Gaseous atom Gaseous cation

$A_{(g)} \longrightarrow A^{+}_{(g)} \quad \Delta H_r=\Delta H_i$

Example :

$C_{(g)} \longrightarrow C^{+}_{(g)}$

$Na_{(g)} \longrightarrow Na^{+}_{(g)}$

$Ca_{(g)} \longrightarrow Ca^{2+}_{(g)}$

VI-4- Electron affinity (Enthalpy affinity ΔH_{Aff} or E_{Aff}):

It's the energy that corresponds to the transformation of a gaseous atom into a gaseous anion (a gaseous atom gains electrons).

$A_{(g)} \longrightarrow A^{-}_{(g)}$

Example:

$Cl_{(g)} \longrightarrow Cl^{-}_{(g)}$

$O_{2(g)} \longrightarrow O^{2-}_{(g)}$

$F_{(g)} \longrightarrow F^{-}_{(g)}$

VI-5- Enthalpy of sublimation (ΔH_{sub}):

This is the energy associated with changing the physical state of an atom from solid to gas.

$A_{(s)} \xrightarrow{\Delta Hr} A_{(g)} \quad \Delta H_r=\Delta H_{sub}$

Example:

$C_{(s)} \longrightarrow C_{(g)}$

$Fe_{(s)} \longrightarrow Fe_{(g)}$

$Na_{(s)} \longrightarrow Na_{(g)}$

VI-6- Lattice Enthalpy (reticular enthalpy /lattice energy ΔH_{ret}):

Lattice enthalpy is the energy required to form a solid crystal from gaseous ions.

$A^{+}_{(g)} + B^{-}(_{g}) \longrightarrow A\text{–}B_{(s)} \quad \Delta H_r=\Delta H_{ret}$

Example:

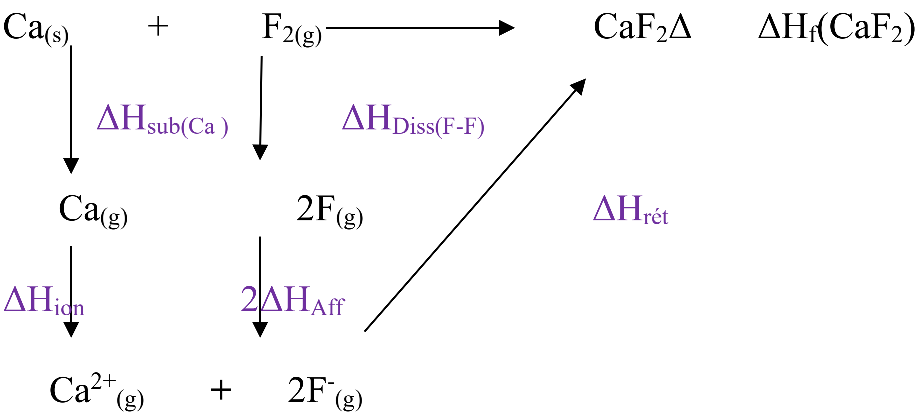
$Na^{+}_{(g)} + Cl^{-}_{(g)} \longrightarrow NaCl_{(s)}$ $K^{+}_{(g)} + I^{-}_{(g)} \longrightarrow KI_{(s)}$

$K^{+}_{(g)} + Cl^{-}_{(g)} \longrightarrow KCl_{(s)}$

Some lattice energy values:

Ionic compounds	NaF	NaCl	CsI
Lattice energy kcal/mole	-217	-184	-141

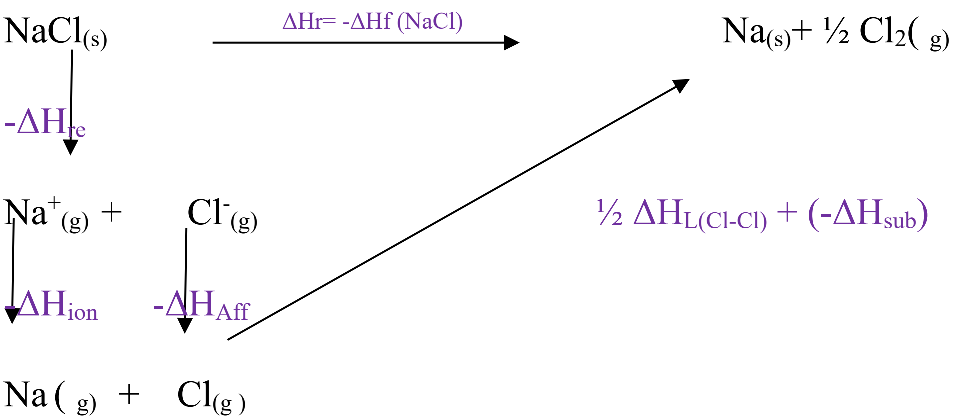
Example 1: Express ΔH_f (CaF_2) in terms of lattice energy $\Delta H_{ré}$ (CaF_2).



The formation reaction is only with pure simple reactants.

So : $\Delta H_{f(CaF_2)} = \Delta H_{sub(Ca)} + \Delta H_{Diss(F-F)} + \Delta H_{ion(Ca)} + 2\,\Delta H_{Aff\,(F)} + \Delta H_{ret}$

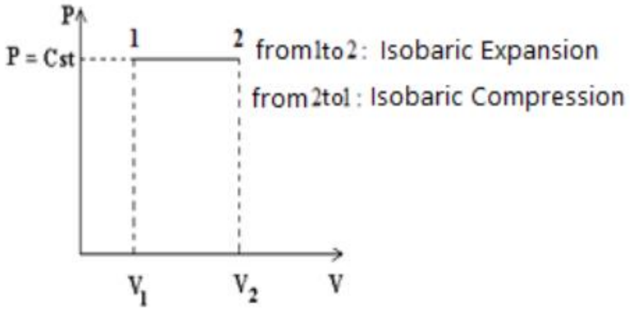
Example 2:



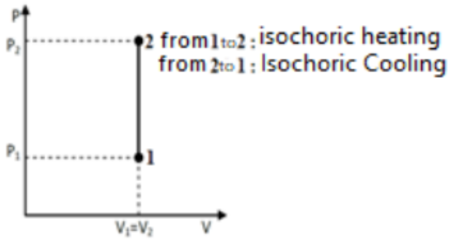
VII- CLAPEYRON diagram:

In this diagram, different transformations (Isobaric, Isothermal, Isochoric, and Adiabatic) are graphically represented by the variation of pressure as a function of volume.

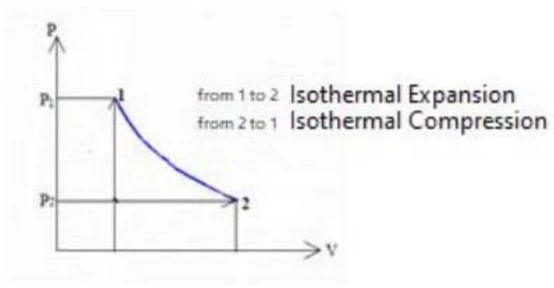
VII-1- ISOBARIC transformation:



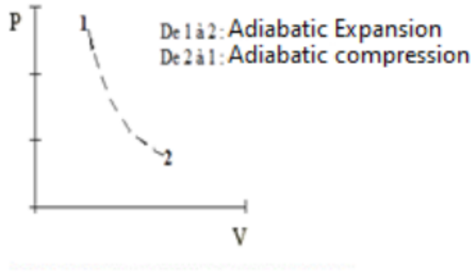
VII-2- ISOCHORIC transformation:



VII-3- ISOTHERMAL transformation:



VII-4- ADIABATIC transformation:



Example :

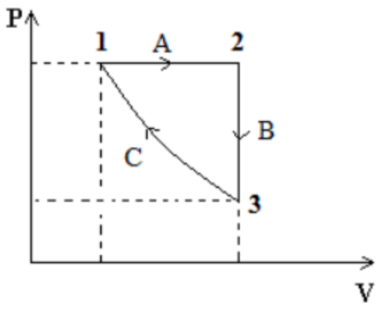
Consider a gas undergoing the following transformations:

Step A1 →2 Isobaric Expansion at constant pressure P= cste.

Step B2 → 3 Isochoric Cooling at constant volume V = cst.

Step C3 → 1 Isothermal Compression at constant temperature T = cste.

Provide the different expressions for W, ΔU, Q, ΔH ?



Step A : Isobaric Expansion

$(P = P_1 = cste)$,

$$W = -\int_{V_1}^{V_2} PdV = -P(V_2 - V_1)$$

$$Q_P = nC_P\Delta T = \Delta H$$

$$\Delta U = W + Q_P$$

Step B : Isochoric Cooling

$V = cst$ therefore $W = -\int PdV \Rightarrow W = 0$

$Q_V = nC_V\Delta T = \Delta U$

$H = U + PV \Rightarrow \Delta H = \Delta U + \Delta(PV)$

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

$\Delta H = \Delta U + nR\,\Delta T = \Delta U + nR\,(T_1 - T_2)$ $(T_1 = T_3)$

Step C : Isothermal Compression

T = cste therefore U = cste => $\Delta U = 0$

W = -Q since $\Delta U = W + Q = 0 \Rightarrow W = -Q$

$$W = -nRT\ln\frac{V_2}{V_1} = -nRT\ln\frac{P_2}{P_1}$$

$$Q = -W = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{P_2}{P_1}$$

Exercise :

We consider an ideal gas undergoing successive transformations represented in a CLAPEYRON diagram, starting from the initial state A characterized by the pressure: PA = 3 atm, VA = 16 L, TA = 300 K.

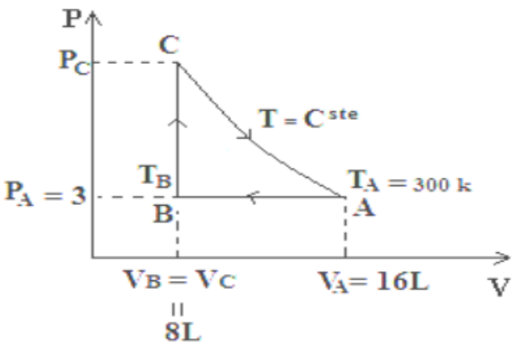
$A \longrightarrow B$ (isobaric compressionV_B = 8L).

$B \longrightarrow C$ (isochoric heating).

$C \longrightarrow A$ (isothermal expansion).

- Represent all these transformations on aCLAPEYRON diagram.
- Calculate the number of moles of gas.
- Calculate the pressure at point C and the temperature T_B.
- Calculate for each transformation the amount of heat exchanged with the surroundings, ΔH, Q, W, ΔU.

  Given $C_P = 11{,}66\ J\ k^{-1}\ mol^{-1}$



- The number of moles :

$$P_AV_A = nRT_A \Rightarrow n = \frac{P_AV_A}{RT_A} = \frac{3,16_3}{0,082 \text{ x } \ 00} = 1,95\text{mole}$$

- The pressure at point C : $T_C = T_A = 300$ k

$$P_CV_C = nRT_C \Rightarrow P_C = \frac{nRT_C}{V_C} = \frac{1,95 \text{ x } 0,\ 82 \text{ x } 300}{8} = 6 \text{ atm}$$

- Calculation of T_B.

$$P_BV_B = nRT_B \Rightarrow T_B = \frac{P_BV_B}{0,082 \text{ x } \ ,95} = 150 \text{ k}$$

VII-The second law of thermodynamics:

In the second law of thermodynamics, we will study the evolution of the reaction (chemical transformation). For this purpose, we introduce a new state function called Entropy (S). This state function allows us to determine whether the reaction is spontaneous or not. The change in entropy ΔS is given by the following relation:

$$\Delta S = \Delta_i S + \Delta_e S$$

$\Delta_i S$: change in internal entropy.

$\Delta_e S$: change in external entropy.

We can calculate ΔS using the relation: $\Delta S = \int \frac{dQ}{T}$

$\Delta_e S = \frac{Q}{T_{ext}}$ Therefore: $\Delta_i S = \Delta S - \Delta_e S$

VII-1- Concept of Entropy :

An isolated system that has undergone an evolution cannot return to the initial state.

Transition from state A(order) to state B (disorder)

$\Delta S = S_B - S_A = \int \frac{dQ}{T}$ In any reversible evolution, the entropy of an isolated system remains constant.

1) Variation of entropy S with temperature and pressure S = f(T,P)

   H= U +PV

   dH= dU +d(PV) = CpdT

   Therefore: $dS = Cp\frac{dT}{T} - R\frac{dP}{P}$ …..(1)

2) Variation of entropy S with temperature and volume S = f(T, V)

   dU = dQ +dW = CvdT

   Therefore: $dS = Cv\frac{dT}{T} + R\frac{dV}{V}$……(2)

3) Variation of entropy S with pressure and volume S = f(P, V)

   (1)= (2)

   We deduce : $\frac{dT}{T} = \frac{dV}{V} + \frac{dP}{P}$

   Replace in (1) or (2)

   If we replace in (2) we will have : $dS = Cv(\frac{dV}{V} + \frac{dP}{P}) + R\frac{dV}{V}$

   $dS = Cp\frac{dV}{V} + Cv\frac{dP}{P}$

   For a reversible cycle, ΔS=0 so dS = 0

$$Cp\frac{dV}{V} + Cv\frac{dP}{P} = 0$$

Divide by Cv, we will have : $\frac{Cp}{Cv}\frac{dV}{V} + \frac{Cv}{Cv}\frac{dP}{P} = 0$

We have : $\frac{Cp}{Cv} = \gamma$

$$\gamma\frac{dV}{V} + \frac{dP}{P} = 0$$

integrate both sides of the equation and obtain:

$\gamma \ln V + \ln P = cst$

$\ln V^{\gamma} + \ln P = cst$

$\ln PV^{\gamma} = cst,$

Therefore : $\mathbf{PV^{\gamma} = cste}$

According to the ideal gas law PV= nRT, we get $P = \frac{nRT}{V}$ and replace it in the previous expression $\frac{nRT}{V}V^{\gamma} = cst$ with n, R cst

We obtain: $\mathbf{TV^{\gamma-1} = cste}$

We derive $V = \frac{nRT}{P}$ and replace it in the same previous expression

$p\frac{(nRT)^{\gamma}}{P^{\gamma}} = cst$

$\frac{PT^{\gamma}}{P^{\gamma}} = cst$ and obtain: $\mathbf{P^{1-\gamma}T^{\gamma} = cste}$

VII-2- Expression of entropy :

VII-2-1- For an isobaric transformation P = cste :

At constant pressure, we have: $\Delta H = Q_P = n\,C_P\,\Delta T$

$dH = dQ = n\,C_P\,dT$

$$\Delta S = \int \frac{dQ}{T} = \int \frac{nC_PdT}{} = nC_P \int_{T_1}^{T_2} \frac{dT}{T} = n\,C_P \ln T \,|_{T_1}^{T_2}$$

$$\Delta S = nC_P(\ln T_2 - \ln T_1)$$

Therefore $\boldsymbol{\Delta S = nC_P ln\frac{T_2}{T_1}}$

VII-2-2- For an isochoric transformation V = cste:

At constant volume, we have $\Delta U = Q_V = n\,C_V\,\Delta T$

$dU = dQ = n\,C_V\,dT$

$$\Delta S = \int \frac{dQ}{T} = \int \frac{nC_VdT}{T} = nC_V \int_{T_1}^{T_2} \frac{dT}{T}$$

Therefore: $\boldsymbol{\Delta S = nC_V ln\frac{T_2}{T_1}}$

VII-2-3- For an isothermal transformation T = cste:

At constant temperature, we have W = -Q

$$W = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

$$\Delta S = \Delta_e S = \frac{Q}{T_{ext}} = \frac{Q}{T}$$

$Q = nRT \ln \frac{V_2}{V_1}$ so $\Delta S = \frac{Q}{T} = \frac{nRT \ln \frac{V_2}{V_1}}{T}$

$$\boldsymbol{\Delta S = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}}$$

VII-3- Entropy calculation:

At 0K (-273°C) we have S°(0k) = 0

At standard stateT= 25°C (298k), we have $\Delta S = S°_{(298k)} - S°_{(0k)} = S°_{(298k)}$

If the temperature T > 298k

H=U + PV

dH= dU +PdV + VdP = TdS –PdV + VdP +PdV

dH= CpdT= TdS+VdP

At P=cste we have CpdT=TdS=>dS $= \frac{CpdT}{T}$

Thus $\Delta S = \int_{298}^{T} \frac{CpdT}{T} = S_T - S_{298}$ and finally, we find:

$$\mathbf{S_T = S_{298} + Cp\ln\frac{T}{298}}$$

VII-4- Entropy of a reaction:

The change in entropy is a state function, dependent only on the final and initial states.

For a chemical reaction, and according to Hess's law, we can write:

$\mathbf{\Delta S_{reaction} = \Sigma S_{products} - \Sigma S_{reactants}}$

VII-4-1- Prediction of the sign of ΔS :

▶ The entropy of a system increases when it evolves towards states that are more disordered than the initial state.

Solid → liquid → gas ΔS increases

► For a given phase, ΔS increases: - When pressure decreases

- When concentration decreases (dilution)

$\Delta_i S$: Variation of internal entropy provides information about intermolecular collisions.

If $\Delta_i S > 0$ (spontaneous reaction).

If $\Delta_i S < 0$ (impossible reaction).

If $\Delta_i S = 0$ (chemical equilibrium).

VII-5- Gibbs free energy G (Free enthalpy) :

Chemical reactions occur due to collisions between reactant molecules. Atoms are released, and their unions in one direction or another depend on:

- Bonding energy
- Molecular disorder

A second state function, relating enthalpy and entropy, is introduced to better understand the second law of thermodynamics. This state function is called Gibbs free energy, G.

$$\mathbf{G = H - TS}$$

At constant temperature and pressure, we can write: $\mathbf{\Delta G = \Delta H - T\,\Delta S}$

The change in Gibbs free energy of a reaction is given by Hess's law.

$$\Delta G_{reaction} = \sum \Delta G_{products} - \sum \Delta G_{reactants}$$

With : $\begin{cases} \Delta G \text{ (pure simple substances/pure elements)} = 0 \\ S \text{ (pure simple substances/pure elements)} \neq 0 \end{cases}$

Pure simple substances/pure elements ($C_{(s)}$, $Fe_{(s)}$, $Na_{(s)}$, $Cu_{(s)}$, $H_{2(g)}$, $Cl_{2(g)}$, $O_{2(g)}$, $N_{2(g)}$,)

The change in Gibbs free energy also informs us about the possibility of the reaction.

If $\Delta G > 0$ (impossible reaction).

If $\Delta G < 0$ (spontaneous reaction).

If $\Delta G = 0$ (chemical equilibrium).

For a chemical reaction, the change in Gibbs free energy can be related to the equilibrium constant by the following expression:

$$\Delta G = \Delta G° + RT \ln k$$

$\Delta G°$: Standard change in Gibbs free energy.

R : Ideal gas constant.

k : Equilibrium constant.

For a chemical equilibrium: $\Delta G = 0$

$\Delta G = \Delta G° + RT \ln k = 0 \Rightarrow \Delta G° = - RT \ln k$

Or: $\ln k = \frac{\Delta G°}{RT}$

Thus, the equilibrium constant can be deduced $k = e^{-\frac{\Delta G°}{RT}}$

VIII- Application exercise

Exercise N° 01:

A mass m of an ideal gas undergoes the following reversible cycle transformations:

- From A to B: isobaric $P1=10^5$ Pa, volume V_1, temperature T_1.
- From B to C: isochoric $V_2=\frac{V_1}{5}$ = 2L, P_2=final pressure at C (C_p= 11,66 JK^{-1}).
- From C to A: isothermal T1=300 K.

Calculate the pressure P_2, the work done, and the heat quantities received during the cycle.

Exercise N° 02:

Consider an ideal gas in the initial conditions PA=3 atm, TA=300 K, VA=16.4 L, which undergoes the following reversible transformations (given γ=1.66):

- From A to B: adiabatic compression until T_B=450 .
- From B to C: isochoric cooling until PC=4.05 atm.

- From C to D: isothermal expansion until P_D=3 atm.
- From D to A: isobaric.

Determine the state variables (P, V, T) at each stage.

Represent the different transformations on a Clapeyron diagram.

Calculate the work done, heat transfer, change in internal energy, and enthalpy for each transformation. Show that the first law of thermodynamics is verified.

Exercise Nº03:

In winter, to avoid freezing, a greenhouse containing 812 g of air (assumed to be an ideal gas) is heated, raising the temperature from 2°C to 16°C. Calculate:

- The change in internal energy of the air during this heating.
- The amount of heat received by the gas if it performed 846.4 Joules of work. Data: The molar mass of air M=29g/mol, R=8.32 J/mol. The ratio of specific heats for air $\gamma = Cp / Cv = 1.4$.

Exercise Nº04:

An ideal gas occupies a volume of 17.40 dm^3 at 300 K under a pressure of 1.05×10^5 Pa. The gas is heated at constant volume (isochoric transformation) until the pressure reaches 1.80×10^5 Pa. Calculate the final temperature of the gas.

a) Demonstrate that for ideal gases, the change in internal energy ΔU and enthalpy ΔH depends only on temperature.

b) Derive Mayer's relation and the molar heat capacity at constant volume Cv for this gas.

c) Calculate ΔU and ΔH.

d) Calculate the heat supplied to the gas to bring it to the final state.

Data: Molar heat capacity of this gas at constant pressure Cp=29.30 J/mol.

Solution

Solution N°01

State of the gas

C P_2, V_2= 2 L, T= 300 K

A P_1, V_1= 10 L, T= 300 K

1- Isothermal from C to A: $P_2 V_2 = P_1 V_1$: from where P_2= 5. 10^5 Pa.
2- work received: dw= -pdv

W_{AB}= -PΔV= 10^5 (2-10) 10^{-3}= 800 J

W_{BC}= 0 isochoric

dW_{CA}= -PdV= $-nRT_1 \frac{dV}{V}$

W_{CA}= $-nRT_1 \ln\frac{V_1}{V_2}$= $-P_1V_1\ln(5) = 10^5\ 2.\ 10^{-3} \ln 5 = -1610$ J.

3- Heat received:

The internal energy does not change over the cycle W + Q= 0 car ΔV= W + Q

D'où ΣQ= -ΣW= 810 J.

The internal energy does not change on the isotherm: Q_{CA}= $-W_{CA}$= 1610 J.

Q_{AB}= C_p ΔT (isobaric) = $C_p (T_B - T_1)$

Calculation T_B: $P_1V_2 = nRT_B$; $P_1V_1 = nRT_1$ D'où $T_B = \frac{V_2T_1}{V_1} = 60$ K.

Q_{AB}= 11,66 (60-300)= -2800 J.

810= -2800 + 1610 + Q_{BC} d'où Q_{BC}= 2000 J.

Solution N°02:

The state variables (P, V, T) of each stage:

A $\longrightarrow$ B: réversible adiabatic $P^{1-\gamma} T^{\gamma}$ = Constant ; $P_A^{1-\gamma} T_A^{\gamma} = P_B^{1-\gamma} T_B^{\gamma} \Rightarrow P_B^{1-\gamma} = \frac{P_A^{1-\gamma} T_A^{\gamma}}{T_B^{\gamma}}$

$$P_B^{1-\gamma} = \left(\frac{T_A}{T_B}\right)^{\gamma} \Rightarrow P_B = \left(P_A^{1-\gamma}\left(\frac{T_A}{T_B}\right)^{\gamma}\right)^{\frac{1}{1-\gamma}}$$

$$P_B = \left(P_A^{1-\gamma}\right)^{\frac{1}{1-\gamma}}\left(\left(\frac{T_A}{T_B}\right)^{\gamma}\right)^{\frac{1}{1-\gamma}}$$

$$P_B = P_A^{\frac{1-\gamma}{1-\gamma}}\left(\frac{T_A}{T_B}\right)^{\frac{\gamma}{1-\gamma}}$$

$$P_B = P_A\left(\frac{T_A}{T_B}\right)^{\frac{\gamma}{1-\gamma}} = 3\left(\frac{300}{450}\right)^{-2{,}52} = 8{,}3 \text{ atm.}$$

Ideal gas law: $V_B = \frac{V_A P_A T_B}{P_B T_A} = \frac{16{,}4\ 3\ 450}{8{,}3\ 300} = 8{,}9$ L.

$P_BV_B = nRT_B \Rightarrow V_B = \frac{nRT_B}{P_B}$ ………….. (1)

$P_AV_A = nRT_A \Rightarrow nR = \frac{P_AV_A}{T_A}$

(1) $V_B = \frac{nRT_B}{P_B} \Rightarrow V_B = \frac{P_AV_A}{T_A}\frac{T_B}{P_B} \Rightarrow V_B = \frac{P_AV_A\,T_B}{T_A\,P_B}$

$P_CV_C = nRT_C \Rightarrow T_C = \frac{P_CV_C}{nR}$ …………… (2)

$P_BV_B = nRT_B \Rightarrow nR = \frac{P_BV_B}{T_B}$

(2) $T_C = \frac{P_CV_C}{nR} \Rightarrow T_C = \frac{P_CV_C}{\frac{P_BV_B}{T_B}} \Rightarrow T_C = \frac{P_C\cancel{V_C}\,T_B}{P_B\cancel{V_B}} \Rightarrow T_C = \frac{P_CT_B}{P_B}$

B ⟶ C: reversible isochoric: VC = 8,9 L= V_B.

Ideal gas law: $T_C = \frac{T_BP_C}{P_B} = \frac{450\ 4{,}05}{8{,}3} = 220$ K.

C ⟶ D: réversible isothermal: $T_D = 220$ K.

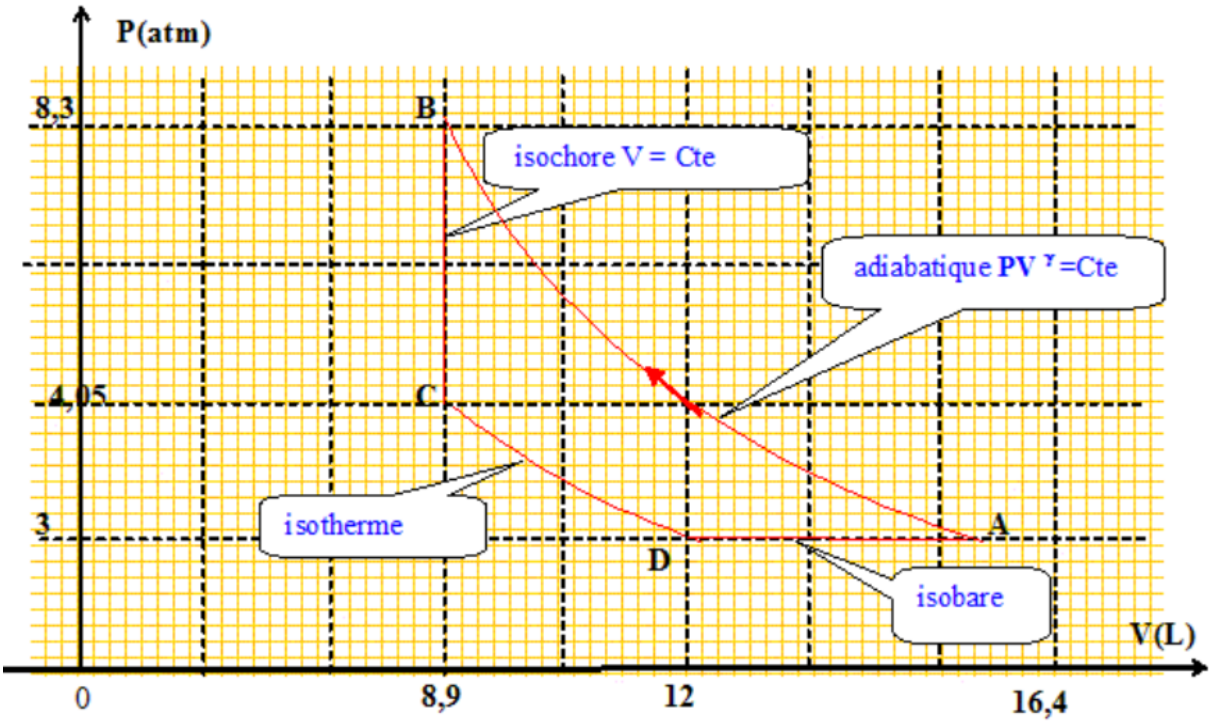
Ideal gas law: $V_D = \frac{V_CP_C}{P_D} = \frac{8{,}9\ 4{,}5}{3} = 12$ L.

$P_DV_D = P_CV_C \Rightarrow VD = \frac{}{PP_C}$

V_C

D

Representation of the different transformations on a Clapeyron diagram:



2-The work, heat, change in internal energy, and enthalpy for each of the transformations:

A ⟶ B : réversible adiabatic Q_{AB}=0 and $P V^{\gamma} = Cste \Rightarrow P_2V_2^{\gamma} = P_1V_1^{\gamma}$

$$\boxed{W = -Cte\int_1^2 \frac{dV}{V^{\gamma}} = -\frac{Cte}{1-\gamma}[V^{1-\gamma}]_1^2 = \frac{Cte}{\gamma-1}(V_2^{1-\gamma} - V_1^{1-\gamma}) = \frac{p_2V_2^{\gamma}\,V_2^{1-\gamma} - p_1V_1^{\gamma}V_1^{1-\gamma}}{\gamma-1} = \frac{p_2V_2 - p_1V_1}{\gamma-1}}$$

$W_{AB}=\frac{8,3\ 10^5.8,9\ 10^{-3} - 3\ 10^5.16,4\ 10^{-3}}{0,66}$; W_{AB}= 3,74 kJ.

ΔU_{AB}= 3,74 kJ ; $\Delta HA\ _B=\frac{nR\gamma}{(\gamma-1)\Delta T}=\frac{8,31\ 1,6\quad 6}{0,66\ 150}$ = 6,3 k J.

$P_AV_A = nRT_A \Rightarrow n=\frac{P_AV_A}{RT_A} \Rightarrow n=\frac{3\ 10^5\ 16\ 10^{-3}}{8,31\ 300} = 1,97 \simeq 2.$

B ⟶ C: réversible isochoric : W_{BC}= 0 et $Q_{BC}= \Delta U_{BC}=\frac{nR}{(\gamma-1)\Delta T}$

$n=\frac{P_AV_A}{RT_A} \Rightarrow n=\frac{3\ 10^5\ 16,4\ 10^{-3}}{8,31\ 300}$= 2mol.

$Q_{BC}=\frac{nR}{(\gamma-1)\Delta T} \Rightarrow Q_{BC}=\frac{2\ 8,31}{0,66\ (200-450)}$ = -5,8 k J.

ΔU_{BC}= -5,8 k J.

$\Delta H_{BC}=\frac{nR\gamma}{(1-\gamma)\Delta T}=\frac{2\ 8{,}31\ 1{,}66}{0{,}66\ (220-450)}$ => ΔH_{BC}= -9,6 k J.

C ⟶ D: réversible isothermal: $\Delta U_{CD}= 0$; $\Delta H_{CD}= 0$

$Q_{CD}= -W_{CD}= nRT\ \ln(\frac{V_D}{V_C})= nRT\ \ln(\frac{P_D}{P_C})$

$Q_{CD}= 2\ 8{,}31\ 220\ \ln(\frac{12}{8{,}9})$ => Q_{CD}= 1,1 k J and W_{CD}= -1,1 k J.

C ⟶ D: réversible isobaric.

$\Delta H_{CD}=\frac{nR\gamma}{(1-\gamma)\Delta T}=\frac{2\ 8{,}31\ 1{,}66}{0{,}66\ (300-220)}$ => ΔH_{CD}= 3,3 k J.

$\Delta U_{CD}=\frac{nR}{(1-\gamma)\Delta T}=\frac{2\ 8{,}31}{0{,}66\ (300-220)}$ => ΔH_{CD}= 2,0 k J.

$W_{DC}= P\ (V_D-V_C) = 3.\ 10^5\ (16{,}4\ 10^{-3} – 12.\ 10^{-3})$ => W_{DC}= 1,3 k J.

$Q_{DC}= \Delta U_{CD} – W_{DC}$ = 2,0 -1,3 => Q_{DC}= 0,7 k J.

1- Show that the first principle is verified:

$\Delta U_{Cycle}= 0$; $\Delta H_{Cycle}= 0$.

Sum of works W_{total}= 3,7 – 1,1 + 1,3 $\simeq$ 3,9 k J.

Sum of heat quantities" Q_{total}= -5,8 + 1,1 + 0,7 $\simeq$ -4 k J.

$W_{total} + Q_{total} = 0$

Solution N°03:

The change in internal energy of n moles of an ideal gas: $\Delta U = n\ C_{(V)}\ \Delta T$ Air is a diatomic ideal gas: $C_V = \frac{5}{2}R$ therefore:

$\Delta U=\frac{812}{29}\ x\ \frac{5}{2}\ x\ 8{,}32\ 14$= 8153,6 J.

a) We have $\Delta U = W + Q$ ou $\Delta U = \Delta W + \Delta Q$

The amount of heat exchanged by the gas (air) is::

$Q = \Delta U - W$ or $W = -846{,}4$ because the air has done work

D'où $Q = 8153{,}6 - (-846{,}4) = 9000$ J.

Solution N°04:

1- At constant volume, for ideal gases, we have: $\frac{P}{T}$ = constant.

therefore: $T_f = \frac{P_f}{P_i} T_i = \frac{1{,}8}{1{,}05}\, 300 = 514{,}28$ K.

2-

a) Par définition $\Delta U = Q + W$, At constant volume, $W = 0$ therfore: $\Delta U = Q_{\upsilon} = n\, C_V\, \Delta T$

ΔU depends only on the temperature.

$$\Delta H = \Delta U + \Delta(PV) \Rightarrow \Delta H = Q_{\upsilon} + P\Delta V + V\Delta P$$

$$= Q_{\upsilon} + V\Delta P \text{ (car } V = \text{constant).}$$

$$= n\, C_V\, \Delta T + V\Delta \frac{nR}{V}\, T$$

$$= n\, C_V\, \Delta T + n\, R\, \Delta T \text{ (car } V = \text{constant).}$$

$$\Delta H = n\,(C_V + R)\, \Delta T$$

ΔH depends only on the temperature.

b) From the expression $\Delta H = n\, C_P\, \Delta T$, we derive Mayer's expression:

$C_P = C_V + R$ From which $C_V = 20{,}986$ J. mol^{-1} K^{-1}.

c) Calculation ΔU et ΔH

$$\Delta U = Q_{\upsilon} = \frac{PV}{RT} C_V\, \Delta T = \frac{1{,}050\ 10^5\ 17{,}4\ 10^{-3}}{8{,}314\ 300}\, 20{,}986\ (514{,}28 - 300) = 3294 \text{ J.}$$

$$\Delta H = Q_P = \frac{PV}{RT} C_P\, \Delta T = \frac{1{,}050\ 10^5\ 17{,}4\ 10^{-3}}{8{,}314\ 300}\, 29{,}300\ (514{,}28 - 300) = 4599 \text{ J.}$$

3- At constant volume $Q_{\upsilon} = \Delta U = 3294$ J.

I- Fundamentals :

In the chemistry of solutions, several definitions have been given for acids and bases.

I-1- Bronsted-Lowry definition :

- A Bronsted acid is a chemical species (ion or molecule) capable of donating a proton **H^+** or **H_3O^+** in a solution; it is a proton donor.

$$\mathbf{AH + H_2O \rightarrow A^- + H_3O^+}$$

- A Bronsted base is a chemical species (ion or molecule) capable of accepting a proton **H^+** in a solution; it is a proton acceptor.

$$\mathbf{B + H_2O \rightarrow BH^+ + OH^-}$$

I-2-Arrhenius definition:

- According to Arrhenius, an acid is a chemical species (ion or molecule) capable of producing hydroxide ion **OH^-**in solution, it is a **OH^-** hydroxide ion acceptor.
- A base, according to Arrhenius, is a chemical species (ion or molecule) capable of producing hydroxide ion **OH^-** in a solution; it is a hydroxide ion donor **OH^-**.

I-3- Lewis definition:

- An acid, as per Lewis, is a chemical species (ion or molecule) that possesses an empty orbital (space).
- A base, as per Lewis, is a chemical species (ion or molecule) that has a lone pair of electrons (a free electron pair) and tends to accept H^+.

Examples:

$HCl + H_2O \rightarrow Cl^- + H_3O^+$

$CH_3COOH + H_2O \;===\; CH_3COO^- + H_3O^+$

$H_3PO_4 + H_2O \;====\; H_2PO^-_4 + H_3O^+$

$H_2PO^-_4 + H_2O \;====\; HPO^{-2}_4 + H_3O^+$

$HPO^{-2}{}_4 + H_2O$ ==== $PO^{-3}{}_4 + H_3O^+$

$H_3O^+ \longrightarrow H^+ + H_2O$ H_3O^+an acid

$HBr + H_2O \longrightarrow H_3O^+ + Br^-$

$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO^-{}_4$

$Na\,OH \longrightarrow Na^+ + OH^-$

$NH_3 + H_2O$ ==== $NH^+{}_4 + OH^-$ NH_3 is a base

$Ca\,(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$

$Ba\,(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$

$H_2O + H^+ \longrightarrow H_3O$ H_2O is a base

$CO^{2-}{}_3 + H_2O$ ==== $HCO^-{}_3 + OH^-$

$HCO^-{}_3 + H_2O$ ==== $H_2CO_3 + OH^-$

Conjugate acid/base pair:

Every acid-base reaction involves 2 conjugate pairs :

⇨ For each acid, a corresponding base is formed as a result of losing an H+ from that acid. This base is called the conjugate base: Acid **HA** / Conjugate Base **A^-** .

⇨ For each base, a corresponding acid is formed as a result of gaining an H+ by the base. This acid is called the conjugate acid: Acid **BH^+** / Conjugate Base **B**.

$HA_{\text{acid 1}} + B_{\text{base 2}}$ == $A^-{}_{\text{base 1}} + BH^+{}_{\text{acid 2}}$ **(HA / A- and BH+/B)**

$HCN + H_2O$ == $CN^- + H_3O^+$ **(HCN / CN^- and H_3O^+ / H_2O)**

$HCOOH + H_2O$ == $HCOO^- + H_3O^+$ **($HCOOH / HCOO^-$ and H_3O^+ / H_2O)**

$H_2SO_4 + H_2O$ ==$HSO^-{}_4 + H_3O^+$ **($H_2SO_4/HSO^-{}_4$ and H_3O^+ / H_2O)**

$HSO^-{}_4 + H2O$ ==$SO^{2-}{}_4 + H_3O^+$ **($HSO^-{}_4 / SO^{2-}{}_4$ and H_3O^+ / H_2O)**

$NH_3 + H_2O$ == $NH^+{}_4 + OH^-$ **($NH^+{}_4 / NH_3$ and H_2O / OH^-)**

$CH_3NH_2 + H_2O$ == $CH_3NH^+{}_3 + OH^-$ **$H_3NH^+{}_3 / CH_3NH_2$ and H_2O / OH^-)**

$C_2H_5NH_2 + H_2O == C_2H_5NH^+_3 + OH^-$ ($C_2H_5NH^+_3$ / $C_2H_5NH_2$ and H_2O / OH^-)

Amphoteric Substances (Ampholytes):

A substance is called amphoteric or ampholytic if it can behave as an acid or a base.

$H_3PO_4 + H_2O \Longrightarrow H_2PO^-_4 + H_3O^+$

$H_2PO^-_4 + H_2O \Longrightarrow HPO^{2-}_4 + H_3O^+$

$HPO^{2-}_4 + H_2O \Longrightarrow PO^{-3}_4 + H_3O^+$

$AH + H_2O \rightarrow A^- + H_3O^+$

$B + H_2O \rightarrow BH^+ + OH^-$

As observed in the previous examples, the molecule H_2O acts as an acid with bases and as a base with acids. Therefore, the water molecule is termed amphoteric or ampholytic.

II- Autoionisation of Water:

The structure of the H_2O molecule imparts amphiprotic (amphoteric) properties to water, which result in the transfer of a proton from one water molecule, acting as an acid, to another water molecule, acting as a base.

$H_2O + H_2O \Leftrightarrow OH^- + H_3O^+$

The existence of equilibrium dictates that the concentrations of $H3O^+$ and OH^- ions cannot vary independently. These quantities are interrelated by the water's ion product, whose value is calculated from the concentrations **$[H3O^+]$** and **$[OH^-]$** in pure water :

$K_e = [H_3O^+] \times [OH^-] = 10^{-14}$ à 25°C

Mathematically, it is possible to take the decimal logarithm of Ke. This leads to the definition of pKe :

$pK_e = -\log K_e$ thus $K_e = 10^{-pKe}$

III- Concept of pH :

III-1- Definition

The pH, or the hydrogen potential, expresses the concentration of hydronium ions in a solution. In a not highly concentrated solution, pH is given by SORENSEN's relation :

$pH = -\log [H_3O^+]$ or $[H_3O^+] = 10^{-pH}$

III-2- pH Scale

For the vast majority of practical applications at temperature of 25°C,

The pH scale ranges from 0 to 14.

- In pure water at 25°C, **$[H_3O^+] = [OH^-] = 10^{-7} molL^{-1}$: neutral medium, $pH = 7$.**
- If **$[H_3O^+] > 10^{-7} molL^{-1}$, $[OH^-] < 10^{-7} molL^{-1}$: acidic medium, $pH < 7$.**
- If **$[H_3O^+] < 10^{-7} molL^{-1}$, $[OH^-] > 10^{-7} molL^{-1}$: basic medium, $pH > 7$.**

Note :

Regardless of the nature of the solution, both: **OH^- and H_3O^+,** ions are present, but in varying proportions.

IV- Strength of acids and bases:

IV-1- Strong acids and bases :

- A strong acid is completely dissociated into H_3O^+ and its conjugate base through a direct reaction.

  $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

- A strong Bronsted base in water is fully dissociated into OH- and its conjugate acid through a direct reaction.

  $NaOH + H_2O \rightarrow Na^+_{aq} + OH^-_{aq}$

If an acid is strong, its conjugate base is weak.

If a base is strong, its conjugate acid is weak.

Any (strong) acid/base pair in aqueous solution does not possess a K_a constant **($K_a \rightarrow \infty$, and pK_a equals 0).**

IV-2- Weak acids and bases :

An acid is weak if its dissociation in water is partial and leads to a chemical equilibrium, a non-total (reversible) reaction. This is the case for organic acids.

$$\mathbf{RCOOH + H_2O \quad == \quad H_3O^+ + RCOO^-}$$

These acids are characterized by a constant that measures the acidity of the medium, known as the acidity constant **K_a**, which is expressed as:

$$\mathbf{k} = \frac{[\text{Base}][H_3O^+]}{[\text{Acid}][H_2O]}\ ;\ [H_20] \sim \text{constant.}$$

So, the acidity constant: $k_a = \frac{[\text{Base}][H_3O^+]}{[\text{Acid}]}$

We can define: **$pK_a = -\log K_a$ or $K_a = 10^{-pKa}$**

The stronger the acid, the larger its K_a and the lower its pK_a.

The weaker the acid, the smaller its K_a and the higher its pK_a.

- A base is weak if its dissociation in water is partial and leads to a chemical equilibrium, a non-total (reversible) reaction. This is the case for amines.

$$\mathbf{RNH_2 + H_2O == RNH^+_3 + OH^-}$$

$$\mathbf{C_2H_5NH_2 + H_2O == C_2H_5NH^+_3 + OH^-}$$

These bases are characterized by a constant that measures the basicity of the medium, known as the basicity constant Kb, expressed as :

The basicity constant: $K_b = \frac{[\text{Acid}][OH^-]}{[\text{Base}]}$

With : **$pK_b = -\log K_b$ or $K_b = 10^{-pKb}$**

The acidity constant **K_a** is related to the basicity constant **K_b** of the acid/base pair.

$$K_a \text{x } K_b = \frac{[\text{Base}][H_3O^+]}{[\text{Acid}]} \text{x} \frac{[\text{Acid}][OH^-]}{[\text{Base}]} = [H_3O^+] \text{ x } [OH^-] = 10^{-14}$$

K_a x $K_b = 10^{-14} = K_e$ thus : **$pK_a + pK_b = 14$ à 25°C**

Any **(weak)** acid/base pair in aqueous solution possesses a **Ka** constant less than 1 and a **pK_a** greater than 0.

The stronger the base, the smaller its K_a and the larger its pK_a .

The weaker the base, the larger its K_a and the smaller its pK_a.

IV-3- Dissociation Coefficient :

The dissociation coefficient **α** of an acid or a base is defined as the ratio of the concentration of the formed entity to the initial concentration.

Acid + H_2O →base + H_3O^+ $\alpha = \frac{[\text{base}]}{C}$

Base + H_2O → Acid + OH^- $\alpha = \frac{[\text{acid}]}{C}$

α : Represents the percentage of dissociated acid or base, its value ranges between 0 and 1.

$$0 \leq \alpha \leq 1$$

- If $\alpha = 1$ dissociation is complete, and both the acid and the base are strong.
- If $\alpha \leq 1$ dissociation is partial, and both the acid and the base are weak.
- If $\alpha = 0$ the reaction does not occur.

Consider the equilibrium: Acid + H_2O === base + H_3O^+

	Acid	base	H_3O^+
t=0	C_0	0	0
teq	$C_0(1 - \alpha)$	$C_0\alpha$	$C_0\alpha$

The expression for the acidity constant K_a becomes:

$$k_a = \frac{[\mathrm{Base}][H_3O^+]}{[\mathrm{Acid}]} = \frac{C0\alpha \text{ x } C0\alpha}{C0\ (1-\ \alpha)}$$

$$\mathbf{k_a = \frac{C\alpha^2}{1-\alpha}}$$

IV-4- The Relationship between pH and pKa: (Henderson-Hasselbalch equation)

Consider the reaction: Acid: $\mathrm{Acid} + H_2O === \mathrm{base} + H_3O^+$

$t=0$	C_0		0	0
t_{eq}	$C_0(1-\alpha)$		$C_0\alpha$	$C_0\alpha$

According to the K_a equation : $k_a = \frac{[\mathrm{Base}][H_3O^+]}{[\mathrm{Acid}]}$

$[H_3O^+] = \frac{[\mathrm{Acid}]\mathrm{Ka}}{[Base]}$ and $\mathrm{pH} = -\log[H_3O^+]$

$$\mathrm{pH} = -\log\frac{[\mathrm{Acid}]\mathrm{Ka}}{[Base]} = -\log\mathrm{Ka} - \log\frac{[\mathrm{Acid}]}{[Base]}$$

Thus, we obtain:

$$\mathbf{pH = pKa + log\frac{[\mathit{Base}]}{[Acid]}}$$

$$\frac{[\mathit{Base}]}{[\mathrm{Acid}]} = 10^{\mathrm{pH-pKa}}$$

Example:

$HCOOH + H_2O == HCOO^- + H_3O^+$ $\quad \mathbf{pH = pKa + log\frac{[HCOO-]}{[HCOOH]}}$

$CH_3NH_2 + H_2O == CH_3NH^+_3 + OH^-$ $\quad \mathbf{pH = pKa + log\frac{[CH3NH2]}{[CH3NH+3]}}$

Dominance of acidic and basic forms:

► If pH <pKa so $\log\frac{[\mathit{Base}]}{[\mathrm{Acid}]} < 0$, $\frac{[\mathit{Base}]}{[\mathrm{Acid}]} < 1$ **indicating dominance of the base.**

▶If **pH >pKa so** $\log\frac{[Base]}{[Acid]} > 0$, $\frac{[Base]}{[Acid]} > 1$ **indicating dominance of the acid.**

▶If **pH = pKa so** $\log\frac{[Base]}{[Acid]} = 0$, $\frac{[Base]}{[Acid]} = 1$ **indicating equivalence.**

IV-5- pH of Aqueous Solutions:

The goal is to establish simple relationships for calculating pH. These relationships require certain approximations, and therefore their validity is generally limited to diluted solutions. These relationships can be used with minimal errors.

IV-6- Solution of a strong acid:

A strong acid with concentration Ca is also completely dissociated in water.

a/ Monoprotic acid case :

$$AH + H_2O \rightarrow A^- + H_3O^+$$

t=0 C_a 0 0

t_f 0 C_a C_a

The dissociation is complete: $[H_3O^+] = [AH] = C_a$.

pH= -log $[H_3O^+]$ = pH= -logC_a

pH = -log C_a

b/ Diprotic acid case :

$$AH_2 + 2H_2O \rightarrow A^{2-} + 2H_3O^+$$

t=0 C_a 0 0

t_f 0 C_a $2C_a$

The dissociation is complete: $[H_3O^+] = 2[AH] = 2C_a$.

pH= -log $[H_3O^+]$ = pH= -log $2C_a$

pH = -log $2C_a$

IV-7- Solution of a strong base:

A strong base with concentration C_b is also completely dissociated in water.

a/ Monobasic case:

B + H_2O → BH^+ + OH^- **Example:** NaOH → Na^+ + OH^-

t=0 C_b 0 0

t_{eq} 0 C_b C_b

The dissociation is complete $[OH^-] = [B] = C_b$

$[H_3O^+]$?

$ke = [H_3O^+]\,[OH^-] = 10^{-14}$

$$[H_3O^+] = \frac{k_e}{[OH^-]} = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{C_b}$$

$$pH = -\log\,[H_3O^+] = -\log\frac{10^{-14}}{C_b}$$

$pH = 14 + \log C_b$

b/ Dibasic case:

B + $2H_2O$ → BH^{2+} +$2OH^-$ **Example:** $Ca(OH)_2$ →Ca^{2+} + 2 OH^-

t=0 C_b 0 0

t_f 0 C_b C_b

The dissociation is complete $[OH^-] = [B] = 2C_b$

$[H_3O^+]$?

$ke = [H_3O^+]\,[OH^-] = 10^{-14}$

$$[H_3O^+] = \frac{k_e}{[OH^-]} = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{2C_b}$$

$pH = 14 + \log 2C_b$

IV-8- Solution of a weak acid:

$RCOOH + H_2O == RCOO^- + H_3O^+$

t=0 C_b 0 0

t_f $C_b\,(1-\alpha)$ $C_b\alpha$ $C_b\alpha$

The dissociation is partial, it involves an equilibrium.

To retrieve the pH expression, we need to write the following equations:

► ***Law of Mass Action:*** $k_a = \frac{[H_3O^+][A^-]}{[HA]}$

- ▶ ***Ionic Product of Water:*** **$k_e = [H_3O^+]\ [OH^-] = 10^{-14}$**

- ▶ ***Electro-neutrality of the solution:*** **$[H_3O^+] = [A^-] + [OH^-]$**

- ▶ ***Conservation of the species A during dissociation:***

$C_a = [HA]_{\text{remaining}} + [A^-]_{\text{formed}}$

- ▶ ***Approximations:***

a/ Nature of the medium: the medium is acidic, so we neglect the concentration of OH^- ions.

=>Electroneutrality : **$[H_3O^+] = [A^-]$**

b/ Acid nature: the acid is weakly dissociated. We can neglect:

⇨ **$[A^-] \lll [HA]$**

⇨ Conservation **$C = [HA]$**

Taking into account all these approximations, we can write:

$$k_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+]^2}{C}$$

$$k_a = \frac{[H_3O^+]^2}{C} \qquad [H_3O^+] = (k_a x\ C)^{1/2}$$

$$pH = -\log [H_3O^+] = -\log (k_a x\ C)^{1/2}$$

$$\mathbf{pH = \frac{1}{2}\, pKa - \frac{1}{2} \log C}$$

IV-9- Solution of a weak base:

The reasoning is analogous, this time we have:

	$B + H_2O$	$== BH^+$	$+ OH^-$
t=0	C_b	0	0
t_f	$C_b(1-\alpha)$	$C_b\alpha$	$C_b\alpha$

The dissociation is partial, involving an equilibrium.

To retrieve the pH expression, we need to write the following equations:

- ▶ ***Law of Mass Action:*** $k_b = \frac{[BH^+][OH^-]}{[B]}$
- ▶ ***Ionic Product of Water:*** $k_e = [H_3O^+]\,[OH^-] = 10^{-14}$
- ▶ ***Electro-neutrality of the solution:*** $[OH^-] = [BH^+] + [H_3O^+]$
- ▶ ***Conservation of species B during dissociation:***

$C_b = [B]_{remaining} + [BH^+]_{formed}$

- ▶ ***Approximations:***

a/ Nature of the medium: the medium is basic, so we neglect the concentration of **H_3O^+** ions**.**

=>Electroneutrality : $[BH^+] = [OH^-]$

b/ Base nature: the base is weakly dissociated. We can neglect:

⇨ $[BH^+] \lll [B]$

⇨ Conservation $C = [B]$

Taking into account all these approximations, we can write:

$k_b = \frac{[BH^+][OH^-]}{[B]} = \frac{[OH^-]^2}{C}$ $[OH^-]^2 = k_b\,C$

$[OH^-] = (k_b\,C)^{1/2}$

$k_e = [H_3O^+]\,[OH^-] = 10^{-14}$ et $K_a \times K_b = 10^{-14}$

$$[H_3O^+] = \frac{K_e}{[OH^-]} = \frac{K_e}{(k_e C)^{1/2}} = \frac{K_e}{\left(\frac{k_e}{k_a}C\right)^{1/2}} = \left(\frac{k_e k_a}{C}\right)^{1/2}$$

$$[H_3O^+] = \left(\frac{k_e k_a}{C}\right)^{1/2}$$

$pH = -\log [H_3O^+] = -\log \left(\frac{k_e k_a}{C}\right)^{1/2} \Longrightarrow -\log [H_3O^+] = -\log \left(\frac{k_e k_a}{C}\right)^{1/2}$

$pH = \frac{1}{2}[14 + Pk_a + \log C]$

$\mathbf{pH = 7 + \frac{1}{2} Pk_a + \frac{1}{2} \log C}$

IV-10- Solution of a diluted strong acid :

Consider a hydrochloric acid solution with $[HCl]$ = **10^{-8}M/L**

$pH = -\log [H_3O^+] = -\log C = -\log 10^{-8}$ thus $pH = 8$

This is a pH > 7 a basic pH ? This result does not correspond to the nature of the medium. Therefore, we must conside:

*$[H_3O^+]_{total} = [H_3O^+]_{acid} + [H_3O^+]_{water}$ and $[Cl^-] = [HCl] = C$

*$k_e = [H_3O^+]_{total} \times [OH^-]$

*$\Sigma C_i z_i = 0$, $[Cl^-] + [OH^-] = [H_3O^+]_{total}$

$$[Cl^-] + \frac{ke}{[H3O+]_{total}} = [H_3O^+]_{total}$$

$$C + \frac{10^{-14}}{[H3O+]_{total}} = [H_3O^+]_{total}$$

We will solve the 2nd degree equation(**the quadratic equation)**:

$$C[H_3O^+]_{total} + 10^{-14} = [H_3O^+]^2_{total}$$

$$[H_3O^+]^2_{total} - C\,[H_3O^+]_{total} - 10^{-14} = 0$$

$$x^2_{total} - C\,x - 10^{-14} = 0$$

We calculate the discriminant $\Delta = b^2 - 4ac$ which results in $x_1 = [H_3O^+]$

$x_2 = [H_3O^+]$

$pH = -\log [H_3O^+]$

IV-11- Solution of a diluted strong base:

Let's consider a solution of sodium hydroxide with a concentration of [NaOH]= **10^{-9}M/l**

pH = 14 +log $[OH^-]$ = 14 + log C = 14 + log 10^{-9} donc pH = 5

This is a pH< 7 so an acidic pH ? This doesn't match the nature of the solution. Hence, we need to consider the following factors:

* $[OH^-]_{total} = [OH^-]_{acid} + [OH^-]_{water}$ and $[Na^+] = [NaOH] = C$

*$k_e = [OH^-]_{total} x[H_3O^+]$

* $\Sigma C_i z_i = 0$, $[Na^+] + [H_3O^+] = [OH^-]_{total}$

$$[Cl^-] + \frac{ke}{[OH-]total} = [OH^-]_{total}$$

$$C + \frac{10^{-14}}{[OH-]total} = [OH^-]_{total}$$

We will solve the 2^{nd} degree equation(**the quadratic equation)**:

$$C[OH^-]_{total} + 10^{-14} = [OH^-]^2_{total}$$

$$[OH^-]^2_{total} - C [OH^-]_{total} - 10^{-14} = 0$$

$$x^2_{total} - C x - 10^{-14} = 0$$

We calculate the discriminant $\Delta = b^2 - 4ac$ which gives $x_1 = [OH^-]$ and $x_2 = [OH^-]$

pH = 14 +log $[OH^-]$

IV-12- Solution of a diacid:

The ionization of a diacid occurs in two steps, resulting in the following equilibrium in solution:

$2H_20$ === $H_3O^+ + OH^-$

(1) $H_2A + H_20$ === $HA^- + H_3O^+$ with acidity constant k_{a1}

(2) $HA^- + H_20$ === $A^{2-} + H_3O^+$ with acidity constant k_{a2}

Usually, $k_{a2} < k_{a1}$ or $Pk_{a2} > Pk_{a1}$

$k_e = [H_3O^+][OH^-] = 10^{-14}$ or $k_e = k_a\, k_b$

$k_{a1} = \frac{[H_3O^+][HA]}{[H_2A]}$, $k_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]}$

$[H_3O^+] = [OH^-] + [HA^-] + 2[A^{2-}]$

$C = [H_2A] + [HA^-] + [A^{2-}]$

Approximation : the environment is acidic=> so we can neglect the concentration of OH^- ions

Hence : $[H_3O^+] = [HA^-] + 2[A^{2-}]$

Nature of the acid is usually $k_2 <<< k_1 <<< 1$

$[A^{2-}] <<< [HA^-] << [H_2A]$, $C = [H_2A]$

Taking $[A^{2-}] = 0$ is equivalent to treating H_2A as a monoacid.

Numerical Application:

Let's determine the concentrations of different species in a solution of H_2S hydrogen sulfide with an initial molarity of 0,1 M = C_0 given $k_1 = 10^{-7}$, $k_2 = 10^{-15}$

1°- Write the Equilibrium Equations:

$2H_20 \Longrightarrow H_3O^+ + OH^-$

$H_2S + H_20 \Longrightarrow HS^- + H_3O^+ \; k_1 = 10^{-7}$

$HS^- + H_20 \Longrightarrow S^{2-} + H_3O^+ \; k_2 = 10^{-15}$

$k_1 = \frac{[H_3O^+][HS^-]}{[H_2S]} = 10^{-7}$, $k_2 = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$

2°- Electroneutrality of the solution:

$[H_3O^+] = [OH^-] + [HS^-] + 2[S^{2-}]$

Conservation of S:

$C = 0{,}1 = [H_2S] + [HS^-] + [S^{2-}]$

Approximation : Considering an acidic environment, we can neglect $[OH^-]$ $\Rightarrow [H_3O^+] = [HS^-] + 2[S^{2-}]$

$k_2 <<< k_1 <<< C_0$

$10^{-15} <<< 10^{-7} <<< 10^{-1} \Rightarrow$ we can neglect $[S^{2-}]$

$[H_3O^+] = [HS^-], C_0 = 10^{-1} = [H_2S]$

$k_1 = \frac{[H_3O^+]^2}{C_0} \Rightarrow [H_3O^+]^2 = k_1C_0 \Rightarrow [H_3O^+] = (k_1C_0)^{1/2}$

$[H_3O^+] = (10^{-7}10^{-1})^{1/2} = (10^{-8})^{1/2} = 10^{-4} \Rightarrow [HS^-] = 10^{-14}$

$[OH^-] = \frac{k_e}{[H_3O^+]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}$

$k_2 = 10^{-15} = \frac{[H_3O^+][S^{2-}]}{[HS^-]} \Rightarrow [S^{2-}] = 10^{-15} <<< 10^{-4}$

V- Discussion of these relationships:

1/ All of these relationships can be deduced from the OSTWALD relation.

$k_a = \frac{C^2\alpha^2}{(1-\alpha)\,C}$; $[H_3O^+] = C^2\alpha^2$

$k_a = \frac{[H_3O^+]^2}{C(1-\alpha)}$ $\Longrightarrow [H_3O^+] = \sqrt{k_a C(1-\alpha)}$

If the acid is weak, then it is poorly dissociated $\alpha <<< 1$

$\Longrightarrow [H_3O^+] = (k_a\ C)^{1/2}$

2/ We can derive from the OSTWALD's law

$k_a = \frac{C\alpha^2}{1-\alpha}$ $\frac{k_a}{C} = \frac{\alpha^2}{1-\alpha}$

The value of α is a direct function of $\frac{k_a}{C}$.

When $[H_3O^+]$ is much smaller than C $[H_3O^+]<<<C$

$\Longrightarrow$ α is no longer small, thus α must be determined by solving a quadratic equation.

$C\,\alpha^2 + k_a\,\alpha + k_a = 0$

α, α' α > 0

$C\,\alpha^2 + k_a\,\alpha - k_a = 0$

$\alpha > 0 : [H_3O^+] \Longrightarrow = \alpha\, C$

Experimentally, α is considered negligible.

- **Acid-base equilibrium resolution :**

Let's consider, for example, a weak acid HA.

1- Write the dissociation equilibrium:

$HA + H_2O \rightleftharpoons A^- + H_3O^+$

We must consider the autoionisation of water.

$H_2O + H_2O \Longrightarrow H_3O^+ + OH^-$

We have four unknowns $[HA]$, $[A^-]$, $[H_3O^+]$, $[OH^-]$

A system of 4 equations.

a/ Law of mass action: $k_a = \frac{[H_3O^+][A^-]}{[HA]}$

b/ Water's ionic product: $k_e = [H_3O^+]\,[OH^-] = 10^{-14}$ and $k_a k_b = k_e$

c/ Electroneutrality of the solution: $\sum_i i^+ = \sum_i i^-$ or $\Sigma C_i z_i = 0$

Note :

It should be noted that an ion carrying a charge n+ or n-$^{-}$ contributes n times its concentration to the overall charge.

$[H_3O^+] = [A^-] + [OH^-]$

d/ Conservation of the species: (Acid /Base)

$C = [HA] + [A^-]$

2-Approximations :

a/ If the medium is acidic, we can neglect the OH^- ions; if it is basic, we can neglect the H_3O^+ ions.

b/ acid or base) weak $\alpha <<< 1$ we can neglect $[A^-]$ compared to $[HA]$.

3-Express all the unknowns in terms of $[H_3O^+]$:

Let solvent $[OH^-] = \frac{k_e}{[H_3O^+]}$

$[H_3O^+] = [A^-] + [OH^-] \Longrightarrow \quad [A^-] = [H_3O^+] - [OH^-]$

$[A^-] = [H_3O^+] - \frac{k_e}{[H_3O^+]}$

$C = [HA] + [A^-]$

$[HA] = C - [A^-]$

$[HA] = C - [H_3O^+] + \frac{k_e}{[H_3O^+]}$

Equilibrium : $k_a = \frac{[H_3O^+][A^-]}{[HA]}$

$$k_a = \frac{[H_3O^+]\left([H_3O^+] - \frac{k_e}{[H_3O^+]}\right)}{\left(C - [H_3O^+] + \frac{k_e}{[H_3O^+]}\right)}$$

k_a is a 3rd-degree equation in terms of $[H_3O^+]$.

For a diacid, we are dealing with a 5th-degree equation.

For a triacid, we are dealing with a 7th-degree equation.

4-Simplification:

Compare the value of $[H_3O^+]$ with $\frac{k_e}{[H_3O^+]}$

When the medium is acidic: Meaning when $[H_3O^+] > 10^{-6}$

$$\frac{k_e}{[H_3O^+]} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

$\frac{k_e}{[H_3O^+]}$ can be neglected compared to $[H_3O^+]$ (1%).

PH < 6: $k_a = \frac{[H_3O^+]^2}{C-[H_3O^+]}$: 2nd-degree equation.

$[H_3O^+]^2 + k_a [H_3O^+] - k_a C = 0; [H_3O^+] > 0$

If $[H_3O^+] << C$

Weak acid $\Rightarrow k_a = \frac{[H_3O^+]^2}{C}$

$k_a C = [H_3O^+]^2 \Rightarrow [H_3O^+] = (k_a C)^{1/2}$

VI- pH of Acid mixtures in solution:

VI-1- Mixture of two strong monoprotic acids:

Consider two strong monoprotic acids (A_1H, A_2H), with respective concentrations C_1 and C_2. In the solution, we have $[H_3O^+] = C_1 + C_2$, and the pH of the solution is given by :

$$pH = -\log[H_3O^+]$$

$$\mathbf{pH = -\log (C_1 + C_2)}$$

VI-1-1-Mixture of a weak monoprotic acid and a strong monoprotic acid:

HA: weak acid, C, k_a, α_0

$HA + H_20 \quad === \quad A^- + H_3O^+$ chemical equilibrium, hence: $k_a = \frac{[H_3O^+][A^-]}{[HA]}$

If the weak acid were alone in the solution, we would have:

$[H_3O^+] = \sqrt{k_a C}, pH = \frac{1}{2} pKa - \frac{1}{2} \log C$

$\alpha_0 = \frac{[H_3O^+]_0}{C} \Rightarrow \alpha_0 = \frac{\sqrt{Ka\, x C}}{C} \Rightarrow \alpha_0 = \sqrt{\frac{k_a}{C}}$

HA' Strong acid with concentration C' α'

$HA' + H_2O \longrightarrow A'^- + H_3O^+$

The strong acid HA introduces a concentration of ions $[H_3O^+] = C'$

Thus, the concentration C' is higher than the concentration of the weak acid, greater than α0C

According to the law of mass action

$HA + H_2O \quad === \quad A^- + H_3O^+$

$HA' + H_2O \longrightarrow A'^- + H_3O^+$

There is a reduction in ionisation of the weak acid (equilibrium), so the equilibrium is shifted to the left=> decrease in [A-] and increase in [HA].

$\alpha < \alpha_0$ the ionised fraction α of the strong acid is smaller than the ionised fraction of the weak acid

$[H_3O^+] = C'$; $[HA] = C$

$\alpha = \frac{[A^-]}{C} = \frac{[A^-]}{[HA]} \qquad k_a = \frac{[H_3O^+][A^-]}{[HA]} = [H_3O^+]\alpha \Rightarrow k_a = \alpha C'$

$\alpha_0 = \sqrt{\frac{k_a}{C}} \Rightarrow \alpha_0^2 = \frac{k_a}{C} \qquad \Rightarrow ka = \alpha_0^2 C$

$k_a = \alpha C' = \alpha_0^2 C \Rightarrow \alpha = \frac{\alpha_0^2 C}{C'}$

$\alpha < 0$ as $C' < 1 \Rightarrow$ reduction

By hypothesis: C, C' are roughly of the same order.

$- \alpha_0 <<< 1 \sim 2\% \Rightarrow 0{,}02 <<< 1$

Thus, the addition of a strong acid to a weak acid causes a reduction in its ionization:

Example : $k_a = 10^{-6}$ $C = C' = 10^{-2}$ µmol /l

$$\left.\begin{array}{lll} Af[H_3O^+]_0 = 10^{-4} & PH = 4 & \alpha_0 = 10^{-2} \alpha < \alpha_0 \\ [H_3O^+] = 10^{-2} & PH = 2 & \alpha = 10^{-4} \end{array}\right\}$$

VI-1-2- Mixture of an acid and its conjugate base in any proportions:

Consider a solution of a pure acid or a mixture with a metal salt (MA) that provides the conjugate base of the acid.

HA C_a

AM C_b

$HA + H_20 === A^- + H_3O^+$ (a)

$A^- + H_20 === HA + OH^-$ (b)

There is a reduction in ionization in (a), leading to the reformation of the acid => decrease in the acid's strength.

$C_a = [HA]$; $C_b = [A^-]$

Apply the law of mass action: $k_a = \frac{[H_3O^+][A^-]}{[HA]}$

$[H_3O^+] = \frac{[HA]}{[A^-]} k_a = \frac{C_a}{C_b} k_a [H_3O^+] = \frac{C_a}{C_b} k_a$

$pH = -\log[H_3O^+] = -\log\left(\frac{C_a}{C_b}k_a\right)$

$pH = -\log\left(\frac{C_a}{C_b}k_a\right) \Rightarrow pH = pka - \log\frac{C_a}{C_b}$

HENDERSON and HASSEL BALCH Relation:

$$\mathbf{pH = pka + \log\frac{[base]}{[acid]}}$$

Note: $C_a = C_b$, so **$pH = Pk_a$**

VI-1-3- Equimolar mixture of 2 weak acid / base pairs:

Let's consider a weak acid **HA/A^-** with acidity constant ka1

And a weak base **BH^+/B** with acidity constant ka2

Equilibrium : $HA + \cancel{H_2}0 \Longrightarrow \cancel{A^- +} H_3O^+$ $\quad ka_1$

$B + \cancel{H_3}O^+ \Longrightarrow BH^+ \cancel{+} H_20$ $\quad ka_2$

Equimolar mixture, thus equal number of moles.

$\Longrightarrow HA + BA^- + BH^+$

$k_{a1} = \frac{[H_3O^+][A^-]}{[HA]}$; $k_{a2} = \frac{[H_3O^+][B]}{[BH^+]}$

$k_{a1}\,k_{a2} = \frac{[H_3O^+]\cancel{[A^-]}}{\cancel{[HA]}}\frac{[H_3O^+][B]}{\cancel{[BH^+]}}$ /

Since the mixture is equimolar: $\underbrace{[HA]\ [A^-]}_{} = \underbrace{[BH^+]\ [B]}_{}$

x moles ; x moles

$k_1k_2 = [H_3O^+]^2 \Rightarrow [H_3O^+] = (ka_1ka_2)^{1/2}$

$pH = -\log[H_3O^+] = -\log(k_1k_2)^{1/2}$

$pH = -\log(ka_1ka_2)^{1/2}$ $\qquad pH = \frac{1}{2}(Pka_1 + Pka_2)$

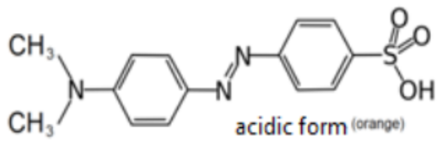
$$pH = \frac{1}{2}\,pKa_1 + \frac{1}{2}\,pKa_2$$

This relation is particularly interesting in the case of an amphoteric substance (ampholyte) like ($H_2PO^-_4$), because it acts as both an acid and a base. This ion simultaneously undergoes ionisation to give $H_2PO^-_4$ and hydrolysis to give H_3PO_4

VII- Colored Indicators:

A colored indicator (In. C) is an acid/base couple with different colors for its acidic and basic forms. These are organic molecules containing one or more benzene rings and protonatable hydrogen atoms.

Example : HELIANTHINE (Methyle-Orange)



$+ H_2O \Longrightarrow HCl\text{-}SO^-_3 + H_3O^+$basic form (yellow)

In general, their reactions are as follows:

$$\text{H-In} + H_2O \;===\; In^- + H_3O^+$$

- If the pH is low (A-F), then [H3O+] is high, leading to the disappearance of the stronger species, idirection 2 acidic form, orange color.
- If the pH is high (basic conditions), with low $[H3O^+]$, direction 1 ,tends toward its basic form and a yellow color.

Note :

The H-In /In- pair constantly coexist in the solution, causing a color change whenever the pH of the solution varies. There is a pH value at which both forms exist at nearly equal concentrations.

For a specific pH, an intermediate color, called the transition color, is observed.

$[In\text{-}H] \geq 10[In^-]$: acidic form.

$[In^-] \geq 10[In\text{-}H]$: basic form.

If we call k_i the acidity constant of this indicator to have the acidic color, we are obliged to $[In\text{-}H] \geq 10[In^-]$

$$\Rightarrow k_i \leq \frac{[H_3O^+]}{10} \quad k_i = \frac{[H_3O^+][In^-]}{[In-H]}$$

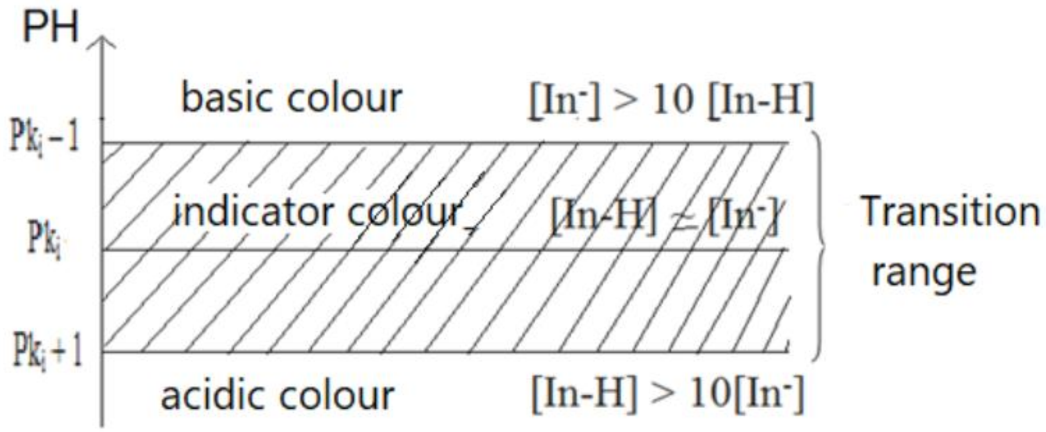
For the basic color, must be $[In^-] \geq 10\ [In\text{-}H]$

$k_i \geq 10\ [H_3O^+]$

$pH \leq pk_i - 1$

$pH \geq pk_i + 1$ so: **$Pk_i - 1 \leq PH \leq Pk_i + 1$**

The transition range (color change range) theoretically extends over 2 pH units.



Name(indicator)	Transition range	Range	Acidic(acid colour)	Basic(base colour)
Thymol Blue	1,2 – 2,8	1,6	Red	Yellow
Helianthine Methyl	3,1 – 4,4	1,3	Orange	Yellow
Red	4,2 – 6,2	2,0	Red	Yellow
Phenolphthalein	8,0 – 9,9	1,9	Colorless	Pink-violet
	9,3 – 10,5	1,2	Colorless	Blue

Thymolphthalein Alizarin Yellow	10,1 – 12	1,9	Yellow	Red

VIII- Acid-base neutralization reactions:

When a solution of acid HA is mixed with a solution of base B, the H3O$^+$ ions and OH- ions react with each other to form water and a salt.

=> This is a neutralisation reaction.

Acie + base $\Longrightarrow$ salt + water

$HA + H_2O \rightarrow H_3O^+ + A^-$

$B + H_2O \rightarrow BH^+ + OH^-$

$H_3O^+ + OH^- === 2H_2O$

If $[H_3O^+] = [OH^-]$ it is said that the neutralisation is complete, and the equivalence point is reached.

If the pH of the mixture (Acid + Base) is measured, the pH increases slightly because the concentration of the acid C_{Acide} decreases due to dilution. There is a reaction between the H3O$^+$ ions from the Acid and the OH$^-$ ions from the Base.

The reaction will continue until the equivalence point $[H_3O^+] = [OH^-]$.

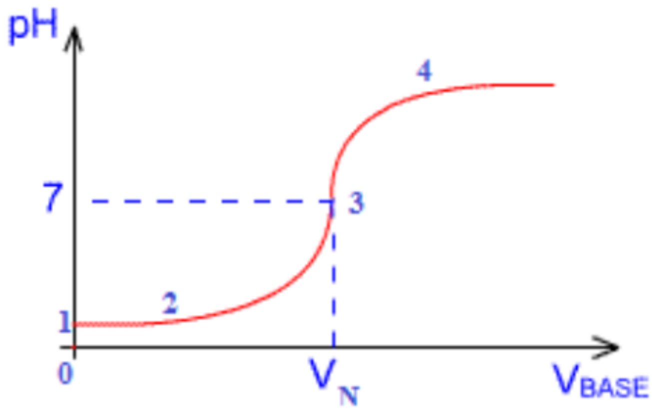
Experimentally, a sudden change in pH is observed when the equivalence point is reached, at which point there is an excess of strong base.

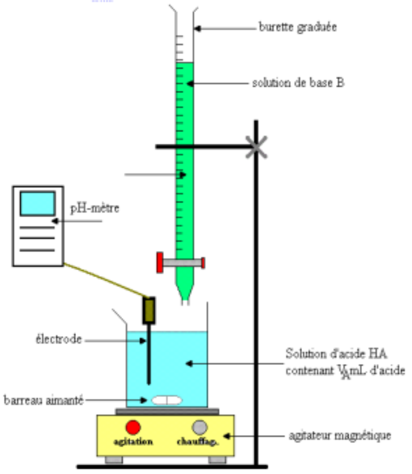
The following cases are distinguished:

- Neutralisation of a strong acid by a strong base.
- Neutralisation of a strong base by a strong acid.
- Neutralisation of a weak acid by a strong base.
- Neutralisation of a weak base by a strong acid.

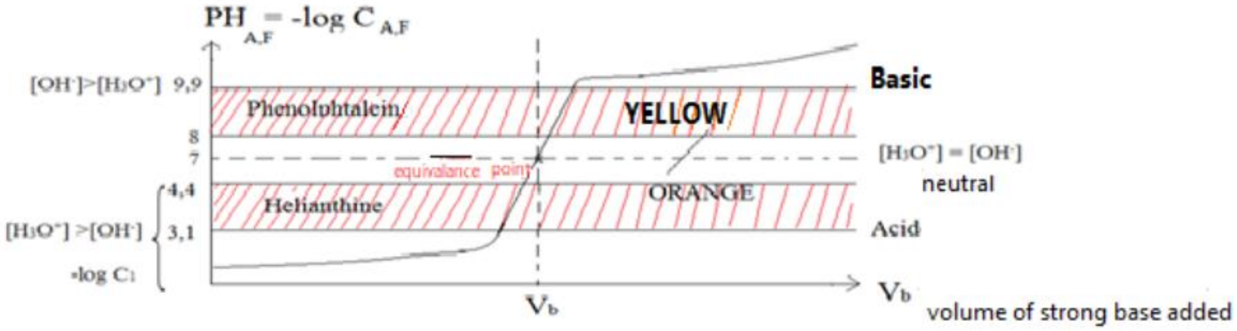
- Neutralisation of a weak acid by a weak base.

VIII-1- Titration of a strong acid with a strong base:





Initially, a strong acid alone :



a- **Before the addition of B: V_b=0** with V_b being the volume of the base added at each moment.

In a strong acidic medium: pH = - log $[H_3O^+]$ = - log C_a

b- Upon addition and before neutralisation: $0 < V_b < V_N$

V_N is the volume of the base required for neutralisation.

$C_a V_a > C_b V_b$ thus $n_{H_3O^+} > n_{OH^-}$

$$n_{H_3O^+} = C_a V_a - C_b V_b$$

$$[H_3O^+] = \frac{C_aV_a - C_bV_b}{V_a + V_b} => pH = -\log\frac{C_aV_a - C_bV_b}{V_a + V_b}$$

c- At neutralisation: $V_b = V_N$

$$[H_3O^+][OH^-] = 10^{-14} C_a\,V_a = C_bC_b$$

$$n_{H_3O^+} = n_{OH^-} => [H_3O^+] = [OH^-] = \frac{10^{-7}M}{l} => pH = 7$$

The solution contains a salt that originates from a strong acid and a strong base, resulting in a neutral substance (non-hydrolyzable salt).

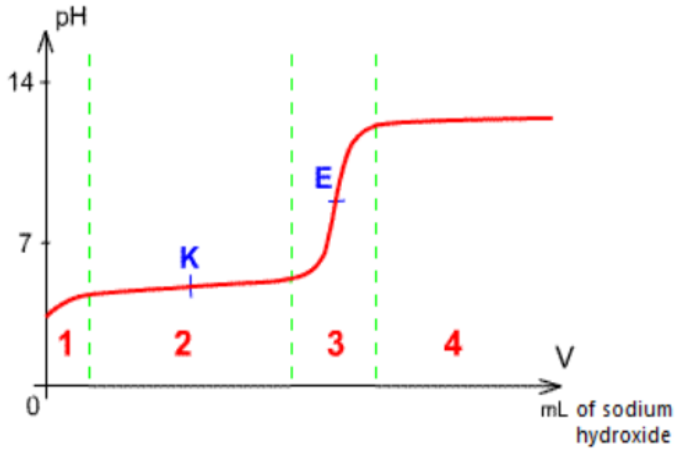
d-After neutralisation: $V_b > V_N$ the base is in excess

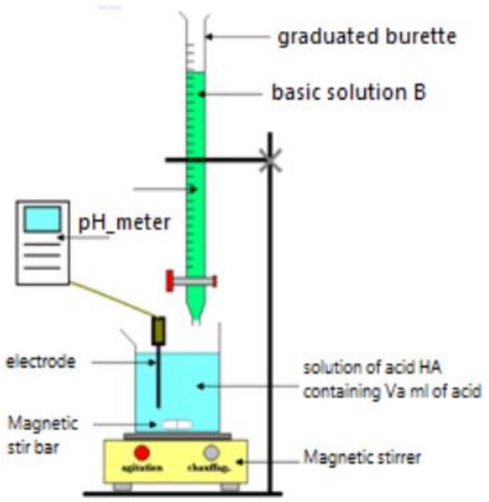
$C_bV_b > Ca\ V_a$ donc $n_{OH^-} > n_{H_3O^+}$

$$n_{OH^-_{water}} = C_bV_b - C_aV_a$$

$$[OH^-] = \frac{C_bV_b - C_aV_a}{V_a + V_b}\ pH = 14 + \log\frac{C_bV_b - C_aV_a}{V_a + V_b}$$

VIII-2- Titration of a weak acid with a strong base:





$HA + H_2O$ ==== $H_3O^+ + A^-$ Partial dissociation.

$B + H_2O \rightarrow OH^- + BH^+$ Complete dissociation.

a- Before adding the base: $V_b = 0$ with V_b the volume of base added at each moment.

In a weak acid medium so : $pH = \frac{1}{2}pKa - \frac{1}{2}\log C$

b- Upon addition and before neutralisation: $0 < V_b < V_N$

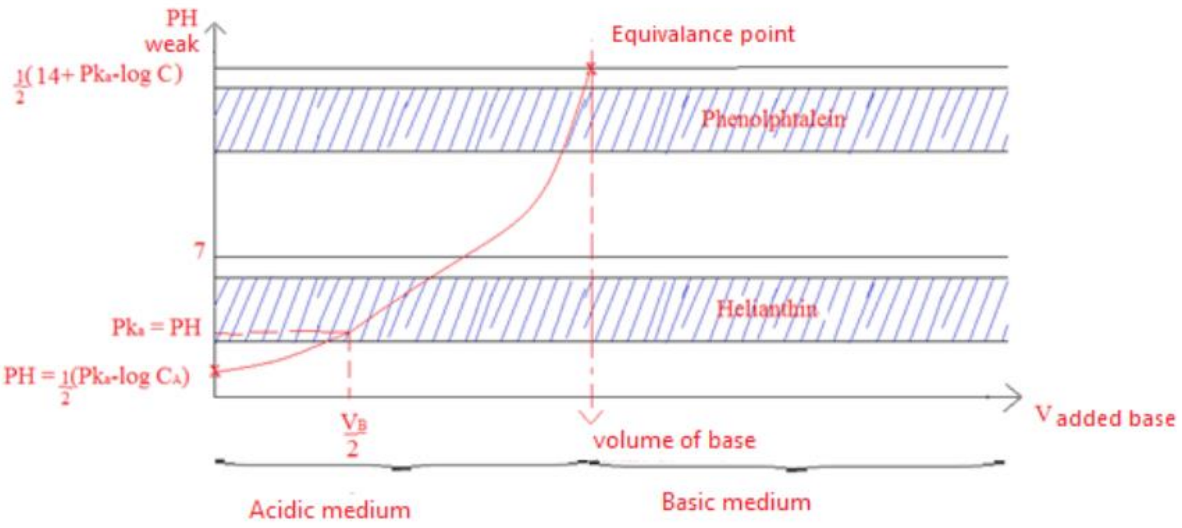
V_N is the volume of base needed for neutralisation.

As long as the acid H_3O^+ is in excess, $[H_3O^+] > [OH^-]$, the pH is that of the mixture of the acid HA and its conjugate base A^-.

$C_a V_a > C_b V_b$

$$n_{H_3O^+} = C_a V_a - C_b V_b \Rightarrow [H_3O^+] = \frac{C_a V_a - C_b V_b}{V_a + V_b}$$

$pH = pk_a + \log\frac{C_B}{C_A}$; $pH = pk_a + \log\frac{[A^-]}{[AH]}$



At half-equivalence :

At half-neutralisation, the volume of the added base is half the volume needed for complete neutralisation$V_b = \frac{V_N}{2}$

$$C_bV_b = \frac{C_aV_a}{2}$$

This solution is known as a buffer solution, where the pH remains relatively stable upon the addition of an acid or a base.

It's a mixture of a weak acid and its salt.

bF af Salt Water

$$NaOH + CH_3COOH \longrightarrow CH_3COO^-Na^+ + H_2O$$

$$pH = pKa - \log\frac{[CH_3COOH]}{[CH_3COO^-]}$$

At half-neutralisation$[CH_3COO^-] = [CH_3COOH] => pH = pKa$

At neutralisation: $V_b = V_N$

$C_a\ V_a = C_bV_b$

The formed salt (CH3COO-, Na+) is weakly basic, hydrolyzable salt.

The hydroxide ions OH- neutralize the hydrogen ions H3O+ from the weak acid, and the dissociation equilibrium proceeds in direction 1 until complete neutralisation is achieved. This means reaching the equivalence point where $[H_3O^+] = [OH^-]$.

$$CH_3COO^- + H_2O \quad === \quad CH_3COOH + OH^- \qquad pH = 8$$

$$pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log C_{salt}$$

c- After neutralisation : **$V_b > V_N$** excess of the base.

In a basic environment, the pH> 7 $C_bV_b > C_aV_a$

$$n_{OH^-} = C_bV_b - C_aV_a$$

$$[OH^-] = \frac{C_bV_b - C_aV_a}{V_a + V_b}$$

Upon addition and before neutralisation

$pH = pKa + \log\frac{[A_1^-]}{[A1H]}$ with $[A_1^-] = [RCOO^-]$ and $[A_1H] = [RCOOH]_{remaining}$

$[A_1^-] + \cancel{[OH^-]} = \cancel{[H_3O^+]} + [BH^+]$ ignoring the concentration of $H30^+$ and OH^-

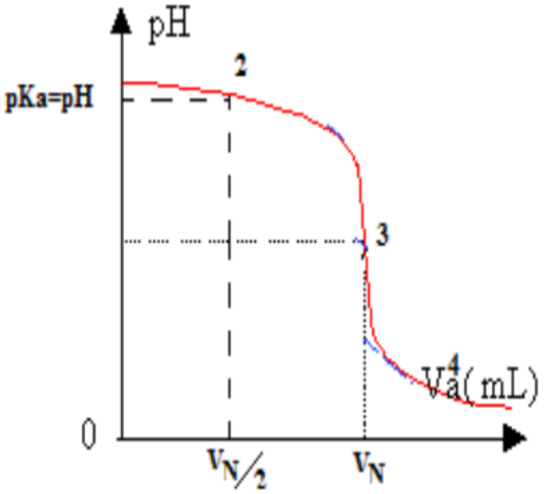
$$[BH^+] = \frac{C_bV_b}{V_a+V_b} et [A_1^-] = \frac{C_bV_b}{V_a+V_b}$$

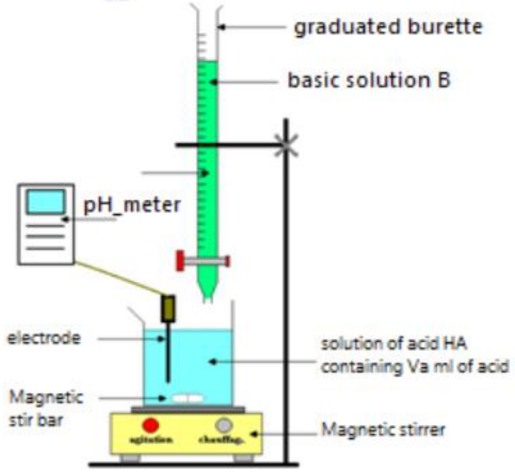
$$[AH]_{res} = [AH]_0 - [A^-]$$

$$\frac{C_aV_a}{V_a + V_b} - \frac{C_bV_b}{V_a + V_b} => [AH] \quad = \frac{C_aV_a - C_bV_b}{V_a + V_b}$$

$$pH = pKa + \log\frac{\frac{C_bV_b}{\cancel{V_a+V_b}}}{\frac{C_aV_a - C_bV_b}{\cancel{V_a+V_b}}} \; pH = pKa + \log\frac{C_bV_b}{C_aV_a - C_bV_b}$$

VIII-3-Titration of a weak base by a strong acid :





a- **Before addition** : **$V_a = 0$** with V_a is the volume of acid added at each moment.

The pH of the medium is basic (weak).

$$pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log C_{NH_4OH}$$

b- **Upon addition and before neutralisation: $0 < V_a < V_N$**

V_N is the volume of base required for neutralisation.

$C_bV_b < C_a V_a$

$pH_{mixture}$ is that of the weak base.

$$pH_{mixture} = \frac{1}{2}\left(14 + Pka + \log\frac{C_A V_A}{V_A+V_B}\right)$$

$$pH = pKa + \log\frac{[Base]}{[Acid]}$$

$$pH = pKa + \log\frac{[NH_4OH]_{res}}{[NH_4^+]}$$