



Unit 2

Use of free energy in chemical equilibria

Thermodynamic functions: energy, entropy and free energy.

Internal energy, Helmholtz free energy, Enthalpy (Definition, expression & explanation)

Gibbs's free energy, Entropy (Definition, expression & explanation)



Background

Thermodynamics Laws

Basic terminologies in thermodynamics



Essential factors for reaction

For a reaction to progress,

- The equilibrium must favour the products
- **Thermodynamics** (energy difference between reactant and product) should be favourable
- Reaction rate must be fast enough to notice product formation in a reasonable period.
- Kinetics (rate of reaction)



- As a subject it is concerned with quantification of the *inter-relation* between energy and the *change of state* of any real world system.
- The extent of such change of state due to transfer of energy *to* or *from* the system is captured through the basic equations of thermodynamics which are derived starting from a set of fundamental observations known as “**Laws of Thermodynamics**”.

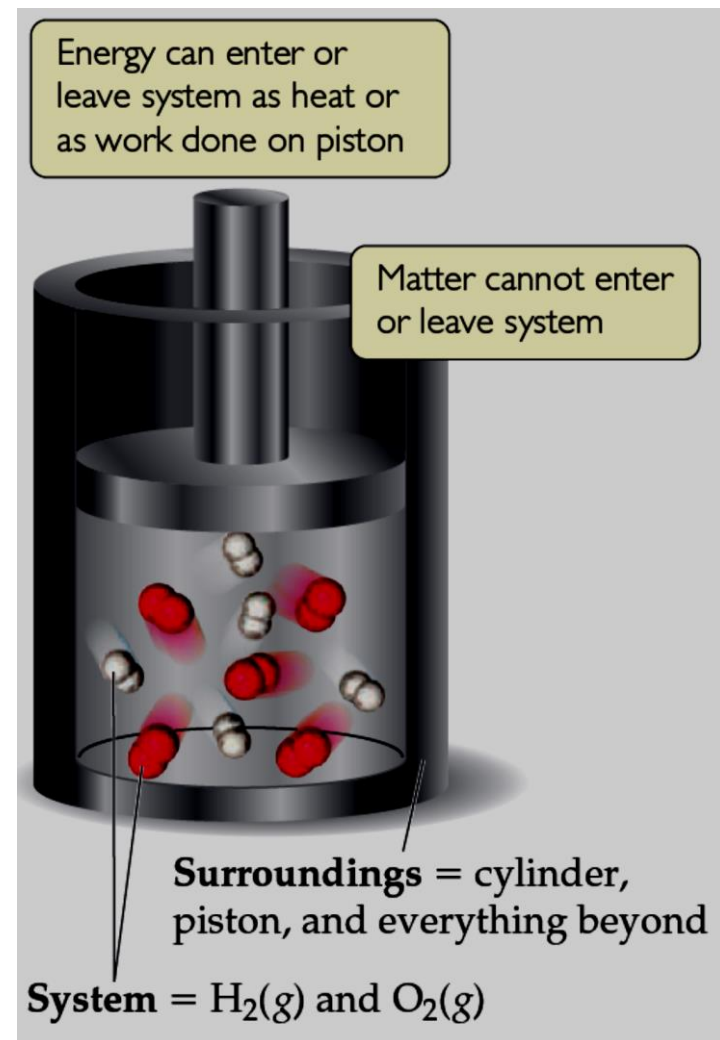


- The laws are essentially ‘postulates’ that govern the nature of interaction of real systems and energy. They are products of human experiential observations to which no exceptions have been found so far, and so are considered to be “laws”.
- The scope of application of the laws of thermodynamics ranges from the microscopic to the macroscopic order, and indeed to cosmological processes.
- Thus, all processes taking place in the universe, whether in non-living or living systems, are subject to the laws of thermodynamics.



Thermodynamic System: Select Definitions

- A **system**, in general, is any part of the universe which may be defined by a boundary which distinguishes it from the rest of the universe.
- Such a thermodynamic system is usually referred to as **control volume** as it would possess a volume and would also contain a definite quantity of matter.
- The **system boundary** may be real or imaginary, and may change in shape as well as in size over time, i.e., increase or decrease.

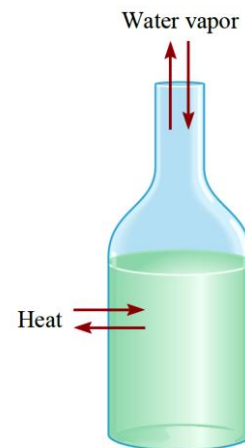




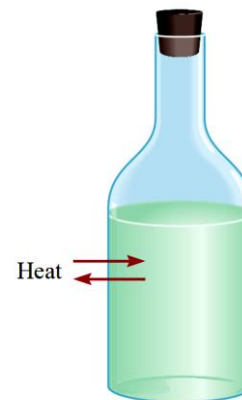
Thermodynamic System

- A system can either be *closed* or *open*.
- A **closed system** does not allow any transfer of mass (material) across its boundary, while an **open system** is one which does.
- In either case energy transfer can occur across the system boundary in any of its various forms; for example, heat, work, electrical / magnetic energy, etc.
- However, for most real world systems of interest to engineers the primary forms of **energy that may transfer across boundaries are heat and work**. In contrast to closed or open systems, a system which is enclosed by a boundary that allows neither mass nor energy transfer is an *isolated* system.

Open system



Closed system



Isolated system



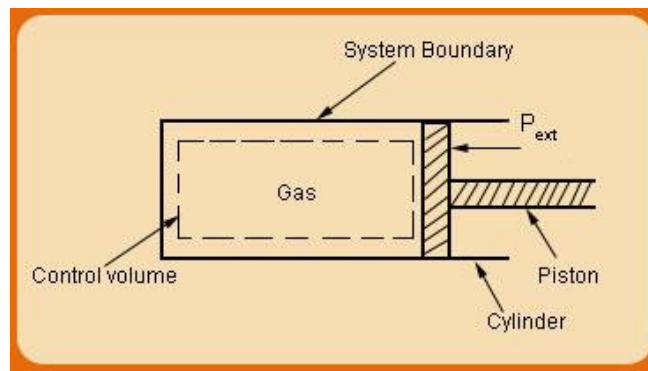


Thermodynamic System

All matter *external* to the system constitutes the ***surroundings***. The combination of the system and surroundings is called the ***universe***.

For all practical purposes, in any thermodynamic analysis of a system it is necessary to include only the immediate surroundings in which the effects are felt.

A very common and simple example of a thermodynamic system is a gas contained in a piston-and-cylinder arrangement derived from the idea of steam engines



Example of simple thermodynamic system



Intensive and extensive properties

Thermodynamic properties can be divided into 2 general classes such as intensive and extensive properties.

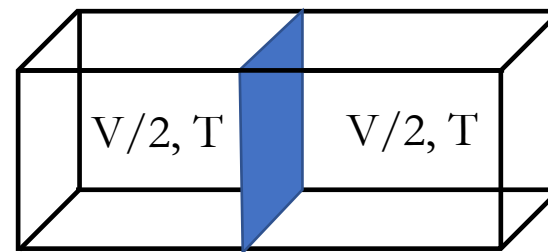
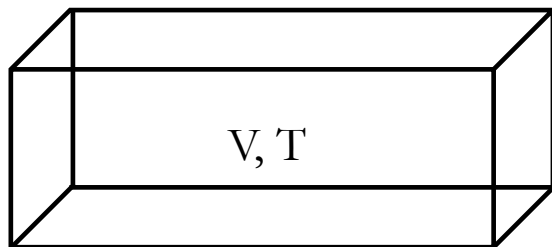
Intensive property, is a physical property of a system that does not depend on the system size or the amount of material in the system.

Examples: density, pressure and temperature

Extensive property of a system does depend on the system size or the amount of material in the system.

Examples: volume, internal energy

Temperature (intensive), mass (extensive), and number of moles (extensive)





Thermodynamic Variables

A **state function** is a quantity whose value is independent of the past history of the substance.

Typical state properties are **altitude, pressure, volume, temperature, and internal energy**.

Path functions are properties or quantities whose values depend on the transition of a system from the initial state to the final state.

The two most common path functions are heat and work.

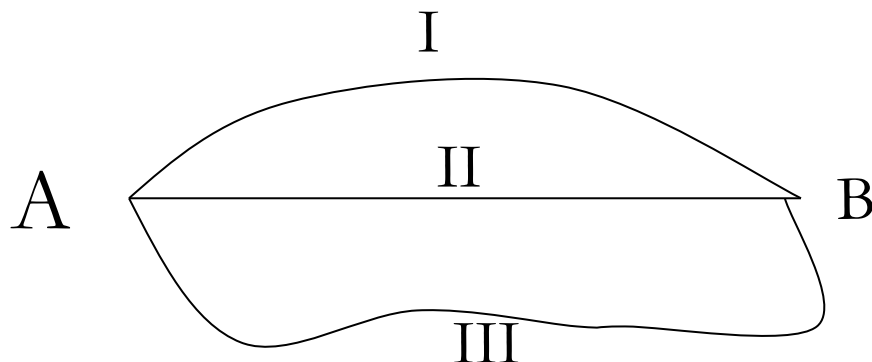
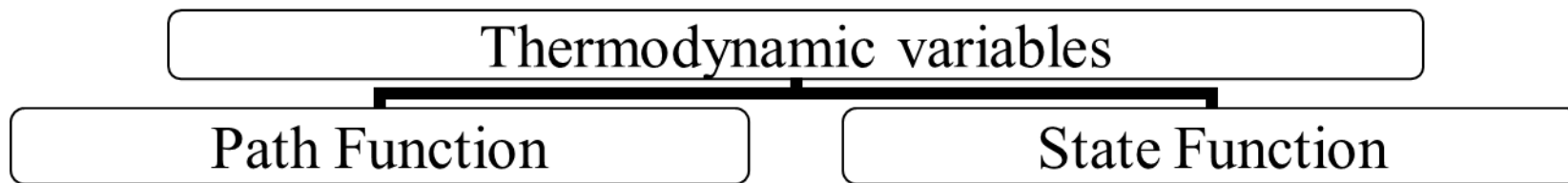
For path functions, the path from an initial state to the final state is crucial.

amount of work done is different





Thermodynamic Variables

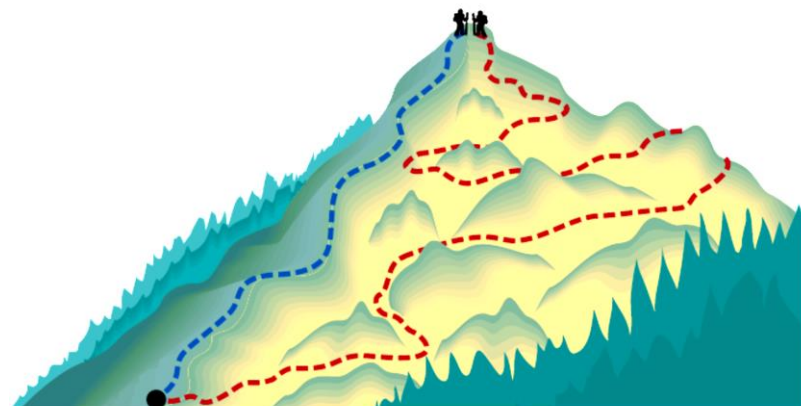


$$W_I \neq W_{II} \neq W_{III}$$

(Path Function)

$$(V_B - V_A)_I = (V_B - V_A)_{II} = (V_B - V_A)_{III}$$

(State Function)



V - Variable



Energy

- The **internal energy**, E (*or* U), of a system is the sum of *all* the kinetic and potential energies of the components of the system.
- Energy is converted to work, energy in the form of heat moves from one place to another, or energy is stored up in the constituent chemicals.
- *Change* in internal energy, denoted ΔE , as the difference between E_{final} and E_{initial} :

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

- We generally cannot determine the actual values of E_{final} and E_{initial} for any system of practical interest.
- Nevertheless, we can determine the value of ΔE experimentally by applying the first law of thermodynamics



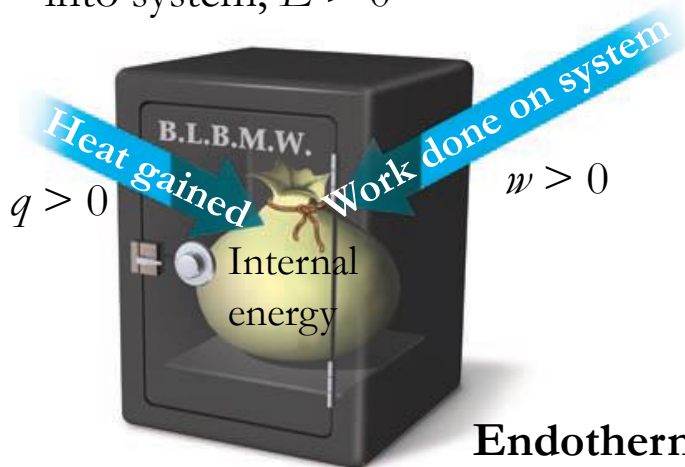
Energy

When a system undergoes any chemical or physical change, the accompanying change in internal energy, ΔE , is the sum of the heat added to or liberated from the system, q , and the work done on or by the system, w :

$$\Delta E = q + w$$

First law of thermodynamics

Energy deposited into system, $E > 0$



$w > 0$

Endothermic



System is interior of vault

Energy withdrawn from system, $E < 0$



$w < 0$

Exothermic

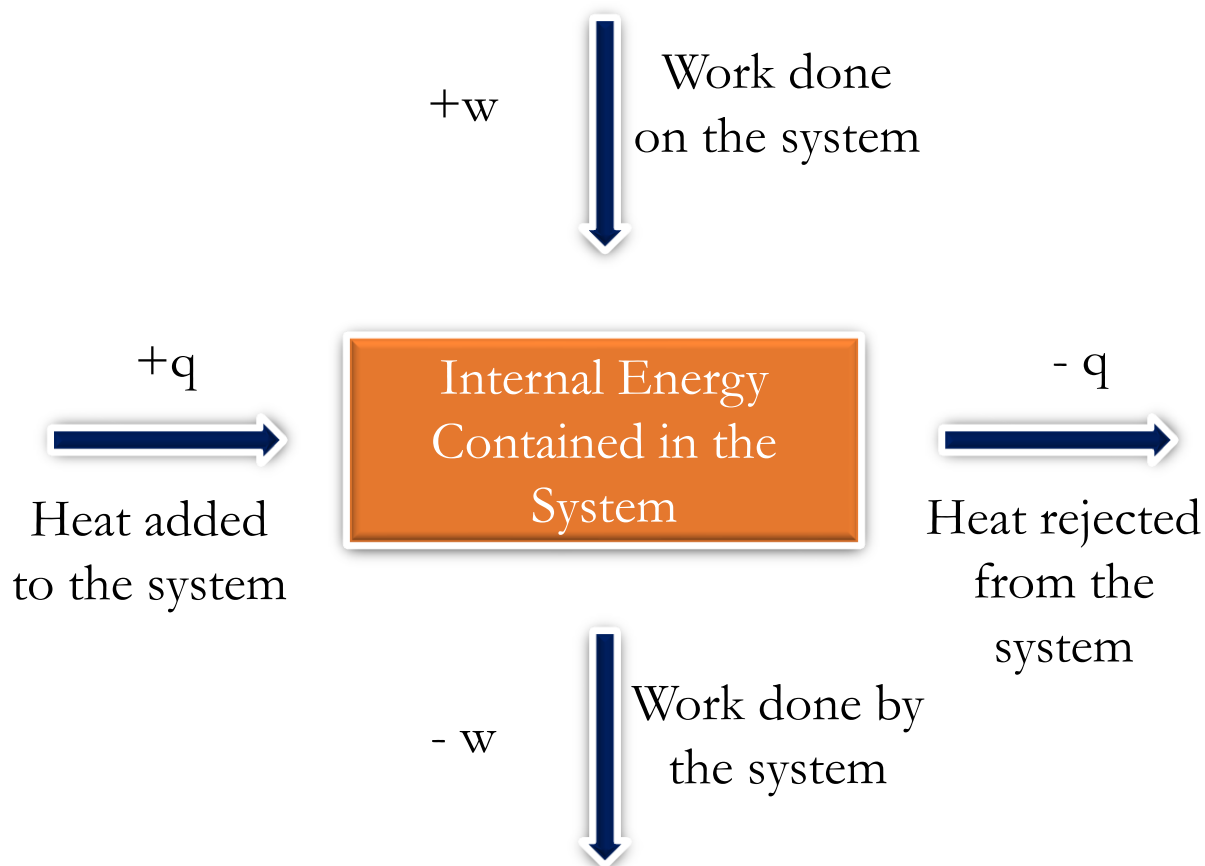


Energy

First law of thermodynamics

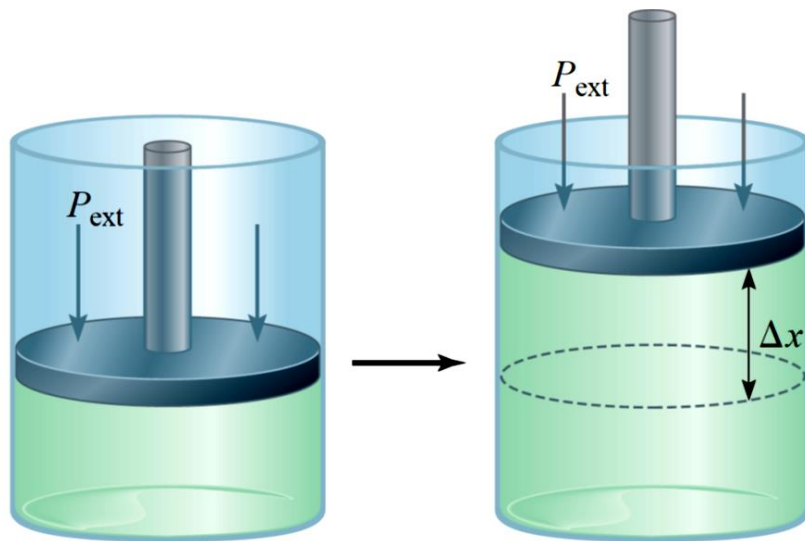
$$\Delta E = q + w$$

Energy neither be created nor be destroyed

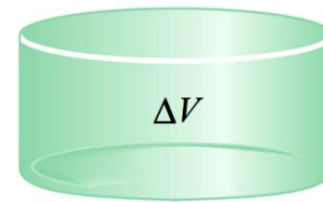




Work done by System



$\Delta V > 0$ for an expansion
work done by the system



$$\text{volume change} = l \times A = \Delta V = (V_f - V_i)$$

Pressure = force / area

$$\text{force on the piston} = p_{\text{ex}} \cdot A$$

$$\text{Work, } w = \text{force} \times \text{distance} = p_{\text{ex}} \cdot A \cdot l$$

$$= p_{\text{ex}} \cdot (-\Delta V) = -p_{\text{ex}} \Delta V = -p_{\text{ex}} (V_f - V_i)$$



Essential terms of thermodynamics.

- **Free energy change** (ΔG) –Overall free energy difference between the reactant and the product
- **Enthalpy** (ΔH) –Heat content of a system under a given pressure.
- **Entropy** (ΔS) – The energy of disorderness



Enthalpy

Enthalpy (heat inside) can be regarded as thermodynamic potential.

- It is a state function and an extensive quantity.
- It also refers to the **difference in bond energies** between the reactant and product.
- In short enthalpy is ‘the heat absorbed (or released) by a chemical reaction’.

If you have a chemical system that undergoes some kind of change but has a fixed volume, the heat output is equal to the change in internal energy ($q = \Delta E$).

We will define the **enthalpy change**, ΔH , of a system as being equal to its heat output at constant pressure:

$$\Delta H = q \text{ at constant pressure}$$

$$H = E + PV$$

H = enthalpy

E = energy of the system

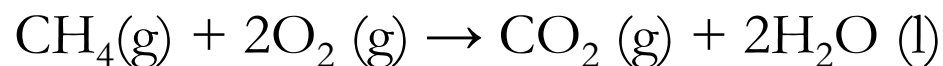
PV = pressure in atm times volume in liters



CALCULATION OF ENTHALPY

- Enthalpy is a measure of difference in bond energy between reactants and products.

E.g. Combustion of methane.



$$\Delta H_{\text{reaction}} = \sum n H(\text{products}) - \sum n H(\text{reactants})$$

$$\begin{aligned}\Delta H^\circ_{\text{comb}} &= [2 \Delta H^\circ_{\text{f,water}} + \Delta H^\circ_{\text{f,carbon dioxide}}] - [\Delta H^\circ_{\text{f,methane}} + 2 \Delta H^\circ_{\text{f,oxygen}}] \\ &= [2*(-286) - 394] - [-75 + 0] \quad (\Delta H^\circ_{\text{f,oxygen}} = 0 \text{ as oxygen is a pure element}) \\ &= -891 \text{ kJ mol}^{-1}.\end{aligned}$$

ΔH° is +ve when reaction is endothermic

ΔH° is -ve when reaction is exothermic



Entropy

- Measure of the disorder of a system
- Entropy comes from the second law of thermodynamics, which states that all systems tend to reach a state of equilibrium.
- The significance of entropy is that when a **spontaneous change occurs** in a system, it will always be found that if the total entropy change for everything involved is calculated, a **positive value** will be obtained.

$$\Delta S = S_{\text{final}} - S_{\text{initial}} \text{ or } \Delta S = S (\text{products}) - S (\text{reactants})$$

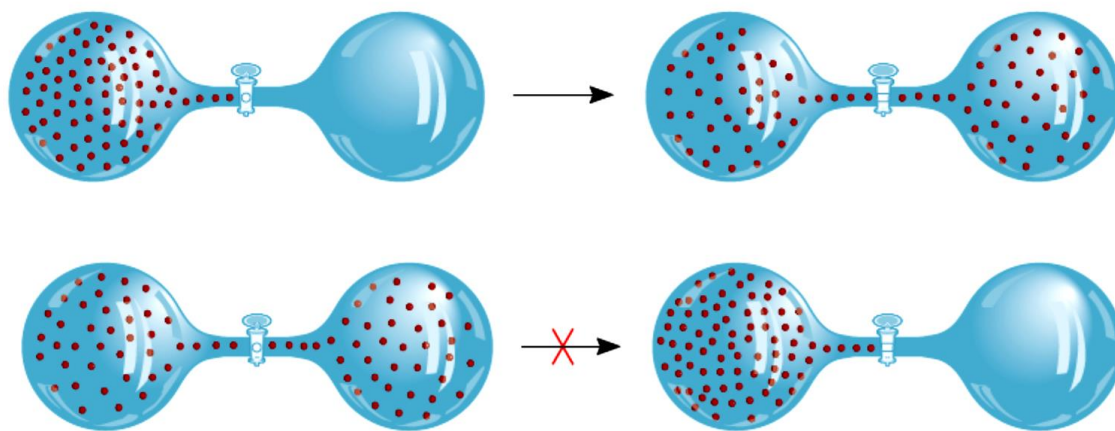
ΔS is change in entropy

S_{final} and S_{initial} are the final and initial entropies, respectively



Entropy

- The second law of thermodynamics states that the **entropy** of any closed system, not in thermal equilibrium, will almost **always increases**.
- Entropy is a thermodynamic property; it is the measure of energy (not used to perform work) but is dependent on temperature as well as volume.
- Entropy is directly proportional to **spontaneity**.





Entropy

- Comparison of entropies: Gases > liquids > solids (bromine gas has greater entropy than when in liquid state)
- Entropy is greater for larger atoms (as we move down in groups in periodic table) and molecules with larger number of atoms.
- Entropy is a measure of the number of ways particles as well as energy can be arranged.
- Entropy of an irreversible system always increases.

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

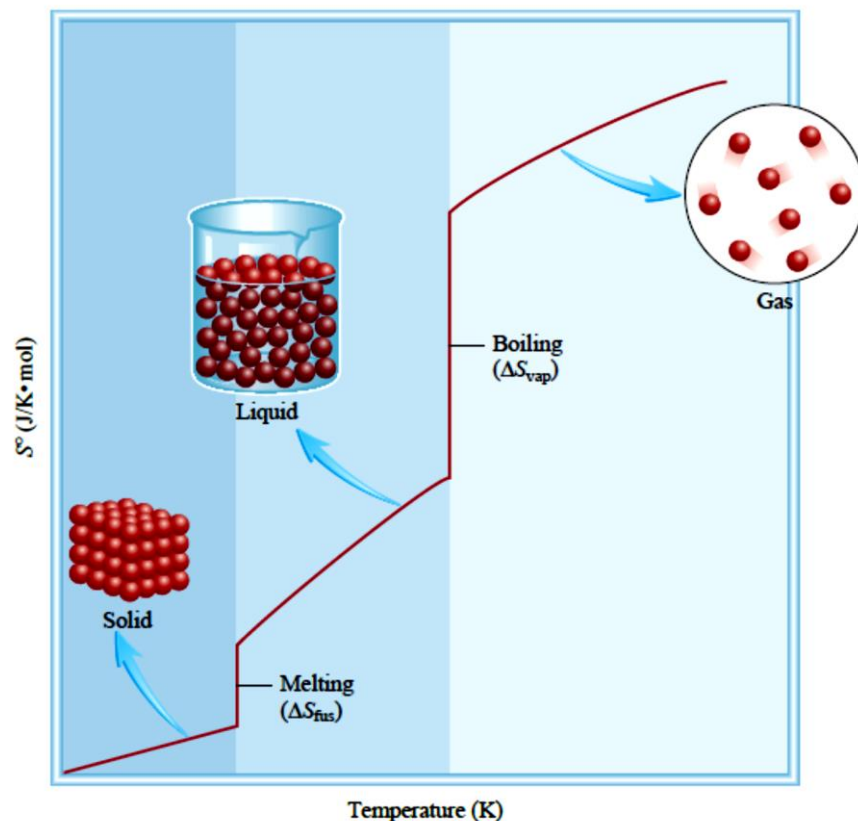
$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$$

For a spontaneous process



Absolute Entropy of a Substance

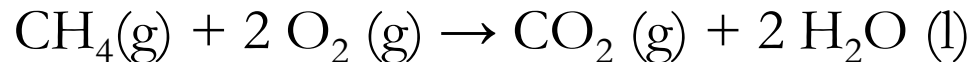
The third law of thermodynamics, which states that the entropy of a *pure substance* in its thermodynamically most stable form is *zero* at the *absolute zero of temperature*, independent of pressure.





CALCULATION OF ENTROPY

The standard entropy (ΔS°) of a substance is the value of entropy of the substance at 298 K and 1 atm.



From the Table of Thermodynamic Data, the Standard entropies of the substances involved in the above reaction are:

| substances | ΔS (J/K.mol) |
|--------------------------------|----------------------|
| $\text{CH}_4(\text{g})$ | 186 |
| $\text{O}_2(\text{g})$ | 205 |
| $\text{CO}_2(\text{g})$ | 214 |
| $\text{H}_2\text{O}(\text{l})$ | 70 |

The entropy change of the reaction can be calculated as:

$$\Delta S^\circ_{\text{reaction}} = \sum n_p S(\text{products}) - \sum n_r S(\text{reactants})$$

$$\Delta S^\circ = [214 + 70 * 2] - [186 + 205 * 2] = -242 \text{ J/K.}$$



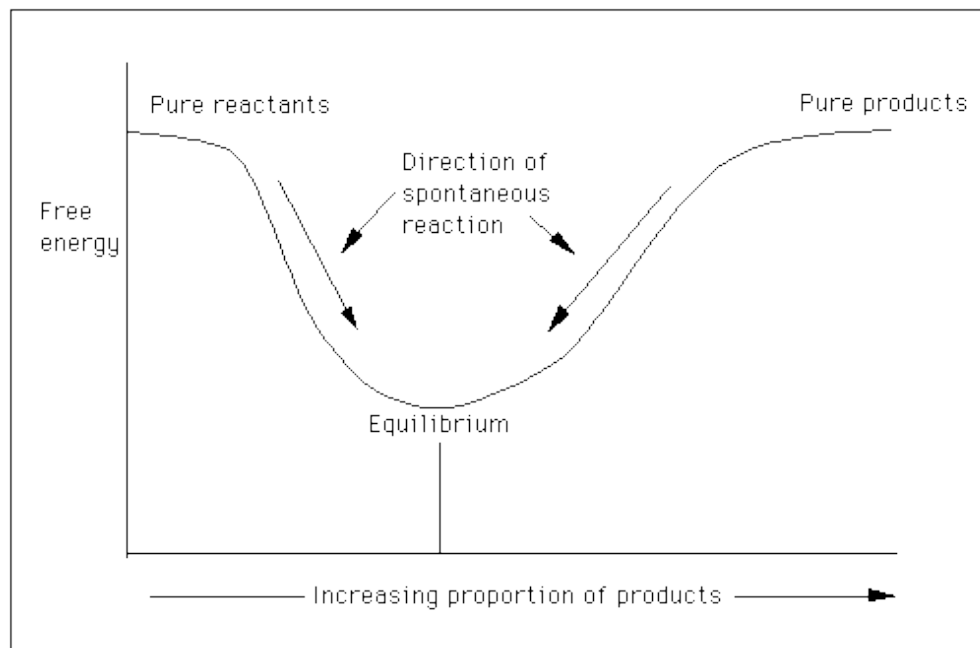
Free energy

- The Gibbs **free energy** is the maximum amount of non-expansion work that can be extracted from a closed system which can be attained only in a completely reversible process.
- The Gibbs free energy change at temperature T is expressed as,
$$\Delta G = \Delta H - T \Delta S$$
- In terms of standard states, when reactants and products at 1 M concentrations (or 1 atmosphere pressure), the free energy change is expressed as,
$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$



Free energy

Given a constant temperature and pressure, the direction of any spontaneous change is toward a lower Gibbs free energy.



The graphic shows that during a reaction, the amount of free energy decreases until the reaction is at equilibrium. If the reaction goes towards completion, the free energy maximum occurs very close to the pure products part of the curve. In other words, the curve moves depending on the conditions of the reaction.



Free energy

- For a reaction to be spontaneous
- The overall free energy at any concentrations of reactant and product is:

$$\Delta G = \Delta G^\circ + RT \ln[\text{product}]/[\text{reactant}]$$

Where R(gas constant) = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and

T(temperature) = in $^\circ\text{K}$

At equilibrium,

$$\Delta G^\circ + RT \ln[\text{product}]/[\text{reactant}] = 0$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$= -2.303 RT \log K_{eq}$$



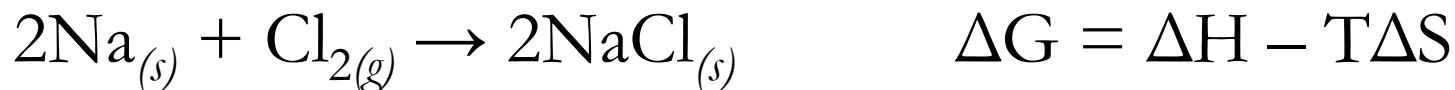
Free energy

For a reaction, equilibrium shifts in the direction of lower species.
Hence,

- $G^\circ (\text{reactant}) > G^\circ (\text{product})$ then,
 - reaction is spontaneous since $\Delta G^\circ < 0$.
 - i.e. **negative** and $K_{eq} > 1$
- $G^\circ (\text{reactant}) < G^\circ (\text{product})$ then,
 - reaction is nonspontaneous since $\Delta G^\circ > 0$
 - i.e. **positive** and $K_{eq} < 1$



Free energy



$$\Delta H = -822.24 \text{ kJ/mol} \quad \Delta S = -181.3 \text{ J/K}\cdot\text{mol} \quad T = 298 \text{ K}$$

- The ΔG for this reaction is -768.2 kJ/mol , so this reaction is **spontaneous** at this temperature.
- Although the entropy of the system decreases in this reaction, it is more than offset by the heat released to the surroundings.



VARIATION OF ΔG IN RELATION WITH ΔH & ΔS

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$$

| Enthalpy Change | Entropy Change | Spontaneous Reaction? |
|--------------------------------|-----------------------------|---|
| Exothermic ($\Delta H < 0$) | Increase ($\Delta S > 0$) | Yes, $\Delta G < 0$ |
| Exothermic ($\Delta H < 0$) | Decrease ($\Delta S < 0$) | Only at low temps, if $ T \Delta S < \Delta H $ |
| Endothermic ($\Delta H > 0$) | Increase ($\Delta S > 0$) | Only at high temps, if $ T \Delta S > \Delta H $ |
| Endothermic ($\Delta H > 0$) | Decrease ($\Delta S < 0$) | No, $\Delta G > 0$ |



Thermodynamic Laws: Outcomes

- **The Zeroth Law** deals with thermal equilibrium and provides a means for measuring temperatures.
- **The First Law** deals with the conservation of energy and introduces the concept of internal energy.
- **The Second Law** of thermodynamics provides with the guidelines on the conversion of internal energy of matter into work. It also introduces the concept of entropy.
- **The Third Law** of thermodynamics defines the absolute zero of entropy. The entropy of a pure crystalline substance at absolute zero temperature is zero.



Acknowledgements

<http://www.shodor.org/UNChem/advanced/thermo/#energy>

<http://nptel.ac.in/courses/103101004/1>