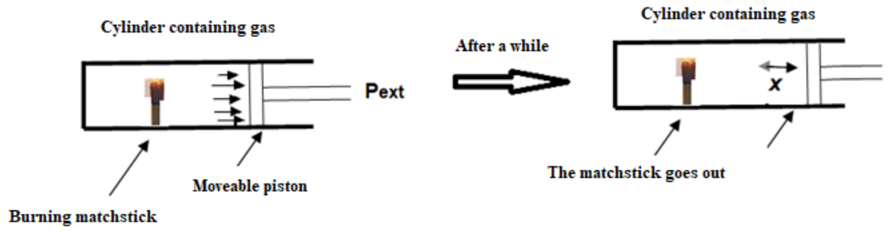
# The first law of thermodynamics

**1-Internal energy:** The internal energy of a system is the energy possessed by that system due to its mass, temperature, chemical composition, and the interactions between its various components. It is related to the forces acting between the molecules and the motion of these molecules (rotation, vibration, etc.). We represent it as U.

In thermodynamics, we cannot calculate the absolute value of internal energy for a system, but we can only calculate the change (ΔU).

**2-Text of the First law**: The first law of thermodynamics is synonymous with the law of conservation of energy and states that energy is neither created nor destroyed (cannot be created from nothing nor vanish into nothingness), but can only be converted from one form to another during reactions or chemical changes. This means that the energy of an isolated system remains constant

**Example:**



During the ignition of the matchstick ⟹ Thermal energy ⟹ Heat quantity ⟹ It works to increase the kinetic energy of gas molecules

And thus, causing the piston to move by a distance x ⟹ Meaning that thermal energy has been converted into mechanical work

- The change in the internal energy of a closed system is equal to the energy exchanged (in the form of work and heat) between the system and the external surroundings.
  Where:

**The integral of the elemental internal energy** →

**Work** $w$

**quantity of heat** $Q$

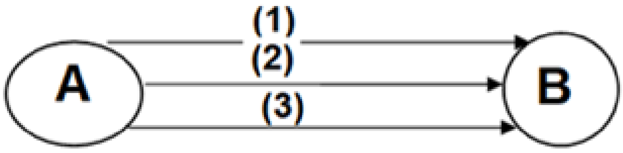
$$\begin{cases} dU = \delta W + \delta Q \\ \Delta U = W_i^f + Q_i^f \\ \Delta U = U_f - U_i \end{cases}$$

**Notes:**

- For an isolated system evolving from state (1) to state (2) (with no heat or work exchange with the external surroundings), it follows that:

$\Delta U = 0 \Rightarrow W + Q = 0 \Rightarrow Q = 0 \ , W = 0$

- The function U is a state function, and its change is independent of the path taken but is solely dependent on the initial and final states.



$$\Delta U_1 = \Delta U_2 = \Delta U_3$$

$$Q_1 + W_1 = Q_2 + W_2 = Q_3 + W_3$$

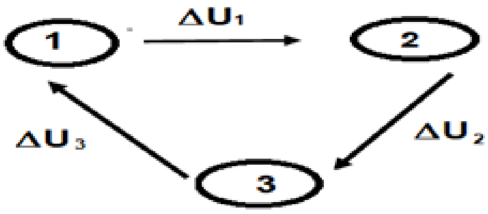
However :

$$Q_1 \neq Q_2 \neq Q_3$$

$$W_1 \neq W_2 \neq W_3$$

Therefore, this principle is known as the principle of initial and final states.

- The change in internal energy for a cyclic process is zero, where a cyclic process is one in which the initial state is the same as the final state.



$$\Delta U_T = \Delta U_1 + \Delta U_2 + \Delta U_3$$

$$= \Delta U_{12} + \Delta U_{23} + \Delta U_{31}$$

$$= \Delta U_{11} = \underset{\text{Cyclic process}}{\Delta U} = 0$$

## 3- Types of Thermodynamic Processes (Closed System):

3-1- Adiabatic transformation (Isentropic): This is a process in which there is no heat exchange between the system and the surroundings. Q = 0.

3-2- Isothermal transformation (Constant Temperature): This is a process that occurs at a constant temperature.

3-3- Isobaric transformation (Constant Pressure): This is a process that occurs at constant pressure.

3-4- Isochoric transformation (Constant Volume): This is a process that occurs at constant volume.

**Note:** If the process is carried out at constant volume:

$$V\ Cst \Rightarrow dV = 0 \Rightarrow W = 0 \Rightarrow dU = \partial Q \Rightarrow \Delta U = Q_V = n\int C_V\, dT$$

**4- Enthalpy**: Most chemical reactions take place at a constant pressure, which is atmospheric pressure (1 atm). In this case, if $Q_P$ is the amount of heat exchanged during a transformation that occurs at constant pressure, it can be expressed as follows:

$$\Delta U = U_f - U_i = W + Q = -p\Delta V + Q_P = -P(V_f - V_i) + Q_P$$

$$\Rightarrow U_f - U_i = Q_P - P(V_f - V_i) \Rightarrow Q_P = (U_f - U_i) + P(V_f - V_i)$$

$$\Rightarrow Q_P = (U_f + PV_f) - (U_i + PV_i) = H_f - H_i = \Delta H$$

## $\Longrightarrow H = U + PV$ Enthalpy function

And thus, the amount of heat exchanged at constant pressure, QP, represents a state function called the enthalpy function, denoted by the symbol H. It is expressed mathematically as: H = U + PV. The enthalpy function plays a crucial role in thermodynamics and has numerous applications, particularly in thermochemistry, given that most chemical reactions occur at atmospheric pressure.

**Notes:**

**1**- H is a state function that changes only with a change in temperature, identical to the function U.
QP = ΔH is the amount of heat exchanged between the system and the surroundings at constant pressure.
QV = ΔU is the amount of heat exchanged between the system and the surroundings at constant volume.

$$H = H(T,P) \Longrightarrow dH = \left(\frac{\sigma H}{\sigma P}\right)_T dP + \left(\frac{\sigma H}{\sigma T}\right)_P dT$$

$$U = U(T,V) \Longrightarrow dU = \left(\frac{\sigma U}{\sigma V}\right)_T dV + \left(\frac{\sigma U}{\sigma T}\right)_V dT$$

2- $\Delta H = \int nC_P dT \quad ; \Delta U = \int nC_V\, dT$

3- $\Delta H_{cyclic\ process} = 0 \ ; \Delta U_{cyclic\ process} = 0$

**5- The relationship between $C_P$ and $C_V$ (for ideal gases):**

$$V\ Cst \Longrightarrow \Delta U = nC_V \Delta T$$

$$P\ Cst \Longrightarrow \Delta H = nC_P \Delta T$$

**According to the ideal gas law: PV = nRT**
**For 1 mole:**

$$PV = RT \Longrightarrow d(PV) = d(RT)$$

$$d(PV) = PdV + VdP = RdT$$

$$dU = dQ + dW$$

$$When\ \ P\ Cst \Longrightarrow dP = 0 \Longrightarrow PdV = RdT$$

$$dU = dQ_P - PdV = C_P\, dT - PdV$$

**And we have:**

$$dU = C_V dT \Longrightarrow dU = C_P\, dT - PdV = C_V dT$$

$$\Longrightarrow (C_P - C_V)dT = PdV = RdT$$

$C_P - C_V = R$ **The Mayer relationship (for ideal gases )**

$$\gamma = \frac{C_P}{C_V} \quad ; \; C_P = \frac{\gamma R}{\gamma - 1} \quad ; \; C_V = \frac{R}{\gamma - 1}$$

## 6- Determining the laws of Laplace for Adiabatic and reversible transformation (ideal gases):

**We have, according to the first principle: dU = dQ + dW**

**Adiabatic transformation ⇒ dQ = 0 ⇒ dU = dW**

$$dW = -P_{ext} dV$$

**Reversible transformation** $\Rightarrow P_{ext} = P_{int} = P_{sys} = P_g = P$

$$\Rightarrow dW = -PdV$$

**So :** $dU = -PdV \, ; dU = nC_V dT \; ; PV = nRT$

$$nC_V dT = -PdV \; ; P = \frac{nRT}{V} \quad \Rightarrow nC_V dT = -nRT \frac{dV}{V}$$

$$\Rightarrow C_V \frac{dT}{T} = -R \frac{dV}{V} \Rightarrow \frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V}$$

$$\Rightarrow \int_{T_1}^{T_2} \frac{dT}{T} = -\frac{R}{C_V} \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow \int_{T_1}^{T_2} \frac{dT}{T} = -\frac{(C_P - C_V)}{C_V} \int_{V_1}^{V_2} \frac{dV}{V} = -(\gamma - 1) \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow Ln\left(\frac{T_2}{T_1}\right) = -(\gamma - 1) Ln\left(\frac{V_2}{V_1}\right) = (\gamma - 1) Ln\left(\frac{V_1}{V_2}\right)$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma - 1)} \quad \Rightarrow T_2 {V_2}^{(\gamma - 1)} = T_1 {V_1}^{(\gamma - 1)}$$

So, in the general case of a transformation for a system (adiabatic) and its reversible counterpart for an ideal gas:

$$TV^{(\gamma - 1)} = Cst$$

Similarly, the following laws can be deduced in the case of a transformation for a system and its reversible counterpart for an ideal gas:

$$T = f(V) \Rightarrow TV^{(\gamma - 1)} = Cst$$

$$P = f(V) \Rightarrow PV^{\gamma} = Cst$$

$$T = f(P) \Rightarrow TP^{\left(\frac{1-\gamma}{\gamma}\right)} = Cst$$

**7- Application of the first law to ideal gases:** When a system evolves from the initial state to the final state, applying the first principle to ideal gases requires us to calculate the quantities ΔH, ΔU, Q, and W**.**

## 7-1- Isobaric transformation (cooling, heating):

$$\begin{matrix}\textbf{The initial state} & \xrightarrow[\Delta P = 0]{P\ Cst} & \textbf{The final state} \\ P, V_1, T_1 & & P, V_2, T_2\end{matrix}$$

**n Constant ( Number of moles ) closed system**

- Calculating the work, W:

$$\textbf{Reversible transformation} \Longrightarrow \begin{matrix} dW = -P_{ext}\, dV \\ P_{ext} = P_{int} = P_{sys} = P_g = P \end{matrix}$$

$$\Longrightarrow W_{12} = -P\int_{V_1}^{V_2} dV \Longrightarrow W_{12} = -P\,(V_2 - V_1)$$

- Calculating the heat quantity Q and the change in enthalpy $\Delta H_{12}$:

$$\text{at } P\ Cst \Longrightarrow Q_{12} = Q_P = \Delta H_{12} = \int nC_P\, dT$$

$$\Longrightarrow Q_{12} = \Delta H_{12} = nC_P\Delta T$$

- Calculating the change in internal energy $\Delta U_{12}$:

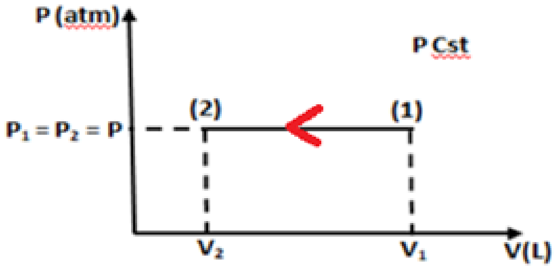
$$\Delta U_{12} = Q_{12} + W_{12} = nC_P\Delta T - P(V_2 - V_1)$$

$$P\ Cst \Longrightarrow PV_1 = nRT_1\ ;\ PV_2 = nRT_2 \Longrightarrow V_1 = nRT_1/P\ ;\ V_2 = nRT_2/P$$

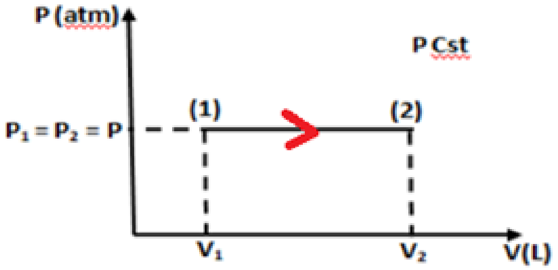
$$\Delta U_{12} = nC_P\Delta T - P\left(\frac{nRT_1}{P} - \frac{nRT_2}{P}\right) = nC_P\Delta T - nR\,(T_2 - T_1)$$

$$\Longrightarrow \Delta U_{12} = nC_v\Delta T$$

**Clapeyron diagram** P = f(V)



Cooling : $T_1 > T_2$ ; $V_2 < V_1$



Heating : $T_2 > T_1$ ; $V_1 < V_2$

## 7-2- Isochoric transformation (cooling, heating):

$$\text{The initial state} \xrightarrow[\Delta V = 0]{V\ Cst} \text{The final state}$$

$$P_1,\ T_1, V \qquad\qquad\qquad P_2\ , T_2,\ V$$

- **Calculating the work, W:**

$$dW = -\,P_{ext}\ dV$$

$$V\ Cst \Longrightarrow dV = 0 \Longrightarrow W_{12} = 0$$

- **Calculating the heat quantity Q and the change in internal energy $\Delta U_{12}$:**

$$V\ Cst \Longrightarrow Q_{12} = Q_V$$

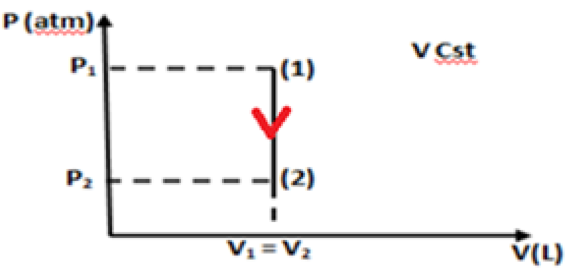
$$\Longrightarrow \Delta U_{12} = Q_{12} + W_{12} = Q_{12} = Q_V = nC_V\Delta T$$

$$\Longrightarrow \Delta U_{12} = Q_{12} = nC_V\Delta T$$

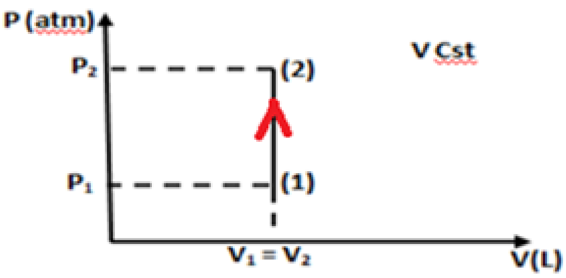
- **Calculating the change in enthalpy $\Delta H_{12}$:**

$$\Delta H_{12} = nC_P\Delta T$$

**Clapeyron diagram** P = f(V)



Cooling : $T_1 > T_2$ ; $P_2 < P_1$



Heating : $T_2 > T_1$ ; $P_1 < P_2$

## 7-3- Isothermal transformation (expansion, compression):

$$\underset{P_1\,,V_1,\ T}{\text{Initial state}} \xrightarrow[\Delta\ T\ =0]{T\ \ Cst} \underset{P_2,\ V_2,\ T}{\text{Final state}}$$

- **Calculation of work W:**

$$dW = -\,P_{ext}\,dV$$

$$\text{Reversible transformation} \Longrightarrow P_{ext} = P_{int} = P_{sys} = P_g = P$$

$$\Longrightarrow W_{12} = -\int_{V_1}^{V_2} P\,dV$$

$$\text{Ideal gas} \Longrightarrow PV = nRT \Longrightarrow P = \frac{nRT}{V} \Longrightarrow W_{12} = -\int_{V_1}^{V_2} nRT\,\frac{dV}{V}$$

$$T\,Cst \Longrightarrow W_{12} = -\ nRT\int_{V_1}^{V_2}\frac{dV}{V} \Longrightarrow W_{12} = -nRT\,Ln(V_2/V_1)$$

$$\text{according to Boyle's Law}:\ \ P_1V_1 = P_2V_2\ \ \text{so}\ :$$

$$W_{12} = -nRT\,Ln(V_2/V_1) = -\,nRT\,Ln(P_1/P_2)$$

- **Calculation of the change in internal energy ($\Delta U_{12}$) and the change in enthalpy ($\Delta H_{12}$):**

  Experimentally, it has been established that the change in internal energy and the change in enthalpy for an ideal gas during a reversible adiabatic process at constant temperature are equal to zero.

$$\text{According to the first law of Joule} \Longrightarrow \Delta U_{12} = 0 \quad \text{at}\ \ T\,Cst$$

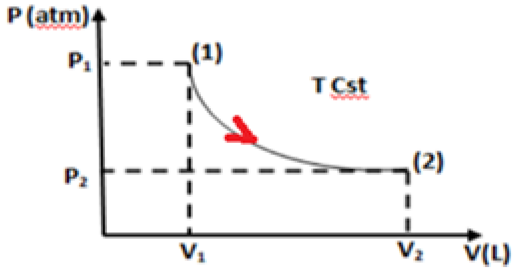
$$\text{According to the second law of Joule} \Longrightarrow \Delta H_{12} = 0 \quad \text{at}\ \ T\,Cst$$

- **Calculation of the heat quantity Q:**

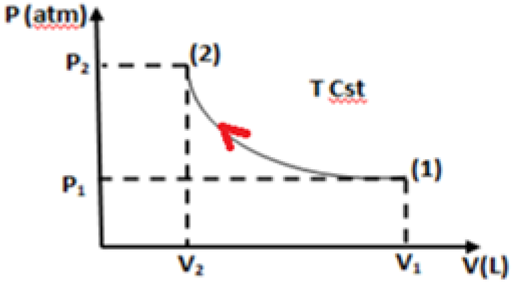
$$\Delta U_{12} = Q_{12} + W_{12} = 0 \Longrightarrow Q_{12} = -\,W_{12}$$

$$\Longrightarrow Q_{12} = -\,W_{12} = nRT\,Ln(V_2/V_1) = nRT\,Ln(P_1/P_2)$$

Clapeyron diagram $P = f(V)$



Expansion : $V_2 > V_1$ ; $P_2 < P_1$



compression : $V_1 > V_2$ ; $P_1 < P_2$

## 7-4- Adiabatic and reversible transformation of an ideal gas:

$$\text{Initial state} \xrightarrow{Q = 0} \text{Final state}$$

$P_1, V_1, T_1$ $\qquad$ $P_2, V_2, T_2$

- **Calculation of work W:**

$$dW = -P_{ext}\,dV$$

Reversible transformation $\Longrightarrow$ $P_{ext} = P_{int} = P_{sys} = P_g = P$

$$\Longrightarrow W_{12} = -\int P\,dV$$

Adiabatic transformation $\Longrightarrow$ $PV^{\gamma} = Cst$ $\Longrightarrow$ $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

$$\Longrightarrow P = \frac{P_1V_1^{\gamma}}{V^{\gamma}} = \frac{P_2V_2^{\gamma}}{V^{\gamma}}$$

$$W_{12} = -\int_{V_1}^{V_2} P_1V_1^{\gamma}\frac{dV}{V^{\gamma}} = -P_1V_1^{\gamma}\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_1}^{V_2} = -P_1V_1^{\gamma}\left[\frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma}\right]$$

$$W_{12} = -\left[\frac{P_1V_1^{\gamma}V_2^{1-\gamma} - P_1V_1^{\gamma}V_1^{1-\gamma}}{1-\gamma}\right] \quad / \quad P_2V_2^{\gamma} = P_1V_1^{\gamma}$$

$$W_{12} = -\left[\frac{P_2V_2^{\gamma}V_2^{1-\gamma} - P_1V_1^{\gamma}V_1^{1-\gamma}}{1-\gamma}\right] = -\left[\frac{P_2V_2 - P_1V_1}{1-\gamma}\right]$$

$$W_{12} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

- **Calculation of the heat quantity Q:**

$$Q_{12} = 0$$

- **Calculation of the change in internal energy ($\Delta U_{12}$)**

$$\Delta U_{12} = Q_{12} + W_{12} = W_{12} = nC_V\,\Delta T = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

**The explanation of the relationship :**

$$P_2V_2 = nRT_2 \quad ; \quad P_1V_1 = nRT_1$$

$$\Longrightarrow W_{12} = \frac{nRT_2 - nRT_1}{\gamma - 1} = \frac{nR}{\gamma - 1}\,\Delta T = nC_V\Delta T$$

- **Calculation of the change in enthalpy ($\Delta H_{12}$):**

$$\Delta H_{12} = nC_p\Delta T$$

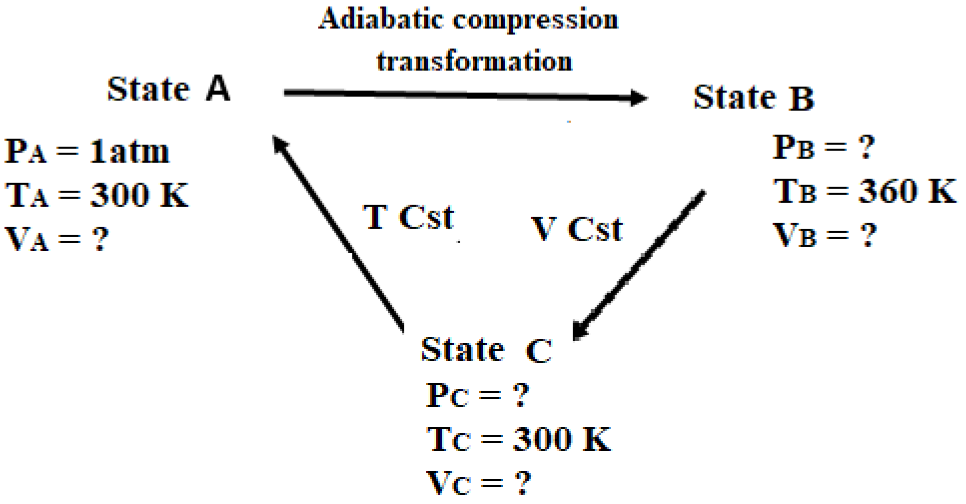
**Application Example:**

One mole of an ideal gas undergoes a series of reversible transformations as follows:

- Adiabatic compression transformation from state A ($T_A$ = 300K, $P_A$ = 1 atm) to state B ($T_B$ = 360 K).
- An isochoric transformation takes the system to state C such that $T_A = T_C$.
- Expansion at constant temperature brings the system back to state A.

- Calculate the variables $V_A$, $V_B$, $P_B$, and $P_C$.
- Represent these transformations on a Clapeyron diagram.
- Calculate for each transformation and for the entire cycle W, Q, ΔU, ΔH summarizing your results in a table. What conclusions can be drawn?
  Given data:
  $C_P = 5/2\ R$, $C_V = 3/2\ R$, R = 0.082 atm.l/mol.K = 8.314 J/mol.K

## Solution to the application example:



**1- Calculate each of VA, VB, PB, PC :**

$$V_A = \frac{nRT_A}{P_A} = \frac{1 \times 0{,}082 \times 300}{1} = 24{,}6\ l$$

Since the transformation from A to B is adiabatic, then:

$$TV^{(\gamma-1)} = Cst$$

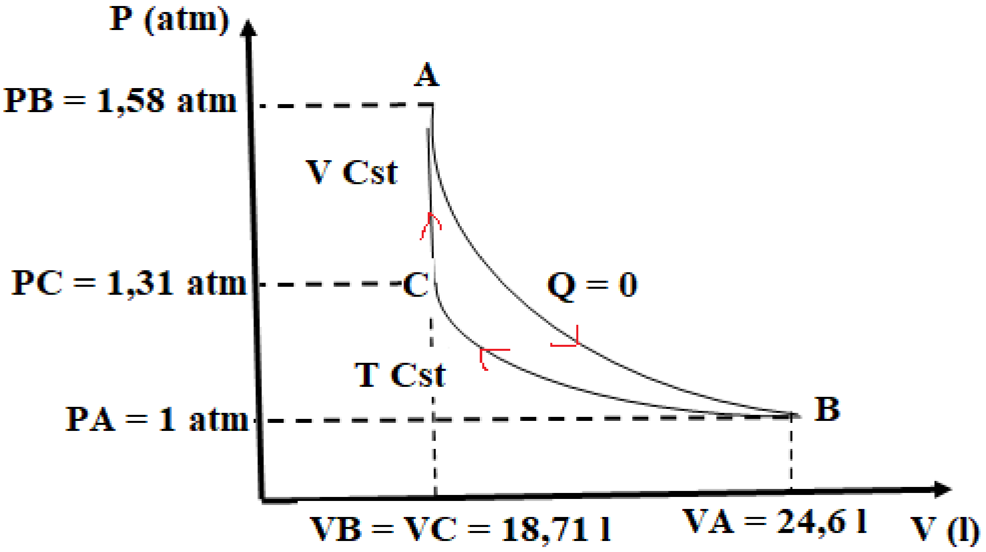
$$T_A V_A^{(\gamma-1)} = T_B V_B^{(\gamma-1)} \Longrightarrow V_B = \left(\frac{T_A}{T_B}\right)^{\left(\frac{1}{\gamma-1}\right)} \times V_A$$

$$V_B = \left(\frac{300}{360}\right)^{\left(\frac{1}{\frac{5}{3}-1}\right)} \times 24,6 = 18,71\ l$$

$$P_B = \frac{nRT_B}{V_B} = \frac{1 \times 0,082 \times 360}{18,71} = 1,58\ atm$$

$$P_C = \frac{nRT_C}{V_C} = \frac{1 \times 0,082 \times 300}{18,71} = 1,31\ atm$$

2- Clapeyron diagram:



3- Calculate Q, W, ΔU , ΔH for each transformation:

__The transformation from A to B :__

$$Q_{AB} = 0$$

$$\Delta U_{AB} = Q_{AB} + W_{AB} = W_{AB} = n.C_V(T_B - T_A)$$

$$\Delta U_{AB} = 1 \times \frac{3}{2} \times 8,314 \times (360 - 300) = 748,26J$$

$$\Delta H_{AB} = n.C_P(T_B - T_A) = 1 \times \frac{5}{2} \times 8,314 \times (360 - 300) = 1247,1J$$

**The transformation from B to C :**

$$W_{BC} = 0$$
$$\Delta U_{BC} = Q_{BC} + W_{BC} = Q_{BC} = n.C_V(T_C - T_B)$$

$$\Delta U_{BC} = 1 \times \frac{3}{2} \times 8,314 \times (300 - 360) = -748,26J$$

$$\Delta H_{BC} = n.C_P(T_C - T_B) = 1 \times \frac{5}{2} \times 8,314 \times (300 - 360) = -1247,1J$$

**The transformation from C to A :**

According to the first law of thermodynamics: $\Delta U_{CA}= 0$

According to the second law of thermodynamics: $\Delta H_{CA}=0$

$$\Delta U_{BC} = Q_{CA} + W_{CA} = 0 \Longrightarrow Q_{CA} = -W_{CA}$$

$$W_{CA} = -nRT_A Ln\left(\frac{V_A}{V_C}\right) = -nRT_A Ln\left(\frac{P_C}{P_A}\right)$$
$$W_{CA} = -nRT_A Ln\left(\frac{V_A}{V_C}\right) = -1 \times 8,314 \times 300 \times Ln\left(\frac{24,6}{18,71}\right) = -682,63J$$
$$Q_{CA} = 682,63J$$

| التحول | Q (J) | W (J) | ΔU (J) | ΔH (J) |
|---|---|---|---|---|
| A الى B | 0 | 748,26 | 748,26 | 1247,1 |
| Bالى C | -748,26 | 0 | -748,26 | -1247,1 |
| Cالى A | 682,63 | -682,63 | 0 | 0 |
| الحلقة | -65,63 | 65,63 | 0 | 0 |

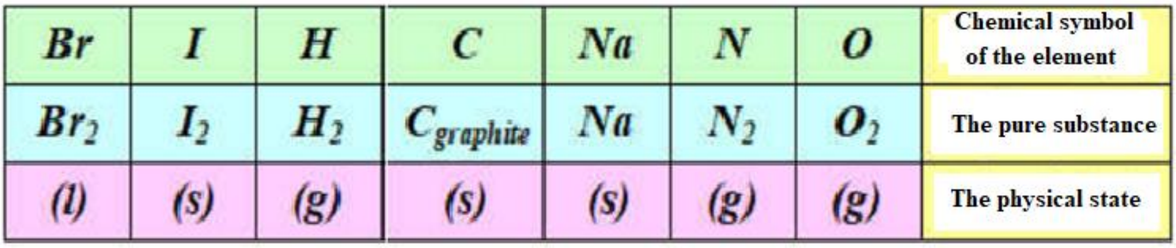
$\Delta U_{cycle}=0$, $\Delta H_{cycle}=0$

Because both functions are state functions

## 8- Application of the First Law to Chemical Reactions:

**8-1- Standard State:** The standard state of a pure substance is the most stable physical state (from a thermodynamic perspective) in which it exists at atmospheric pressure (P = 1 atm) and at standard temperature (usually equal to 298 K).

The following table provides the physical state of some elements under standard conditions.



| Br | I | H | C | Na | N | O | Chemical symbol of the element |
|---|---|---|---|---|---|---|---|
| $Br_2$ | $I_2$ | $H_2$ | $C_{graphite}$ | Na | $N_2$ | $O_2$ | The pure substance |
| (l) | (s) | (g) | (s) | (s) | (g) | (g) | The physical state |

- **Based on this definition, the standard-state enthalpy of formation for pure simple substances is equal to zero.**

**Examples :**

$$\Delta H^{\circ}_{298}(O_2)_g = 0;\ \Delta H^{\circ}_{298}(N_2)_g = 0;\ \Delta H^{\circ}_{298}(H_2)_g = 0$$

$$\Delta H^{o}_{298}\ \text{(graphite)} = 0 \quad \text{but} \quad \Delta H^{o}_{298}\ \text{(diamant)} \neq 0$$

## 2- Enthalpy of Formation of a Compound ΔHf:

**The enthalpy of formation of a compound is the enthalpy change for the reaction that forms the compound from its elements in their standard states.**

**Example:**

**Formation reaction of water:**

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(L)} \qquad \Delta H_f(H_2O_{(L)})$$

**Formation reaction of ethanol:**

$$2C_{grahite\ (S)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3CH_2OH_{(L)} \qquad \Delta H_f(CH_3CH_2OH_{(L)})$$

**Notes:**

**• At standard conditions (1 atm, 298 K), the enthalpy of formation is called the standard enthalpy of formation.**

**• Enthalpies of formation are temperature-dependent.**

**Example:**

$$T_1 = 298\text{ K} \quad \frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)} \quad Q_1 = -22,08\text{ Kcal} = \Delta H^0_{f,298}(NH_{3(g)})$$

$$T_2 = 398\text{ K} \quad \frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)} \quad Q_2 = -23,05\text{ Kcal} = \Delta H^0_{f,398}(NH_{3(g)})$$

- **The enthalpy change can be positive or negative:**

$$\text{Endothermic reaction} \Longrightarrow \Delta H > 0$$

$$\text{Exothermic reaction} \Longrightarrow \Delta H < 0$$

**Examples:**

$$C_{graphite\ (S)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_1^\circ = -94,05\ \text{Kcal} \quad \text{Exothermic}$$
$$2C_{graphite\ (S)} + H_{2(g)} \rightarrow C_2H_{2(g)} \qquad \Delta H_2^\circ = 54\ \text{Kcal} \quad \text{Endothermic}$$

**Note:**

The reaction can cause a change in the physical state of the substance, so it is necessary to specify the physical state of the reactants and products.

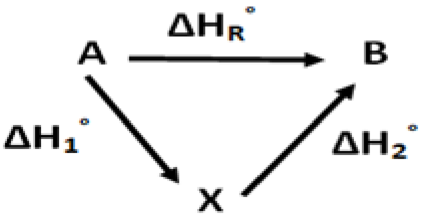
**Example:**

$$T_1 = 25\,°C \quad H_{2(g)} + \frac{1}{2}O_{2(g)} \xrightarrow{\Delta H_R^\circ} H_2O_{(L)} \quad \Delta H_R^\circ = \Delta H_f^\circ(H_2O_{(L)}) = -67,5\ \text{Kcal}$$
$$T_2 = 110\,°C \quad H_{2(g)} + \frac{1}{2}O_{2(g)} \xrightarrow{\Delta H_R^\circ} H_2O_{(g)} \quad \Delta H_R^\circ = \Delta H_f^\circ(H_2O_{(g)}) = -57,8\ \text{Kcal}$$

## 9- How to calculate the change in enthalpy for a reaction ($\Delta H_R^\circ = \Delta H_f^\circ$):

**9-1- Direct Method:** The change in enthalpy for a reaction can be calculated using calorimetry by relying on the zeroth law of thermodynamics ($\sum Q_i$), treating the reaction as an isolated system.

**9-2- Indirect Method:** In this case, we resort to an indirect method to calculate the change in enthalpy for a reaction, knowing that enthalpy is a state function that depends only on the initial and final states.



$$\Delta H_R^\circ = \Delta H_1^\circ + \Delta H_2^\circ$$

**Example:**

Consider the following reaction at T = 298 K:

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \xrightarrow{\Delta H_R^\circ} CO_{2(g)} \qquad *$$

$$(1) \qquad C_{graphite(S)} + \frac{1}{2}O_{2(g)} \xrightarrow{\Delta H_1^\circ} CO_{(g)} \quad \Delta H_1^\circ = \Delta H_f^\circ(CO_{(g)}) = -26,42\ \text{Kcal/mol}$$

$$(2) \qquad C_{graphite(S)} + O_{2(g)} \xrightarrow{\Delta H_2^\circ} CO_{2(g)} \quad \Delta H_2^\circ = \Delta H_f^\circ(CO_{2(g)}) = -94,05\ \text{Kcal/mol}$$

To obtain the change in enthalpy for the reaction (*), we do the following:

We reverse equation (1):

$$(3) \qquad CO_{(g)} \xrightarrow{\Delta H_3^\circ} C_{graphite(S)} + \frac{1}{2}O_{2(g)} \quad \Delta H_3^\circ = -\Delta H_1^\circ = 26,42\ \text{Kcal/mol}$$

$$* = (3) + (2) \Rightarrow \Delta H_R^\circ = \Delta H_3^\circ + \Delta H_2^\circ = -\Delta H_1^\circ + \Delta H_2^\circ$$
$$\Delta H_R^\circ = -(-26,42) + (-94,05) = -67,63\ Kcal/mol$$

## 9-3- Hess's Law: Consider the following reaction:

$$aA + \mathrm{bB} \xrightarrow{\Delta H_R^\circ} \mathrm{cC} + \mathrm{dD}$$

$$\Delta H_R^\circ = c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D) - a\Delta H_f^\circ(A) - b\Delta H_f^\circ(B)$$

**That is, in the general case:**

$$\Delta H_R^\circ = \sum \alpha_i \, \Delta H_f^\circ(\,products) - \sum \beta_i \, \Delta H_f^\circ(Reactants)$$

**$\alpha_i$ و $\beta_i$ are the stoichiometric coefficients**

**Notes:**

- The change in enthalpy corresponding to a reaction is independent of the number of intermediate steps and equals the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants.

- The enthalpy of formation of a compound when the formation reaction occurs under standard conditions (T = 298 K, P = 1 atm) is: $\Delta Hf^\circ_{298}$.

**Example:**

$$C_{graphite(S)} + O_{2(g)} \xrightarrow{\Delta H_{R,298}^\circ} CO_{2(g)}$$

$$\Delta H_{R,298}^\circ = \Delta H_{f,298}^\circ(CO_{2(g)}) - \underbrace{\Delta H_{f,298}^\circ(C_{graphite(S)})}_{=\,0} - \underbrace{\Delta H_{f,298}^\circ(O_{2(g)})}_{=\,0} = \Delta H_{f,298}^\circ(CO_{2(g)})$$

A simple and pure compound under standard conditions

A simple and pure compound under standard conditions

- The compound is more stable if the absolute value of $\Delta H^\circ_f$ is large.

**Example:** **at 298 K:**

$$\Delta H_f^\circ(CO_{(g)}) = -26,42 \ \mathrm{Kcal/mol}$$
$$\Delta H_f^\circ(CO_{2(g)}) = -94,05 \ \mathrm{Kcal/mol}$$

Therefore, $CO_{2(g)}$ is more stable than $CO_{(g)}$.

### Dissociation enthalpy, $\Delta H_d^\circ$:

Dissociation enthalpy is the enthalpy change for the reverse reaction of the formation reaction, and it is equal in magnitude to the enthalpy of formation.

**Example:**

$$H_{2(g)} + ½\, O_{2(g)} \underset{(2)}{\overset{(1)}{\rightleftarrows}} H_2O_{(g)}$$

Direction (1) corresponds to $\Delta H^\circ_f(H_2O_{(g)})$

Direction (2) corresponds to $\Delta H^\circ_d(H_2O_{(g)})$

$$\Delta H_{Cycle} = 0 \Longrightarrow \Delta H^\circ_f(H_2O_{(g)}) + \Delta H^\circ_d(H_2O_{(g)}) = 0$$

$$\Longrightarrow \Delta H^\circ_f(H_2O_{(g)}) = - \Delta H^\circ_d(H_2O_{(g)})$$

**Example:** **Let the following reactions occur at P = 1 atm, T = 298 K:**

$$(1) \qquad C_2H_{2(g)} + 2H_{2(g)} \xrightarrow{\Delta H^\circ_1} C_2H_{6(g)}$$

$$(2) \qquad CO_{2(g)} + H_{2(g)} \xrightarrow{\Delta H^\circ_2} CO_{(g)} + H_2O_{(g)}$$

$$(3) \qquad CH_{4(g)} + 2O_{2(g)} \xrightarrow{\Delta H^\circ_3} CO_{2(g)} + 2H_2O_{(g)}$$

Calculate the change in enthalpy for the previous reactions.

Data:

| The compound | $C_2H_{2(g)}$ | $H_2O_{(g)}$ | $H_2O_{(L)}$ | $CH_{4(g)}$ | $CO_{(g)}$ | $C_2H_{6(g)}$ | $CO_{2(g)}$ |
|---|---|---|---|---|---|---|---|
| $\Delta H^\circ_{f,298}$ (Kcal/mol) | 54,19 | -57,80 | -68,32 | -17,89 | -26,42 | -24,86 | -94,05 |

**Solution:**

$$\Delta H^\circ_1 = \Delta H^\circ_f(C_2H_{6(g)}) - \Delta H^\circ_f(C_2H_{2(g)}) - 2\underset{= 0}{\Delta H^\circ_f(H_{2(g)})}$$

$$\Delta H^\circ_1 = -24,86 - (-54,19) = -79,05 \text{ Kcal} \quad \text{Exothermic reaction}$$

$$\Delta H^\circ_2 = \Delta H^\circ_f(CO_{(g)}) + \Delta H^\circ_f(H_2O_{(g)}) - \Delta H^\circ_f(CO_{2(g)}) - \underset{= 0}{\Delta H^\circ_f(H_{2(g)})}$$

$$\Delta H^\circ_2 = -26,42 + (-57,80) - (-94,05) = 9,83 \text{ Kcal/mol} \quad \text{Endothermic reaction}$$

$$\Delta H^\circ_3 = \Delta H^\circ_f(CO_{2(g)}) + 2\Delta H^\circ_f(H_2O_{(g)}) - \Delta H^\circ_f(CH_{4(g)}) - \underset{= 0}{2\Delta H^\circ_f(O_{2(g)})}$$

$$\Delta H^\circ_3 = -94,05 + 2(-57,80) - (-17,89) = -191,76 \text{ Kcal/mol} \quad \text{Exothermic reaction}$$

## The enthalpy change for a reaction of physical state change.

It concerns a physical transformation of matter (a change in its physical state):

**Fusion:** It is the transformation of matter from the solid state to the liquid state, such as:

$$H_2O_{(s)} \rightarrow H_2O_{(l)}$$

And it is represented by the change in enthalpy for this transformation $\Delta H°_{fus}$ or $L_{fus}$, and the reverse process of this transformation is freezing.

**Vaporization:** It is the transformation of matter from the liquid state to the gaseous state, such as:

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

And it is represented by the change in enthalpy for this transformation $\Delta H°_{Vap}$ or $L_{Vap}$, and the reverse process of this transformation is condensation.

**Sublimation:** It is the transformation of matter from the solid state directly to the gaseous state without passing through the liquid state, such as:

$$I_{2(s)} \rightarrow I_{2(g)}$$

And the reverse process of this transformation is condensation.

• It is also possible to include within the change in physical state the alterations that occur in the crystalline structure of the substance, such as the transformation of graphite carbon into diamond carbon.

$$C_{(g)} \rightarrow C_{(d)}$$

Note: The change in enthalpy for any physical transformation differs from the change in enthalpy for the reverse transformation only in sign. For example, if $\Delta H_{fus}° = -248$ kJ/mol, then the change in enthalpy for the reverse transformation is $\Delta H_{cond}° = +248$ kJ/mol.

## 9-4 The relationship between $\Delta H_R$ and $\Delta U_R$ in chemical reactions:

We have the following reaction at temperature T:

$$aA \ + \ bB \longrightarrow cC \ + \ dD$$

If this transformation (reaction) occurs at constant pressure, then:

$$H = U + PV \ \Rightarrow dH = dU + d(PV)$$

$$\Rightarrow \Delta H = \ \Delta U + P\Delta V \qquad P\ Cst$$

- If the reaction occurs between liquid or solid substances, then the total volume does not change, where the initial volume is approximately equal to the final volume.

$$\Rightarrow V_f = \ V_i \Rightarrow \Delta V = 0$$

$$\Rightarrow \ \Delta H_R = \Delta U_R \ \Rightarrow \ Q_P = \ Q_V$$

- If gases are present among the reactants or products, then:

$$PV = nRT \Rightarrow \ \Delta(PV) = \ \Delta(nRT) = RT\Delta n \qquad (\ T\ Cst)$$

$$\Delta n = (c + d) - (a + b)$$

So :

$$\Delta H_R = \Delta U_R + RT\Delta n_g$$

And only the coefficients of gaseous elements are considered in the calculation of Δn.

**Example:** Consider the following reaction at T = 25°C and P = 1 atm.

$$\mathrm{H_{2(g)}} + \frac{1}{2}\mathrm{O_{2(g)}} \xrightarrow{\Delta H_R^\circ} \mathrm{H_2O_{(L)}} \quad \Delta H_R^\circ = \Delta H_f^\circ\left(\mathrm{H_2O_{(L)}}\right) = -68,32\ \mathrm{Kcal}$$

Calculate $\Delta U_R°$

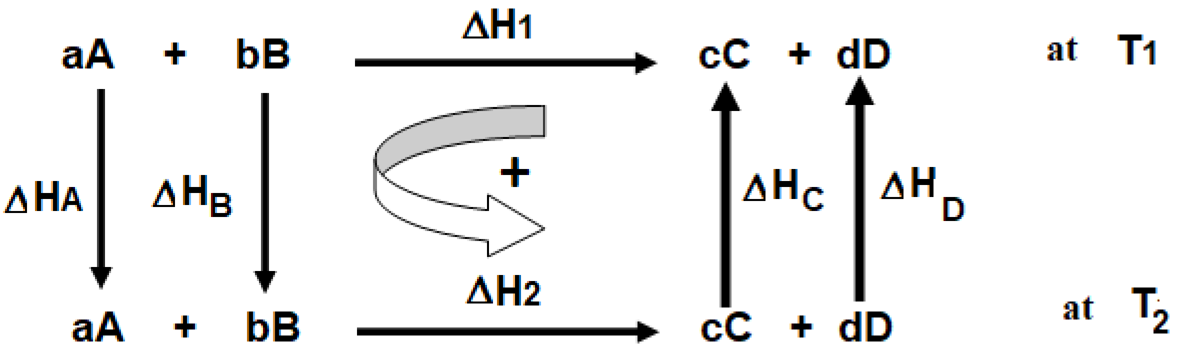
$$\Delta H_R = \Delta U_R + RT\Delta n_g \Longrightarrow \Delta U_R = \Delta H_R - RT\Delta n_g$$

$$\Delta n_g = 0 - \left(1 + \frac{1}{2}\right) = -\frac{3}{2}$$

$$\Longrightarrow \Delta U_R = -68,32 - (2\times 10^{-3}) \times 298 \times \left(-\frac{3}{2}\right) = -67,426\ Kcal/mol$$

## 9- 5. Kirchhoff's Law - Enthalpy Change Law with Temperature Variation:

Consider the following chemical reactions at $T_1$ and $T_2$ under constant pressure of 1 atm.



Based on our diagram: $\boldsymbol{\Delta H_1 = \Delta H_A + \Delta H_B + \Delta H_2 + \Delta H_C + \Delta H_D}$

$C_{PA} \longrightarrow A$ ; $C_{PB} \longrightarrow B$ ; $C_{PC} \longrightarrow C$ ; $C_{PD} \longrightarrow D$

$\Delta H_2 = \Delta H_1 - \Delta H_A - \Delta H_B - \Delta H_C - \Delta H_D$

$$\Delta H = nC_P\,\Delta T \quad \Longrightarrow \begin{cases} \Delta H_A = aC_{PA}(T_2 - T_1) \\ \Delta H_B = bC_{PB}(T_2 - T_1) \\ \Delta H_C = cC_{PC}(T_1 - T_2) \\ \Delta H_D = dC_{PD}(T_1 - T_2) \end{cases}$$

$$\Rightarrow \Delta H_2 = \Delta H_1 - \int_{T_1}^{T_2} (aC_{PA} + bC_{PB})\, dT - \int_{T_2}^{T_1} (cC_{PC} + dC_{PD})\, dT$$

$$\Rightarrow \Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} [(cC_{PC} + dC_{PD}) - (aC_{PA} + bC_{PB})]\, dT$$

And from this, we deduce Kirchhoff's law:

$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_P\, dT$ **In the absence of state transformations for both reactants and products**

$$\Delta C_P = \sum_{i=1}^{n} \alpha_i C_{Pi}(\,Products) - \sum_{i=1}^{n} \beta_i C_{Pi}(\,reactants)$$

$\beta_i$ و $\alpha_i$ $stoichiometric\ coefficients$

- Kirchhoff's relationship allows us to calculate the change in enthalpy for a reaction at any temperature if we know $\Delta H_1° = \Delta H_{298}°$ for that reaction.
- In the presence of state transformations, then:

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_P\, dT + \Delta Q$$

**Practical Example 1:** Calculate the change in enthalpy for the following reaction at T = 50°C and at T = 120°C, knowing that the change in enthalpy for this reaction at T = 298 K is $\Delta H_{R,298}° = -136.62$ Kcal.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(L)}$$

The data:

| The element | $H_2O_{(g)}$ | $H_2O_{(L)}$ | $O_{2(g)}$ | $H_{2(g)}$ |
|---|---|---|---|---|
| $C_P$ ( cal/mol.K) | 8 | 18 | 8,29 | 6,86 |

$\Delta H_{vap,373K}°(H_2O_{(L)}) = 9702$ cal/mol

**Solution:**

• At T = 50°C, there are no changes in the physical state for both reactants and products. Therefore, we can apply Kirchhoff's law:

$$\Delta H^{\circ}_{R,323} = \Delta H^{\circ}_{R,298} + \int_{298}^{323} \Delta C_P\, dT$$

$$\Delta C_P = 2C_P(\mathrm{H_2O_{(L)}}) - 2C_P(\mathrm{H_{2(g)}}) - C_P(\mathrm{O_{2(g)}}) = 2(18) - 2(6,86) - (8,29) = 13,99\ \mathrm{cal/mol\ K}.$$

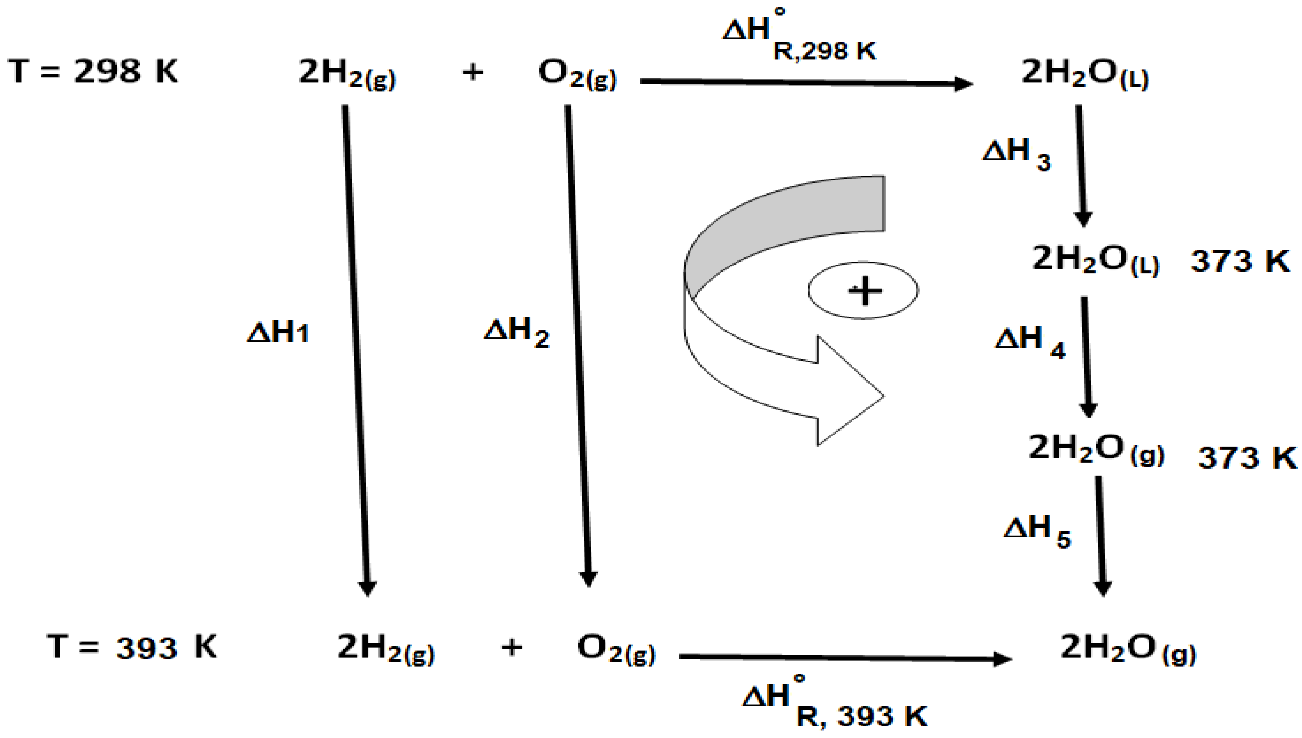
$$\Delta H^{\circ}_{R,323} = -136,62 + \int_{298}^{323}(13,99 \times 10^{-3)}\, dT = -136,62 + 0,01399(323 - 298)$$

$$\Delta H^{\circ}_{R,323} = -136,270\ Kcal$$

:$\Delta H^{\circ}_{R,393}$ Calculation

At a temperature of 120°C, there is a change in the physical state of water, where at this temperature, water is in the gaseous state, and thus we cannot apply the Kirchhoff's Law.

We proceed with the following cycle:



$$\Delta H_{\mathrm{cycle}} = 0 \implies \Delta H_1 + \Delta H_2 - \Delta H^{\circ}_{R,393\ K} - \Delta H_3 - \Delta H_4 - \Delta H_5 - \Delta H^{\circ}_{R,298\ K} = 0$$

$$\implies \Delta H^{\circ}_{R,393\ K} = \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H^{\circ}_{R,298\ K} - \Delta H_1 - \Delta H_2$$

$$\Delta H_1 = \int_{298}^{393} 2C_P(H_{2(g)})dT = 2(6,86)(393 - 298) = 1303,4\ cal$$

$$\Delta H_2 = \int_{298}^{393} C_P(O_{2(g)})dT = (8,29)(393 - 298) = 787,55\ cal$$

$$\Delta H_3 = \int_{298}^{373} 2C_P(H_2O_{(L)})dT = 2(18)(373 - 298) = 2700\ cal$$

$$\Delta H_4 = 2\Delta H_{Vap}(H_2O_{(L)}) = 2(9702) = 19404\ cal$$

$$\Delta H_5 = \int_{373}^{393} 2C_P(H_2O_{(g)})dT = 2(8)(393 - 373) = 320\ cal$$

$$\Delta H^{\circ}_{R,393\,K} = 2700 + 19404 + 320 + (-136,62.10^{3}) - 1303,4 - 787,55$$

$$\Delta H^{\circ}_{R,393\,K} = -116,28\,Kcal$$

Application Example 2: Let the following reaction be:

$$CH_{4(g)} + 3Cl_{2(g)} \rightarrow CHCl_{3(L)} + 3HCl_{(g)}$$

And which occurs at a temperature T = 298 K and releases a heat amount of 302.3 kJ. Calculate the change in enthalpy for this reaction at T = 330 K and the heat under constant volume, $\Delta U^{\circ}_{R,330K}$.

Given data.

| The compound | $HCl_{(g)}$ | $CHCl_{3(L)}$ | $Cl_{2(g)}$ | $CH_{4(g)}$ |
|---|---|---|---|---|
| $C_P$ (J/mol K) | 29,1 | 112,2 | 33,9 | 35,7 |

**T boiling ($CHCl_{3(L)}$) = 61,17 °C =334,17 K**

## Solution:

$$\Delta H^{\circ}_{R,298\,K} = -302,3\,Kj \quad Negative\ sign\ because\ the\ reaction\ releases\ heat$$

$$\Delta H^{\circ}_{R,330} = \Delta H^{\circ}_{R,298} + \int_{298}^{330} \Delta C_P\, dT$$

$$\Delta C_P = C_P(CHCl_{3(L)}) + 3C_P(HCl_{(g)}) - C_P(CH_{4(g)}) - 3C_P(Cl_{2(g)})$$

$$\Delta C_P = 112,2 + 3(29,1) - 35,7 - 3(33,9) = 62,1 j/molK$$

$$\Delta H^{\circ}_{R,330} = -302,3 + \int_{298}^{330} (62,1.10^{-3})\, dT = -302,3 + 0,0621(330 - 298) = -300,31Kj$$

**Calculate $\Delta U^{\circ}_{R,330\,K}$ :**

$$\Delta H^{\circ}_{R,330\,K} = \Delta U^{\circ}_{R,330\,K} + R\,(330)\Delta n_g$$

$$\Delta n_g = 3 - 4 = -1$$

$$\Rightarrow \Delta U^{\circ}_{R,330\,K} = \Delta H^{\circ}_{R,330\,K} - R\,(330)\Delta n_g$$

$$\Rightarrow \Delta U^{\circ}_{R,330\,K} = -300,31 - (8,314) \times 330 \times 10^{-3} \times (-1) = -297,57\,KJ$$

**9-6 Chemical Bonding Enthalpy:** The enthalpy of formation of the chemical bond A-B is the energy accompanying the formation of the bond starting from the two atoms in their free and gaseous state.

$$A_{\text{atom (g)}} + B_{\text{atom (g)}} \underset{E\,(A-B)}{\overset{\Delta H_f^\circ\,(A-B)}{\rightleftarrows}} A-B_{(g)} \quad \text{at} \quad T = 25°C \text{ , } P = 1 \text{ atm}$$

$\Delta H_f^\circ\,(A-B)$ : It is the energy required to form the bond $A-B$

$E\,(A-B)$ : It is the energy required to break the bond $A-B$

$\Delta H_f^\circ\,(A-B) < 0 \quad \Rightarrow$ Because elements in the state of free and gaseous atoms are less stable

We have : $\Delta H_f^\circ\,(A-B) + E\,(A-B) = 0$

$$\Rightarrow \Delta H_f^\circ\,(A-B) = -\,E\,(A-B)$$

$E\,(A-B) > 0 \quad \Rightarrow$ It is the energy required to break the bond $A-B$

**Note:** The greater the absolute value of $\Delta H_f^\circ(A-B)$ indicate that the bond A-B is more stable.

## Calculating the energy of the chemical bond using the thermodynamic method:

This method enables the calculation of bond energies in complex molecules.

**Example (1):**

$$\begin{tikzcd}
H_{2(g)} \arrow[d, "\Delta H^\circ_{\text{dissociation}}(H\text{-}H) = E\,(H\text{-}H)"'] & + & \frac{1}{2}O_{2(g)} \arrow[d, "\frac{1}{2}E\,(O=O)"'] \arrow[rr, "\Delta H^\circ_{R,298}", "\Delta H_f^\circ\,(H_2O_{(L)})"'] & & H_2O_{(L)} \\
2\,H_{(g)} & + & O_{(g)} \arrow[rr, "2\,\Delta H_f^\circ\,(O\text{-}H)"'] & & H_2O_{(g)} \arrow[u, "\Delta H^\circ_{\text{liquefaction}}(H_2O_{(g)})"']
\end{tikzcd}$$

Lewis structures :

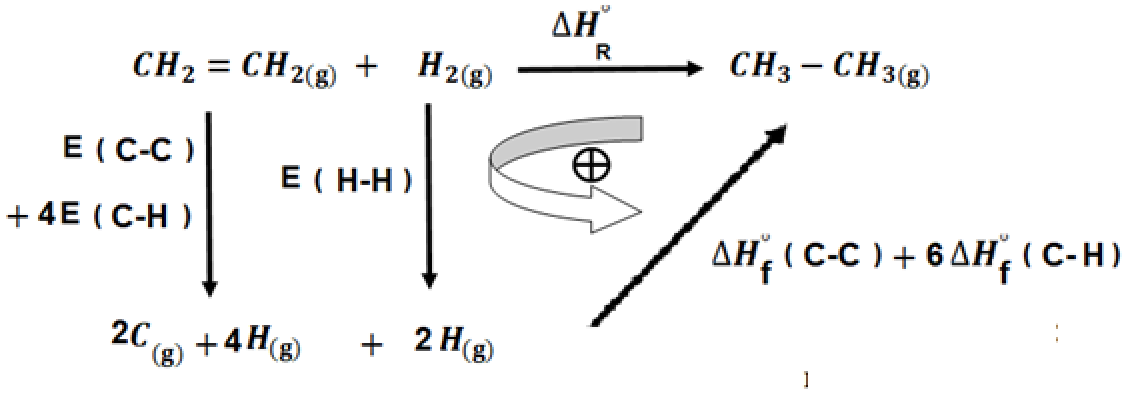
$H_2O$ : $H-\overline{\underline{O}}-H$

$H_2$ : $H-H$

$O_2$ : $|\overline{O}=\overline{O}|$

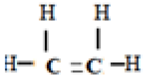
$$\Delta H_f^\circ\,(H_2O_{(L)}) = E\,(H\text{-}H) + 1/2\,E\,(O=O) + 2\,\Delta H_f^\circ\,(O\text{-}H) + \Delta H^\circ_{\text{liquefaction}}(H_2O_{(g)})$$

**Example (2):** **Let the following reaction be:**



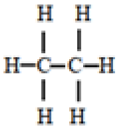
Lewis structures :

$CH_2=CH_2$ :



$H_2$ : H-H

$CH_3-CH_3$ :



$$\Delta H^\circ_R = E(C\text{-}C) + 4E(C\text{-}H) + E(H\text{-}H) + \Delta H^\circ_f(C\text{-}C) + 6\Delta H^\circ_f(C\text{-}H)$$

## Applied Example 1:

The combustion of 1 mole of ethylene under standard conditions (T = 298 K , P = 1 atm), according to the following equation, releases a quantity of heat equal to 1387.87 kilojoules to the surroundings.

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ_{R,298°K} = ?$$

Using standard molar enthalpies of formation, bond energies, and the sublimation enthalpy of carbon:

- Calculate the standard molar enthalpy of formation for the formation of $C_2H_{4(g)}$.
- Calculate the bond energy of the C=C bond in $C_2H_{4(g)}$.
  Data: at 298 K

**$\Delta H^\circ_{f(CO2(g))} = -392.9\ kJ.mol^{-1}$, $\Delta H^\circ_{f(H2O)L} = -284.2 kJ.mol^{-1}$. $\Delta H^\circ_{Sub(C)} = 716.2\ kJ.mol^{-1}$**

| Bond | C-H | H-H |
|---|---|---|
| $\Delta H^\circ_{f,298}$ (Kj/mol) | -413.8 | -434.7 |

## Solution:

- Calculate $\Delta H_f(C_2H_{4(g)})$
  According to Hess's law:

$$\Delta H^\circ_{R,298} = 2\Delta H^\circ_f(CO_{2(g)}) + 2\Delta H^\circ_f(H_2O_L) - \Delta H^\circ_f(C_2H_{4(g)}) - 3\cancel{\Delta H^\circ_f(O_{2(g)})}$$

= 0

A simple and pure compound under standard conditions

$$\Rightarrow \Delta H^\circ_f(C_2H_{4\,(g)}) = 2\Delta H^\circ_f(CO_{2(g)}) + 2\Delta H^\circ_f(H_2O_L) - \Delta H^\circ_{R,298}$$

$$\Rightarrow \Delta H^\circ_f(C_2H_{4\,(g)}) = 2\,(-392{,}9) + 2(-284{,}2) - (-1387{,}87) = 33{,}6\ \text{Kj/mol}$$

- Calculate the bond energy of C=C in the molecule $C_2H_{4(g)}$:

We have the formation reaction equation for $C_2H_{4(g)}$ as follows (under standard conditions T = 298 K and P = 1 atm):

$$\begin{tikzcd}
2C_{graphite\,(s)} \arrow[d, "2\Delta H_{Sub\,(Cs)}"'] & + & 2\,H_{2(g)} \arrow[r, "\Delta H^\circ_{R,298}"] \arrow[d, "-\,2\,\Delta H^\circ_f\ (H\text{-}H)"'] & C_2H_{4(g)} \\
2C_{(g)} & + & 4\,H_{(g)} \arrow[ur, "\Delta H^\circ_f\ (C{=}C)\ +\ 4\,\Delta H^\circ_f(C\text{-}H)"'] \arrow[r, phantom, "\oplus"] &
\end{tikzcd}$$

$$\Delta H^\circ_{R,298} = \Delta H^\circ_{f\ 298}\,(C_2H_{4(g)})$$

$$\Rightarrow 2\,\Delta H_{Sub\,(Cs)} - \Delta H^\circ_f\ (H\text{-}H) + \Delta H^\circ_f\ (C{=}C) + 4\,\Delta H^\circ_f(C\text{-}H) - \Delta H^\circ_{f\ 298}\,(C_2H_{4(g)}) = 0$$

$$\Rightarrow \Delta H^\circ_f\ (C{=}C) = \Delta H^\circ_{f\ 298}\,(C_2H_{4(g)}) - 2\,\Delta H_{Sub\,(Cs)} + 2\,\Delta H^\circ_f\ (H\text{-}H) - 4\,\Delta H^\circ_f(C\text{-}H)$$

$$\Rightarrow \Delta H^\circ_f\ (C{=}C) = 33{,}6 - 2(\ 716{,}2\ ) + 2(-434{,}7) - 4(-413{,}8) = -613\ \text{KJ/mol}$$

**Note:** The bond energy A-B is related to the environment of these two atoms, and thus the C-H bond energy is not the same in $CH_3$-H or $CH_3$-OH. Therefore, the thermodynamic method for calculating bond energy provides approximate results and is not precise.

**Example 3:**
Consider the following reaction at a temperature of 298 K:

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl\ (g) + HCl\ (g)$$

- Calculate the standard molar enthalpy change for this reaction, $\Delta H^\circ_{R,298}$.
- Calculate the bond energy of C-H at a temperature of 298 K.
- Calculate the standard molar enthalpy of sublimation for carbon at a temperature of 298 K.

Data:

| The compound | $CH_4(g)$ | $CH_3Cl$ (g) | HCl (g) |
|---|---|---|---|
| $\Delta H^\circ_{f,298}$ (Kcal/mol) | -17.9 | -20 | -22 |

| Bond | Cl-Cl | C-Cl | H-Cl | H-H |
|---|---|---|---|---|
| $\Delta H^{\circ}_{f}$ (Kcal/mol) | -58 | -78 | -103 | -104 |

**Solution:**

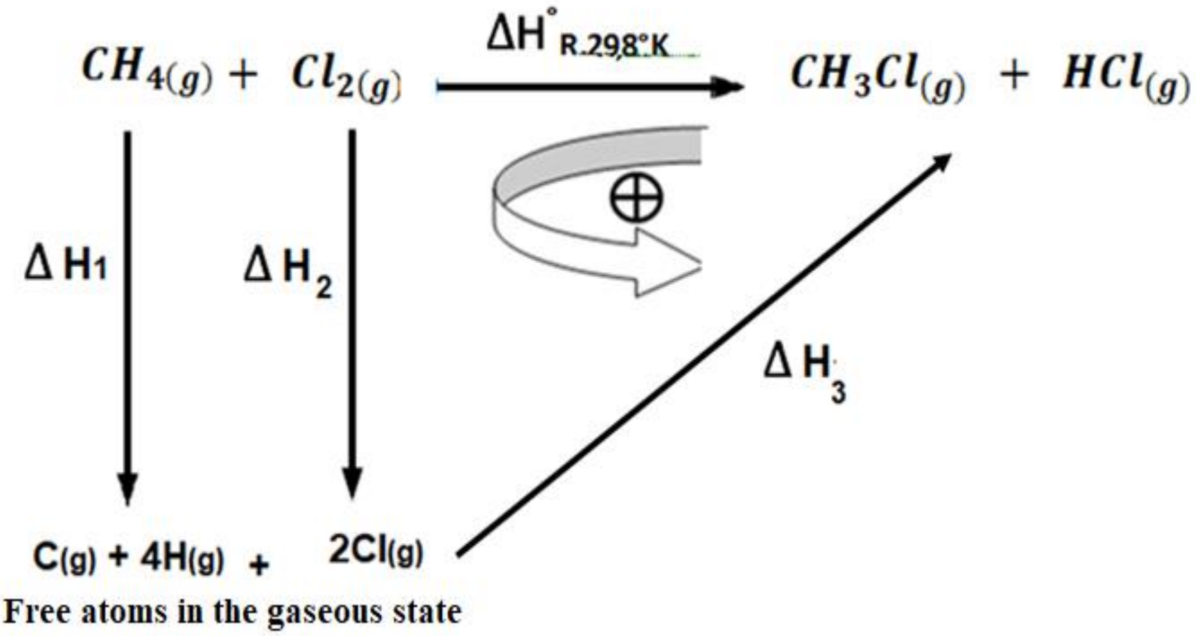
- Calculate $\Delta H^{\circ}_{R,298°K}$ :

  According to Hess's law:

$$\Rightarrow \Delta H^{\circ}_{R,298} = \Delta H^{\circ}_{f}(HCl\ (g)) + \Delta H^{\circ}_{f}(CH_3Cl\ (g)) - \Delta H^{\circ}_{f}(CH_4(g)) - \underbrace{\Delta H^{\circ}_{f}(Cl_2(g))}_{=0}$$

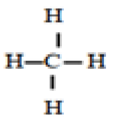
$$\Rightarrow \Delta H^{\circ}_{R,298} = (-22) + (-20) - (-17{,}9) = -24{,}1\ Kcal$$

- Calculating the bond energy of C-H in the molecule $CH_{4(g)}$



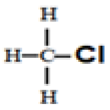
$$\Delta H_1 = 4E_{C-H}$$
$$\Delta H_2 = E_{Cl-Cl}$$
$$\Delta H_3 = -3E_{C-H} - E_{C-Cl} - E_{H-Cl}$$

**Lewis structures**


: $CH_4$

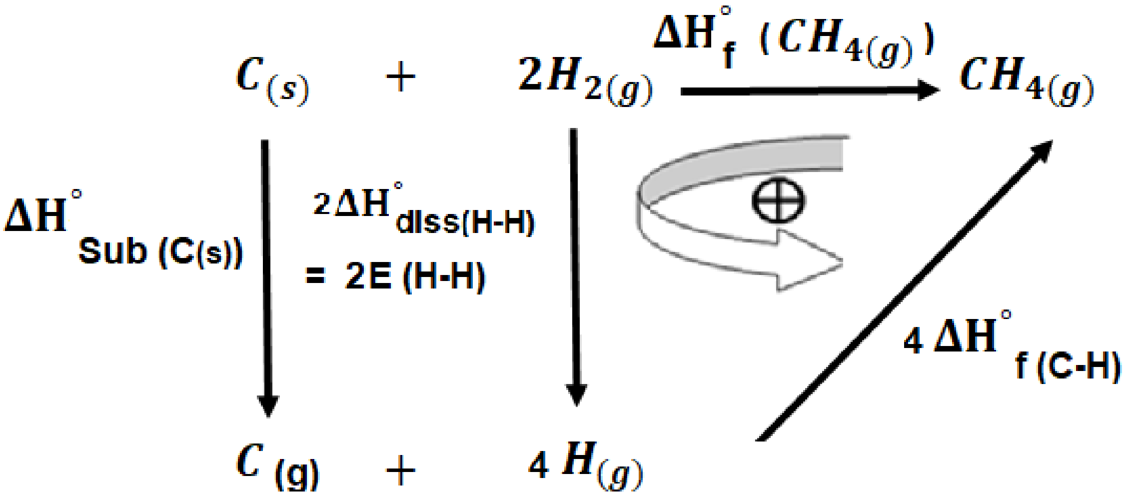
Cl-Cl : $Cl_2$

H-Cl : $HCl$


: $CH_3Cl$

$$\Rightarrow \Delta H^\circ_{R,298} = \Delta H_1 + \Delta H_2 + \Delta H_3 = 4E_{C-H} + E_{Cl-Cl} - 3E_{C-H} - E_{C-Cl} - E_{H-Cl}$$
$$\Rightarrow \Delta H^\circ_{R,298} = E_{C-H} + E_{Cl-Cl} - E_{C-Cl} - E_{H-Cl}$$
$$\Rightarrow E_{C-H} = \Delta H^\circ_{R,298} - E_{Cl-Cl} + E_{C-Cl} + E_{H-Cl} = -24,1 - 58 + 78 + 103$$
$$\Rightarrow E_{C-H} = 98,9\ Kcal/mol$$

- Calculating the standard molar enthalpy of sublimation for carbon :



$$\Delta H^\circ_f\ (CH_{4(g)}) = \Delta H^\circ_{Sub\ (C(s))} + 2E\ (H\text{-}H) + 4\ \Delta H^\circ_{f\ (C\text{-}H)}$$

$$\Delta H^\circ_{Sub\ (C(s))} = \Delta H^\circ_f\ (CH_{4(g)}) - 2E\ (H\text{-}H) - 4\ \Delta H^\circ_{f\ (C\text{-}H)}$$

$$\Delta H^\circ_{Sub\ (C(s))} = -17{,}9 - 2(104) - 4(-98{,}9) = 169{,}7\ Kcal/mol$$