

Introduction to Thermodynamics

Chapter 1: Introduction to Thermodynamics (THD)

- I- Concept of system, quantities and state function (application to ideal gases)
- II- 1st principle of THD (Energy, work and heat (U,W,Q))
- III- Thermochemistry (enthalpy and heat of reaction)
- IV- 2nd Principle of THD: entropy and free enthalpy.

Every science has its own unique vocabulary associated with it. Precise definition of basic concepts forms a sound foundation for development of a science and prevents possible misunderstandings. Careful study of these concepts is essential for a good understanding of topics in thermodynamics.

I. Concept of system, quantities and state function (application to ideal gases)

I.1. Thermodynamics and energy

The name thermodynamics stems from the Greek words therme (heat) and dynamis (power). Thermodynamics can be defined as the study of energy, energy transformations and its relation to matter. Energy can be viewed as the ability to cause changes.

The analysis of thermal systems is achieved through the application of the governing conservation equations, namely *Conservation of Mass*, *Conservation of Energy* (1st law of thermodynamics), the 2nd law of thermodynamics and the property relations.

- First law of thermodynamics: An expression of the conservation of energy principle.
« During an interaction, energy can change from one form to another but the total amount of energy remains constant » \implies Energy cannot be created or destroyed.

- Second law of thermodynamics: energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy.

Whenever there is an interaction between energy and matter, thermodynamics is involved. Some examples include heating and air-conditioning systems, refrigerators, water heaters, etc.

I.2. Dimensions and Units

Any physical quantity can be characterized by dimensions. The arbitrary magnitudes assigned to the dimensions are called units. There are two types of dimensions, *primary* or *fundamental* and *secondary* or *derived* dimensions.

Primary dimensions are: mass, m ; length, L ; time, t ; temperature, T

Secondary dimensions are the ones that can be derived from primary dimensions such as: velocity (m/s²), pressure (Pa = kg/m.s²).

There are two unit systems currently available SI (International System) and USCS

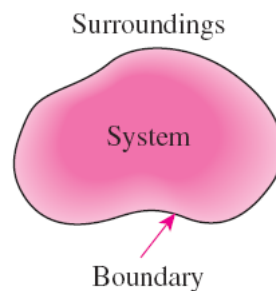
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(United States Customary System) or English system. We, however, will use SI units exclusively in this course. **The SI units are based on decimal relationship between units. The prefixes used to express the multiples of the various units are listed in Table 1-1.**

Important note: in engineering all equations must be dimensionally homogenous. This means that every term in an equation must have the same units. It can be used as a sanity check for your solution.

I.3. Definition of system

- **System:** A quantity of matter or a region in space chosen for study.
 - **Surroundings:** The mass or region outside the system
 - **Boundary:** The real or imaginary surface that separates the system from its surroundings.
- The boundary of a system can be *fixed* or *movable*.



- Systems may be considered to be *closed* or *open*.
- **Closed system or control mass :** consists of a fixed amount of mass, and no mass can cross its boundary. But, energy in the form of heat or work, can cross the boundary, and the volume of a closed system does not have to be fixed.
- **Open system or control volume :** is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor. Both mass and energy can cross the boundary of a control volume.
- **Isolated system :** A closed system that does not communicate with the surroundings by any means.



System	Matter exchange	Energy exchange	Example
opened	Yes	Yes	Living being
closed	No	Yes	Electric cells, closed reactor
isolated	No	No	Sealed bulb (Thermally insulated), universal

• **Properties of a System**

Any characteristic of a system is called a *property*.

- **Intensive properties** : are those that are independent of the size (mass) of a system, such as temperature, pressure, and density. They are not additive.
- **Extensive properties** : values that are dependant on size of the system such as mass, volume, and total energy U. They are additive.

◆ Generally, uppercase letters are used to denote extensive properties (except mass m), and lower case letters are used for intensive properties (except pressure P, temperature T).

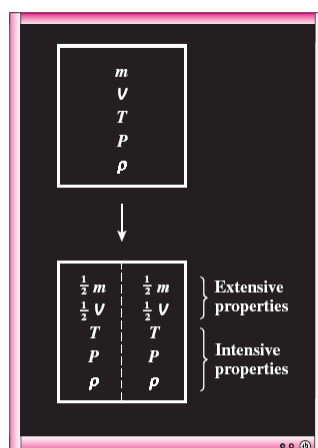


FIGURE 1-24
Criterion to differentiate intensive and extensive properties.

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◆ Extensive properties per unit mass are called specific properties, e.g. specific volume ($v=V/m$).

I.4. State and Equilibrium

The State of a system is defined by the values of the various intensive and extensive properties of the system (eg : P,T, V).

At a given *state*, all the properties of a system have fixed values. Thus, if the value of even one property changes, the state will change to different one.

- **Equilibrium** : is a state of balance, states variable have well defined, constant values.

State function :

Thermodynamic properties which depend on initial state and final state. Usually, we require at least 2 state variables to specify the state of system

For a perfect gas: $P.V - n R T = 0$ or ; $P V = n RT$

Variables	Functions
P ;V	$T = P.V / n.R \rightarrow f (P,V) = T$
V,T	$P = n.R.T / V \rightarrow f (V,T) = P$
P,T	$V = n.R.T / P \rightarrow f (P,T) = V$

- **Equation of state** :

The mathematical relationship between state variables is called the equation of state.

I.5. Equation of state for ideal gases:

- **Ideal gas** : An ideal gas is a theoretical concept in thermodynamics that describes a gas with certain idealized properties. These properties include negligible intermolecular interactions, perfectly elastic collisions between molecules.
- **Equation of state for ideal gases:**

Are relationships linking several state variables to each other, enabling a system to be described completely without knowing all the variables. The equation of state for a perfect gas is:

$$PV = nRT$$

Where **P** is the pressure, **V** is the volume; **R** is the molar gas constant

Eg : for a perfect gas : $PV = nRT$

Where: P: gas pressure;

V: volume of the gas;

n: number of moles of the gas;

T: gas temperature.

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R: perfect gas constant; $R = 8.31451 \text{ JK}^{-1}\text{mol}^{-1} = 2 \text{ cal K}^{-1}\text{mol}^{-1} = 0.082 \text{ l.atm K}^{-1}\text{mol}^{-1}$

State variables	P	V	T
SI	Pascale (Pa) 1 atm = 1,1325.105 Pa ; 1atm = 1,01325 Bar ; 1 atm = 760 mmHg.	m^3 $1\text{l} = 10^{-3} \text{ m}^3 = 1\text{dm}^3$	Kelven (K) ; $T(\text{K}) = t(^{\circ}\text{C}) + 273$

Note:

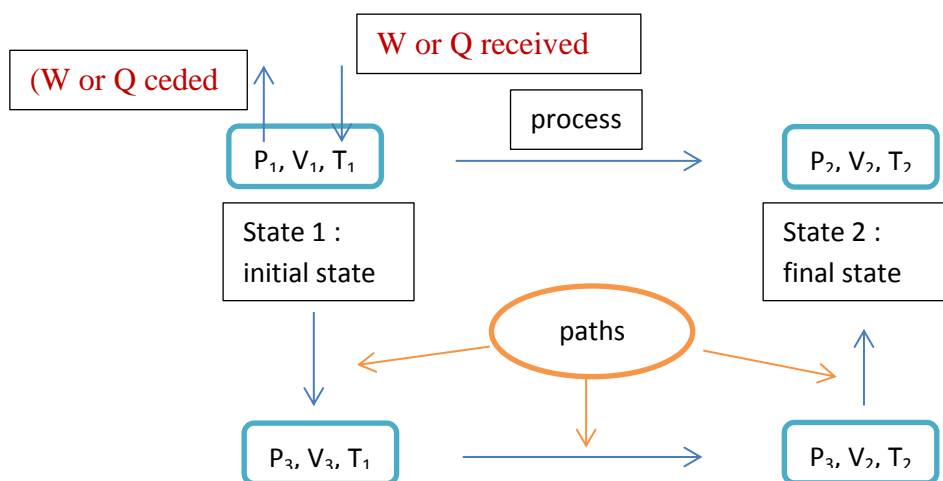
Standard temperature and pressure (STP):

$P = 1 \text{ atm} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg}$; $T = 0^{\circ}\text{C} = 273.15 \text{ K}$

I.6. Processes and Cycles

Process: Any change that a system undergoes from one equilibrium state to another.

Path: The series of states through which a system passes during a process.



- **State Functions :** Those thermodynamic properties which depend on initial and final state. e.g : $\Delta E, \Delta U, \Delta H, \Delta S, \Delta G$ etc.
- **Path function :** Those properties which depend on path

e.g : Work and heat

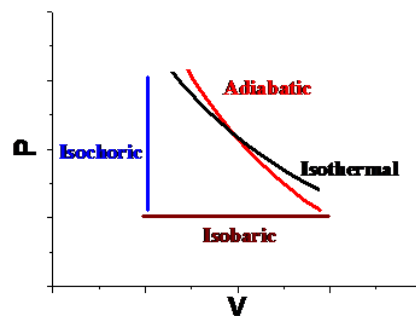
Typically, there are many possible paths that a system may take between two states.

I.7. Transformations of the state of a system (operation, evolution) (Thermodynamic Processes)

A system undergoes a thermodynamic process when there is some energetic change within the system that is associated with changes in pressure, volume, internal energy, temperature, or any sort of heat transfer.

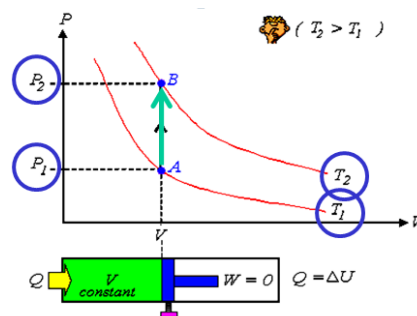
I.8. Graphical representation of perfect gas transformations :

Variations in the state of the system following a transformation are represented in various diagrams like Clapeyron. This is a simple graphical representation of pressure as a function of volume, $P = f(V)$.

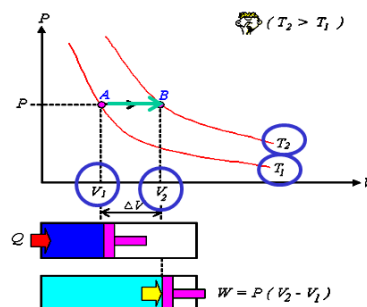


There are four types of thermodynamic processes that have their unique properties, and they are:

- Isochoric Process :** A process where no change in volume occurs and the system does no work.

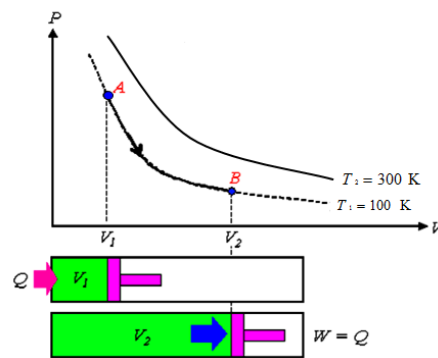


- Isobaric Process :** A process in which no change in pressure occurs.

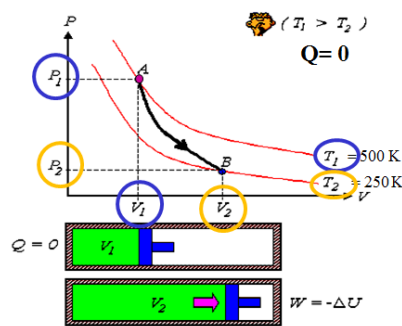


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- c. **Isothermal Process** : A process in which no change in temperature occurs.



- d. **Adiabatic Process** : A process where no heats transfer into or out of the system occurs.



- e. **Cyclic Processes** : These are series of processes in which after certain interchanges of heat and work, the system is restored to its initial state. $(P_i, V_i, T_i) = (P_f, V_f, T_f)$.

For ideal gass :

$(R=8.314 \text{ J/K.mol})$, T is temperature in Kelvin, and n is the number of mole of gas.

The ideal gas equation $PV = nRT$ encompasses the three laws that perfect gases obey:

a) Charles's Law:

At constant volume (V), the pressure (P) of a gas is proportional to its temperature (T).

$$P/T = \text{constant}, P_1/T_1 = P_2/T_2.$$

b) Gay-Lussac's Law:

At constant pressure (P), the volume (V) of a gas is proportional to its temperature (T).

$$V/T = \text{constant}, V_1/T_1 = V_2/T_2 \text{ (law of isobaric expansion).}$$

c) Boyle-Mariotte law

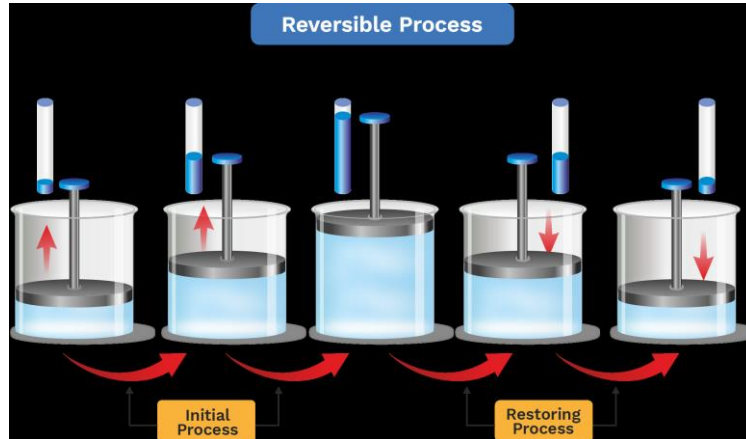
At constant temperature (T), the volume (V) of a gas is inversely proportional to its pressure (P).

$$PV = \text{constant}, P_1V_1 = P_2V_2 \text{ (law of isothermal compressibility).}$$

I.9. Reversible and irreversible transformation

Reversible transformation :

A transformation is reversible if the opposite transformation passes through the same intermediate states in reverse order. It is an infinitely slow transformation.



Irreversible transformation

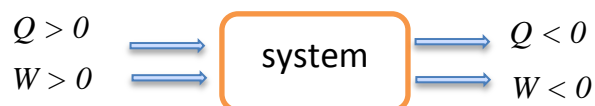
Any non-reversible transformation is irreversible. One of the main causes of irreversibility is the presence of friction, which degrades energy in the form of heat. During a transformation, the system's state variables change to reach a new equilibrium state.



I.10. Possible transfers between the system and the external environment

The transfer between the system and the external environment can be either energy transfer (*work and heat*)

During an exchange with the external environment, the system can either give or receive energy.



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➤ Sign convention for heat, Q :

$Q = \text{positive value}$ \Rightarrow heat enters the system (endothermic process)

$Q = \text{negative value}$ \Rightarrow the system gives up heat to the outside environment

➤ Sign convention for work, W :

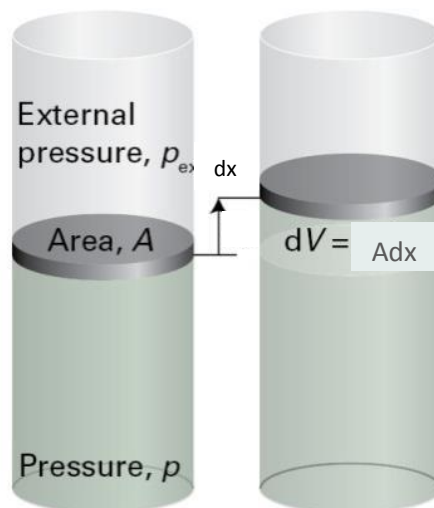
$W = \text{positive value}$ \Rightarrow the system receives work (receiving system);

$W = \text{negative value}$ \Rightarrow system supplies work (driving system).

Unit: [W]: Joule ; [Q]: Joule or calorie; with: **1 calorie = 4.18 joules.**

Concept of work: Expression of the work of the pressure forces:

Work is defined as the action of an external force on an object over a distance. It is equal to the product of the force (F) times the displacement (x).



For a small displacement dx due to force F , work done on the system.

$$\left\{ \begin{array}{l} dW = F \cdot dx \\ F = PA \end{array} \right. \Rightarrow \boxed{dW = PA \cdot dx}$$

[Here P = pressure, A = Area, V = volume]

$$\left\{ \begin{array}{l} V = (l-x)A \\ \Rightarrow dV = -A \cdot dx \\ \Rightarrow dW = -P_{\text{ext}} \cdot dV \end{array} \right. \Rightarrow \boxed{W_{PV} = -P_{\text{ext}} \int_{V_1}^{V_2} dV}$$

Units of work :
 [W] = Pa.m³ = Joules
 [W] = l. atm (**1 l.atm = 101.325 J**)
 [W] = Cal (**1 Cal = 4.185 J**)

Note:

$$W = - \int_1^2 p dV$$

- If $V_2 < V_1$ (compression), $\Delta V < 0$ and $W > 0$, indicating that the system receives work from the external surroundings.
- If $V_2 > V_1$ (expansion), $\Delta V > 0$ and $W < 0$, indicating that the system provides work to the external surroundings.
- **Work for the different transformations for an ideal gas: (Reversible case):**

a. Isochoric Transformation : (V constant , dV =0) :

$$W = 0$$

b. Isobaric Transformation : (p constant)

$$W = -P (V_2 - V_1) = -nR (T_2 - T_1)$$

c. Isothermal Transformation:

$$W = - \int p dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{p_2}{p_1} = P_1 V_1 \ln \frac{p_2}{p_1}$$

$$(P_1 V_1 = P_2 V_2)$$

Concept of Heat Q :

- **Définition :**

Heat (Q) is a form of energy that is transferred from one part of a system to another or to another system by virtue of a difference in temperature.

In this case, the amount of heat exchanged is proportional to the temperature difference. ($\Delta T = T_2 - T_1$) and to the mass (m) of the system.

The expression for the quantity of heat (or heat) is:

$$\delta Q = m \cdot c' \cdot dT$$

$$Q = \int_{T_1}^{T_2} mc' dT \quad \Rightarrow$$

m: mass of the substance (g or Kg).

c': Specific heat capacity (cal (J) / g(Kg).°C(K)).

ΔT : temperature variation (°C or K).

T₁: initial temperature (K).

T₂: final temperature (K).

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We can also write:

$$\delta Q = n \cdot c \cdot dT$$
$$Q = \int_{T_1}^{T_2} n c dT$$



Units of heat :

[Q] = Joule (J)

[Q] = calorie (cal)

With :

n: number of moles.

c: Molar specific heat capacity (cal (J) / mol.°C(K)).

Note:

If c' (c) is constant, we will have:

$$Q = mc'\Delta T \text{ Or } Q = n c \Delta T$$

$$\text{With : } \Delta T = T_2 - T_1$$

Note:

Q<0 the reaction is exothermic.

Q>0 the reaction is endothermic

Q = 0 the reaction is athermic

II. First law of thermodynamics : (The Law of Conservation of Energy)

The first law of Thermodynamics. The total energy of an isolated system is conserved under any thermodynamical change. This means that energy cannot be created or destroyed, but it can be converted from one form to another

II.1. Change in Internal energy (ΔU)

Suppose gas starts from state A, undergoes thermodynamic changes & attains a final state B.

The change in internal energy :

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

Note : For an isolated system, from the 1st Law $\Delta U = 0$.

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For a non-isolated system, the variation in its internal energy is equal to the quantity of energy exchanged with the external environment the variation in its internal energy is equal to the quantity of energy exchanged with the external environment, by thermal transfer (heat) and mechanical transfer (work)".

$$\begin{aligned}\Delta U &= Q + W \\ \text{And} \\ \Delta U &= n c_v \Delta T \\ \text{So that} \\ \Delta U_{\text{system}} &= - \Delta U_{\text{surrounding}}\end{aligned}$$

Notes :

ΔU independent of the path taken but **dependent** only on the **initial** and **final states** of the system (ΔU is state functions).

Work done on or by system and heat exanged depend on the path taken (Q and W are not state functions).

Internal energy for the different transformations for an ideal gas: Reversible case:

For an elemental transformation, we have: $dU = \delta Q + \delta W$

a. At constant volume:

$$\Delta U = U_2 - U_1 = Q_v + W = Q_v - \int_1^2 p dV$$

Isochoric transformation $V = \text{constant}$ $dV = 0 \Rightarrow W = 0$

$$\Delta U = U_2 - U_1 = Q_v = n c_v \Delta T$$

ΔU represents the heat exchanged at constant volume.

b. At constant pressure:

$$\Delta U = U_2 - U_1 = Q_p + W = Q_p - p (V_2 - V_1) \quad (Q_p = n c_p \Delta T \text{ as we will see down})$$

c. At constant temperature :

$$\Delta U = n c_v \Delta T = 0 \Rightarrow Q = - W$$

II.2. Enthalpy of the system :

We define a new state function $dH = dU + d(PV)$; **H : Enthalpy of the system.**

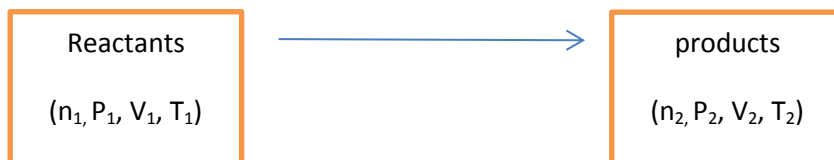
$$\Delta H = H_2 - H_1 = n c_p \Delta T = Q_p$$

$\Delta H < 0$ the reaction is exothermic.

$\Delta H > 0$ the reaction is endothermic.

III. Applications of the first principle of thermodynamics to thermochemistry

The study of thermal changes accompanying chemical transformations is known as thermochemistry



III.1. Heat of reaction

The heat of reaction is defined as the amount of heat liberated or absorbed at a given temperature when the reactants are converted into products as represented by the balanced chemical equation.

Let's consider a closed system undergoing a chemical reaction assumed to be complete:



Generally, chemical reactions are carried out at constant pressure ($p = \text{constant}$).

If: $\Delta H < 0$ The reaction is exothermic

If: $\Delta H > 0$ The reaction is endothermic

Relationship between ΔH et ΔU :

$$H = U + PV \longrightarrow \Delta H = \Delta U + \Delta(PV) ;$$

For an ideal gas, $PV = nRT$, by replacing PV with its expression, we obtain.

$$\Delta H = \Delta U + \Delta(nRT) \longrightarrow \Delta H = \Delta U + \Delta nRT$$

The relationship between enthalpy and internal energy is expressed as:

$$\Delta H = \Delta U + \Delta n_g RT \text{ with } \Delta n_g = \sum n_i (\text{gaseous products}) - \sum n_i (\text{gaseous reactants})$$

In order to compare the heats of different reactions, it is necessary to specify the conditions under which these reactions are carried out. We then define the standard enthalpy of reaction ΔH°_R for each reaction, which represents the change in enthalpy accompanying the reaction under standard conditions.

Standard state and heat of reaction

is the physical state under which a pure substance is most stable. A substance is in the standard state when it is taken at $P^\circ = 1 \text{ bar} = 10^5 \text{ Pa} = 0.9872 \text{ atm} = 750 \text{ mmHg}$ and at a temperature T (typically $T = 25^\circ\text{C}$).

Internal energy and standard enthalpy: The internal energy ΔU and standard enthalpy ΔH characterize a substance in its standard state at $P^\circ = 1 \text{ bar}$, and they are denoted as ΔU° and ΔH° .

Standard enthalpy types :

ΔH°	Definition	Example
3. Standard enthalpy of formation: ΔH_f°	is the enthalpy change accompanying the formation of one mole of the compound from its elements in their most stable state, all substances being in their standard state.	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g})$ $\Delta H_f^\circ = -57,88 \text{ Kcal/mol}$ $\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$ $\Delta H_f^\circ = -17,89 \text{ Kcal/mol}$
	<p>Note : the standard enthalpy of formation of elemental substances = 0</p> <p>eg : $\Delta H_f^\circ(\text{O}_2) = 0$; $\Delta H_f^\circ(\text{Cl}_2) = 0$; $\Delta H_f^\circ(\text{C}) = 0$</p>	
Enthalpy of phase change	It corresponds to the latent heat L of the phase change if the given temperature is the temperature of the phase change.	$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g}) \Delta H_{\text{vap}}^\circ, \text{H}_2\text{O} = L_v$ $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l}) \Delta H_{\text{fus}}^\circ, \text{H}_2\text{O} = L_f$ $\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{g}) \Delta H_{\text{sub}}^\circ, \text{I}_2 = L_s$
Bond energy	Enthalpy of formation of a chemical bond : Atom A(g) + Atom B(g) \longrightarrow Molecule AB(g) Similarly, we define the dissociation energy, which	$\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$ $\Delta H_f(\text{H}_2\text{O})$ $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g}) (\Delta H_{\text{diss}}(\text{H-H}))$ $\frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{O}(\text{g}) (1/2\Delta H_{\text{diss}}(\text{O-O}))$ $2 \text{H}(\text{g}) + \text{O}(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g})$

corresponds to the energy $2\Delta H_L(\text{OH})$ required to break a covalent bond. It has the same absolute value as the bonding energy but with the opposite sign. $\Delta H^\circ_{\text{diss}} = -\Delta H^\circ_L$

Calculation of Reaction Enthalpies: Hess's Law

a) Direct method:

Determination of reaction heats from the enthalpies of formation of compounds:

Consider the following reaction: $aA + bB \longrightarrow cC + dD$

The knowledge of the enthalpies of formation of the products and reactants allows us to determine the enthalpy of the reaction:

$$\Delta H^\circ_{R,298} = [(c \Delta H^\circ_f(\text{C}) + d \Delta H^\circ_f(\text{D})) - (a \Delta H^\circ_f(\text{A}) + b \Delta H^\circ_f(\text{B}))]$$

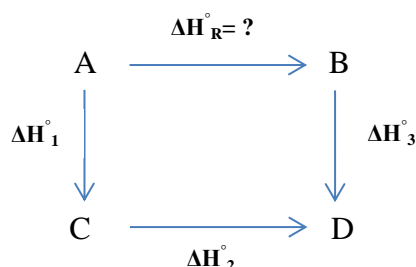
In the general case:

$$\Delta H^\circ_{R,298} = \sum v_j \Delta H^\circ_{f,298K}(\text{products}) - \sum v_i \Delta H^\circ_{f,298K}(\text{reactants})$$

Where v_i and v_j are the stoichiometric coefficients of the reactants and products of the reaction.

b) Indirect method:

When a global reaction can be replaced by a series of reactions occurring at the same temperature, the overall enthalpy change is the sum of the enthalpy changes of the individual reactions.



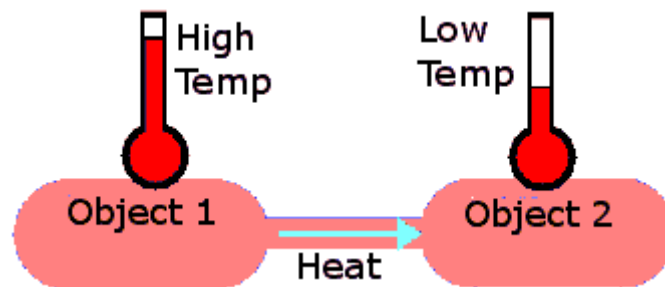
$$\Delta H^\circ_R = \sum \Delta H^\circ_i \longrightarrow \Delta H^\circ_R = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3$$

Hess's law: "If a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps."

- Because ΔH is a state function, the total enthalpy change depends only on the initial state (reactants) and the final state (products) of the reaction. It doesn't matter how you get there.

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does not guarantee that the process will occur. Thus, we need another general principle (second law) to identify whether a process can occur or not.



When a hot body comes into contact with a cold body, heat transfers from the hot body to the cold body until thermal equilibrium is reached. The reverse transformation never occurs spontaneously. However, the first principle of thermodynamics does not prohibit this transformation; it only requires the conservation of energy. In chemistry, it is important to determine the direction of the reaction's evolution. The second principle of thermodynamics is a principle of evolution based on the concept of **entropy**.

Concept of entropy:

4.2.1. Thermodynamic definition:

Let's consider a closed system, the degree of randomness or disorderness is known as entropy.

The elementary variation in entropy is the sum of two terms:

$$\Delta S_{univers} = \Delta S_{sys} + \Delta S_{ext}$$

ΔS_{sys} : Entropy of the system.

ΔS_{ext} : Entropy of the external environment.

Total entropy change for the universe is always (positive)

- If $\Delta S_{univers} < 0 \Rightarrow$ Impossible transformation ;
- If $\Delta S_{univers} = 0 \Rightarrow$ Reversible transformation ;
- If $\Delta S_{univers} > 0$ Irreversible transformation.
- **Entropy (S)**

1. Degree of randomness or disorderness is known as entropy and is an extensive quantity expressed in **J/K**.

2. Entropy change for a system

$$\Delta S_{syst} = S_2 - S_1 = \int_1^2 \frac{dq}{T}$$

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- ✚ If $\Delta S > 0$ corresponds to an increase in disorder;
- ✚ If $\Delta S < 0$ corresponds to an increase in order;
- ✚ The variable ' ΔS ' depends only on the initial and final states of the system.

Variation of entropy during transformations of a system

III-2-2-1-Entropy of an isolated system

- ✚ The entropy of an isolated system is zero.

$$dS = 0$$

a. Reversible transformation

The entropy of an isolated system remains constant during a reversible transformation.

$$\Delta S_{\text{sys}} = S_2 - S_1 = \int_1^2 \frac{dq}{T} = 0 \Rightarrow S_2 = S_1$$

b.

Irreversible transformation

The entropy of an isolated system increases during an irreversible transformation.

$$\Delta S_{\text{sys}} = S_2 - S_1 = \int_1^2 \frac{dq}{T} > 0 \Rightarrow S_2 > S_1$$

III-2-2-2- Entropy of a non-isolated system (Entropy of ideal gases):

a. Isobaric transformation

$$P = \text{Cte} \Rightarrow dQ_p = nC_p dT \Rightarrow \Delta S = \int_1^2 \frac{dQ_p}{T} = \int_{T_1}^{T_2} \frac{nC_p dT}{T} = n.C_p \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S = n.C_p \ln \frac{T_2}{T_1} = n.C_p \ln \frac{V_2}{V_1}$$

b. Isochore transformation

$$V = \text{Cte}, dQ_v = nC_v dT \Rightarrow \Delta S = \int_1^2 \frac{dQ_v}{T} = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = n.C_v \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S = n.C_v \ln \frac{T_2}{T_1} = n.C_v \ln \frac{p_2}{p_1}$$

c. Isothermal transformation

$$T = \text{Cte} \Rightarrow \Delta U = 0 \Rightarrow W + Q = 0 \Rightarrow Q = -W = \int_1^2 P dV = nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = \int_1^2 \frac{dQ}{T} = \frac{nRT}{T} \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{p_1}{p_2}$$

d. Adiabatic transformation

$$dQ = 0 \Rightarrow \Delta S = 0$$

III-2-2-3- Entropy variation in a chemical reaction

Consider a chemical reaction taking place at constant temperature and pressure:



$$\Delta S_R = S_{\text{final}} - S_{\text{initial}} = cS(C) + dS(D) - aS(A) - bS(B)$$

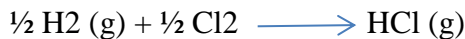
$$\Delta S_R = \sum v_j S^{\circ} T (\text{products}) - \sum v_i S^{\circ} T (\text{reactants})$$

Under standard conditions at 298 K, the entropy change $\Delta S^{\circ} 298K$ is:

$$\Delta S^{\circ} 298 = \sum v_j S^{\circ} 298 (\text{products}) - \sum v_i S^{\circ} 298 (\text{reactants})$$

Example 1:

Let's determine the entropy change $\Delta S^{\circ} 298$ during the formation of one mole of hydrochloric acid according to the following reaction carried out at 298 K, under a pressure of 1 atmosphere:



$$\Delta S^{\circ} 298 = S^{\circ} 298(HCl) - \frac{1}{2} S^{\circ} 298 (Cl_2) - \frac{1}{2} S^{\circ} 298(H_2) = 2,35 \text{ cal/mol.K} > 0$$

4.7. Variation of $\Delta S^{\circ} R$ with temperature:

Consider a chemical reaction taking place at constant pressure:



By knowing $\Delta S^{\circ} 298$ of this reaction, we can determine $\Delta S^{\circ} T$ using the following Kirchhoff's equation:

$$\Delta S^{\circ} T = \Delta S^{\circ} 298 + \int_{298}^T C_p \frac{dT}{T} \quad \text{at } p = \text{constant}$$

$$\Delta C_p = \sum v_j c_{p,j} (\text{products}) - \sum v_i c_{p,i} (\text{reactants})$$

If the reaction occurs at constant volume, Kirchhoff's relation becomes:

$$\Delta S^{\circ} T = \Delta S^{\circ} 298 + \int_{298}^T C_V \frac{dT}{T} \quad \text{at } V = \text{constant}$$

$$\Delta C_p = \sum v_j c_{v,j} (\text{products}) - \sum v_i c_{v,i} (\text{reactants})$$

Introduction to Thermodynamics

Free energy and enthalpy:

6.1.1. Free enthalpy:

1. Definition :

According to the 2nd law of thermodynamics, a transformation is spontaneous (irreversible) if:

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{ext}} > 0$$

Or: $\Delta S_{\text{ext}} = \frac{Q_{\text{sys}}}{T}$ ($Q_{\text{ext}} = -Q_{\text{sys}}$) when the transformation is carried out at a constant temperature T.

For an isobaric transformation: $Q_{\text{sys}} = \Delta H_{\text{sys}}$ $\Delta S_{\text{ext}} =$

From where: $\Delta S_{\text{sys}} > 0$ $T \Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$ $\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} < 0$

By definition the term: $\Delta H - T \Delta S$ is called “free enthalpy” or “GIBBS function” denoted ΔG hence

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

$$G = H - TS$$

$$dG = dH - TdS$$