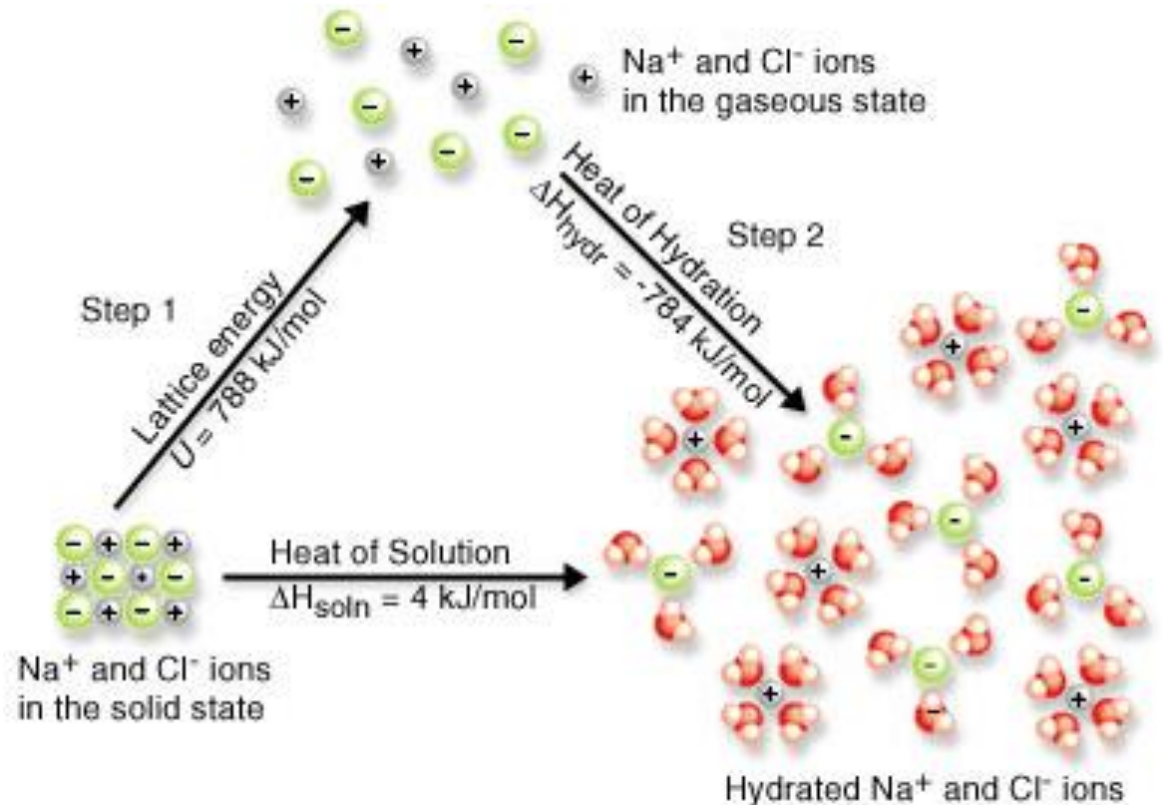
Then ΔH_{sol} is positive
(endothermic process)

e.g. NH_4NO_3

If $\Delta H_{\text{lattice}} < \Delta H_{\text{solv}}$

Then ΔH_{sol} is negative
(exothermic process)

e.g. CaCl_2



Enthalpy change

Enthalpy of solution

Example

The lattice enthalpy of potassium bromide KBr is 689 kJ/mol. The enthalpy of hydration of potassium bromide is -670 kJ/mol. Calculate the enthalpy of solution of KBr and indicate whether the process of KBr solution is endothermic or exothermic.

Heat capacity

Definition

Heat capacity is designated as C_p at constant pressure, and designated as C_v at constant volume.

The unit of heat capacity is a unit of energy per temperature (e.g. J/K and cal/K)

Heat capacity is an **extensive property** because it depends on the amount of the substance (e.g. 100 g of water has 100 times the heat capacity of 1 g of water)

Heat capacity

Types of heat capacity

Specific heat capacity is the amount of heat required to raise the temperature of 1 g of a substance by 1 K. Unit is $\text{J K}^{-1} \text{g}^{-1}$.

$$Q = C_s \times m \times \Delta T$$

Molar heat capacity is the amount of heat required to raise the temperature of 1 mole of a substance by 1 K. Unit is $\text{J K}^{-1} \text{mol}^{-1}$.

$$Q = C_s \times n \times \Delta T$$

Molar and specific heat capacities are **intensive properties** because they do not depend on the amount of the substance (all molar quantities are intensive).

Thermochemistry

Thermochemistry is a part of thermodynamic deals with the heat changes (ΔH) accompanying isothermal chemical reactions at constant pressure or volume.

The enthalpy of the reaction depends on the states of reactants and products and the temperature, therefore these factors are specified:



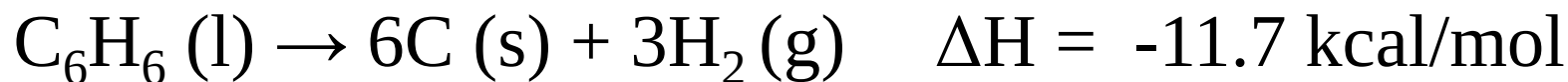
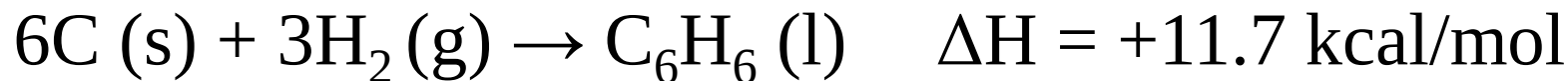
Enthalpy of reaction ΔH

For a chemical reaction ΔH is called a *enthalpy of reaction or heat of reaction*.

The enthalpy of reaction may be positive (heat is absorbed) or negative (heat is evolved).

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

By writing a reaction on paper in reverse direction, its ΔH changes sign:



Enthalpy is a *state function* (independent of the path).

Enthalpy of reaction ΔH

Standard enthalpy of reaction

The standard enthalpy of reaction ΔH° is the heat change when the chemical reaction occur under standard conditions.

The standard enthalpy of combustion ΔH°_c is the heat change when 1 mole of a substance is completely burnt in oxygen under standard conditions.

Combustion is always exothermic (ΔH°_c values are always negative)

The standard enthalpy of formation (ΔH°_f) is the heat change when 1 mole of a substance is formed from its elements in their most stable form.



ΔH°_f (water) = -571.6 kJ / 2 mole then 1 mole H_2O = -285.8 kJ mol⁻¹

Enthalpy of formation values can be either negative or positive

Thermodynamic reversibility

- A *thermodynamic equilibrium* is a state in which the system properties **are not undergoing** any changes with time.
- A **reversible process** is a process in which the system and environment can be restored to exactly the same initial states that they were in before the process occurred, if we go backward along the path of the process.

Thermodynamic reversibility

When an energy is permanently lost during a process (not converted to an internal energy), **the process is irreversible.**

An example of irreversible process is the conversion of mechanical work into frictional heat; there is no way, by reversing the motion of a weight along a surface, that the heat released due to friction can be restored to the system.

All real processes are **irreversible process**

Thermodynamic spontaneity

Some processes happen spontaneously, other processes don't.

E.g. Objects fall down spontaneously, but throwing them up requires an external work)

A *spontaneous process* is one that occurs “naturally” (without intervention). E.g. diamond converts to graphite.

A *non-spontaneous process* is one that does not occur “naturally” (needs intervention to occur). E.g. throwing objects up.

All spontaneous processes are **irreversible**.

2nd law of thermodynamics

This inability to predict the natural direction of a process based on energy considerations alone (e.g. ΔH) requires another state function.

The second law uses a new state function called entropy change (ΔS).

Entropy change (ΔS) represents the probability of the occurrence of a process and the tendency of a system to approach a certain state of energy equilibrium.

Entropy, S , is a thermodynamic quantity that is a measure of the randomness or disorder for the system or surroundings

2nd law of thermodynamics

The entropy change ΔS is equal to the heat change in an **isothermal reversible process** divided by the absolute temperature at which the heat change occurs.

$$\Delta S = \frac{Q_{rev}}{T}$$

Q_{rev} is the heat change in an isothermal reversible process (Joule)

T is the absolute temperature (Kelvin)

The units of entropy are energy per degree kelvin (J K^{-1} or cal K^{-1}).

The entropy change for the system depends only on its current state and is independent of the path.

Entropy change **ΔS is a state function**

Entropy change **ΔS is an extensive property**

2nd law of thermodynamics

The second law of thermodynamics states that *all natural processes are accompanied by a net gain in entropy of the system and its surroundings (i.e. $\Delta S > 0$).*

$$\Delta S_{\text{net}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Then the second law says

$\Delta S_{\text{net}} > 0$ (spontaneous processes ‘irreversible process’)

$\Delta S_{\text{net}} = 0$ (system at equilibrium ‘reversible processes’)

Since heat is added to the system, all entropy values are positive at temperatures above 0K.

Standard molar entropy values are indicated as S° and are for substances at 1 bar pressure and 1 molar solution concentration. The units for entropy are in J/K.mol.

ΔS° is calculated as

$$\sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants})$$

For similar substances: $S^\circ \text{ gas} > S^\circ \text{ liquid} > S^\circ \text{ solid}$

An increase in molecular weight lead to an increase in S°

CH₄ $S^\circ = 186.3 \text{ J K}^{-1} \text{ mol}^{-1}$

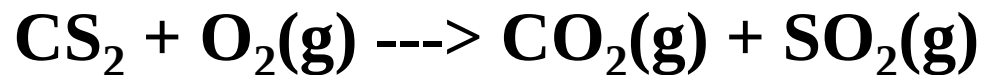
C₂H₆ $S^\circ = 229.6 \text{ J K}^{-1} \text{ mol}^{-1}$

C₃H₈ $S^\circ = 269.9 \text{ J K}^{-1} \text{ mol}^{-1}$

Which substance has the higher entropy in each of the following pairs? Explain your answers.

- CO_2 (at -78°C) or CO_2 at 0°C ?
- HF , HCl or HBr

Calculate the entropy change ΔS° for the following:



S(J/mole-K)

CO₂(g) 213.7

O₂(g) 205

CS₂(g) 151

SO₂(g) 248.1

Gibb's free energy

Free energy function ΔG

Free energy application

Free energy function ΔG

Definition

There are two factors involved in determining the direction of chemical change:

The system seeks to minimize its energy (ΔH)

The system seeks to maximize its entropy (ΔS).

Gibbs free energy ΔG , is a state function that links the first and second law of thermodynamics and determine the direction of a chemical change

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

Difference in energies
between products and
reactants

Change in thermal
energy spreading

Free energy function ΔG

Interpretation

If ΔG is **negative** it means that the process is **spontaneous**

If ΔG is **zero**, it means that the system is at **equilibrium**.

If ΔG is **positive** it means that the process is **not spontaneous**.

A more negative ΔH and a more positive ΔS favors spontaneous reaction, by making ΔG more negative.

If $T \Delta S < \Delta H$, and ΔH is negative, then ΔG will be negative (i.e. the process is spontaneous).

If $T \Delta S < \Delta H$, and ΔH is positive, then ΔG will be positive (i.e. the process is not spontaneous).

If $T \Delta S > \Delta H$, then ΔG will be negative (i.e. the process is spontaneous regardless whether ΔH is negative or positive).

Free energy application

Example 1

ΔH and ΔS for the transition from ice to liquid water at 25 °C and 1 atm are +1650 cal/mole and +6 cal/mole deg), respectively. Compute ΔG for the phase change and indicate whether the process is spontaneous.

The process leads to:

An increased freedom of molecular movement (ΔS is positive)

A increased molecular energy (ΔH is positive)

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

$$\Delta G = 1650 - (298 \times 6) = -138 \text{ cal/mole}$$

The process is spontaneous because $T \Delta S$ is sufficiently larger than the positive value of ΔH to make ΔG negative

Free energy application

Example 2

ΔH and ΔS for the transition from liquid water to ice at -10°C and at 1 atm pressure are -1343 cal/mole and -4.91 cal/mole deg, respectively. Compute ΔG for the phase change and indicate whether the process is spontaneous.

The process leads to:

A decreased freedom of molecular movement (ΔS is negative)

A decreased molecular energy (ΔH is negative)

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

$$\Delta G = (-1343) - [263 \times (-4.91)] = -51.67 \text{ cal/mole}$$

The process is spontaneous, as reflected by the negative value of ΔG .

References

- Connors, K. A. 2003. *Thermodynamics of Pharmaceutical Systems: An Introduction for Students of Pharmacy*, Wiley.
- Sinko, P. J. M. A. N. 2006. *Martin's physical pharmacy and pharmaceutical sciences: physical chemical and biopharmaceutical principles in the pharmaceutical sciences*, Philadelphia, Lippincott Williams & Wilkins.