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## I Aromaticity

Huckel Rule: The compounds with odd number of pairs of electrons, ( $w$ hich is mathematically written as $4 n+2$ ( $n=0,1,2,3$ etc),show aromaticty .Molecules $w$ hich do not obey these rules partially fall in the category of anti-aromatic and non aromatic compounds. The porbital array (A) and delocalization (B) in benzene can be pictorially represented as show $n$ below .


A


B

Fig :1

## Molecular orbital description of arematicity and antiaromaticity

According to molecular orbital theory, the six p orbeats conitine to form six molecular orbitals, three of $w$ hich are bonding and threse anti-bondigg. Six $\pi$ electrons occupy the bonding orbitals, $w$ hich are lower in energy comistred to the un-hybridized $p$ orbitals (atomic orbitals). The relative energies of atomierbitals and miecular orbitals are show n in Figure.


Fig:2

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Figute: 3
The relative energies of $p$ n脊ecular orbitals in planar cyclic conjugated systems can be determined by a simplified apprơ納 dev,foped by Frost. This involves the follow ing steps:

1) First of all we draw *aycle,
2) Then place. of its vertices pötritios, n . Each point where the polygon touches the circle represents an energy/kyel.


14 andygon touches the circle at a horizontal diameter, that point would represent a nonbonding orbital . Energy levels below this line indicate bonding MOs and those above are anti-bonding.

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Frost diagrams - Illustrative examples


Fig:4
Po ints to remember while making predictions on aromaticity using Frost's circle

- Aromatic compounds will have all occupied molecular orbitals completely filled $w$ here as antiaro matic compounds w ould have incompletely filled orbitals.

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- If an antiaromatic system (4n electrons) has the freedom to undergo conformational change and become nonaromatic that would do so. Remember that antiaromatic state is less stable than aromatic and nonaromatic forms. A comparison of molecular orbitals in aromatic and antiaromatic systems is presented in figure 5 .


Fig 5

## Aromaticity in higher Annulenes

Completely conjugate, monocyclic thyfocarbons are called annulenes.

## Examples,


[4] Annulene

[6] Annulene

[8] Annulene

[10] Annulene

Fig: 6
The criterk for aromaticity that we discussed earlier can be applied to higher annulenes as well. How ever, achieving planarity is a hurdle for many larger rings due to potential steric clashes or angle strains. If the ring (w ith $4 n+2 \pi$ electrons) is sufficiently large such that planarity does not cause steric or angle strains, the systemwould adopt that conformation, get stabilization through electron delocalization and becomes aromatic. Larger annulenes w ith 4 n

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$\pi$ electrons are not antiaromatic because they are flexible enough to become non-planar and become non-aromatic.
h [10]-annulene, there is considerable steric interaction betw een hydrogens at 1 and 6 positions. Further, a planar form (regular decagon) requires an angle of $144^{\circ}$ between carbon atoms which is too large to accommodate in a sp ${ }^{2}$ framew ork. The system prefers a nonplanar conformation and is not aromatic (the fact that angle strain need NOT alwayshe aproblem in achieving planarity is evident from examples such as cyclooctatetraenyl daniel Which is stable and aromatic). Bridging C1 and C6 in [10]-annulene leads to the compound V II (Fgure) which is reasonably planar w ith all the bond distances in the range of $13-1.42 \AA$ and show aromaticity (In NMR, outer protons are found at 6.9-7.3 ä and the bridgehed fiethylene at 5.0 ä).


Fig :7

## [12]-annu*ere

[12]-annfiene $4 \mathrm{n}, \mathrm{n}=3$ ) is antiaromatic and hence is not stable above $-50^{\circ} \mathrm{C}$. Its dianion $\left(4 n+2, n=3\right.$ ) is how eveer stable up to $30^{\circ} \mathrm{C}$ and is aromatic.


Fig : 8

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## [14]-annulene

Bond lengths in [14]-annulene range from 1.35-1.41 Å but do not show the alternating pattern of localized polyenes. It is aromatic (except for the isomers that are not planar). NMR shows that it is in conformational equilibrium as show n below Figure. The steric interactions associated with internal hydrogens can be minimized if $\mathrm{C} 3, \mathrm{C} 6, \mathrm{C} 10$ and C 13 positions are locked using suitable bridging units. Thus trans-15,16-dimethyldihydropyrerie and its diethyl and dipropyl homologs are aromatic with C-C bond distances betmeeeram. my Conformational flexibility in [14]-annulene can be restricted by insertirg triple bone in pace of one of the more double bonds. Here, the triple bond contribetes ory two for delocalization leaving the other tw o localized.

## Homoaromaticity

If a stabilized cyclic conjugated system $\left(4 n+2 \mathrm{e}^{-s}\right)$ can beemerned by bypassing one saturated atom, that lead to homoaromaticity. Compared true aromatic $y^{3}$ stems, the net stabilization here may be low due to poorer overlap of orbitals cycyesetatriènylcation (homotropyliumion) formed when cyclooctatetraene is dissolved in conentrated sulfuric acid is the best example to demonstrate homoaromaticity. Here, six electrons)arre spread over seven carbon atoms as in Tropylium cation.

## II Coordination complexes

## CFT : APPLICATIONs

(1) Colour of transition inetal complexes

CFT provides ar, ", atanation the observed colours of transition metal complexes. When the light fallson a eomplex, the folow ing observations may occur :
(i) Themompay abserb the whole of white light. In this case complex appears black.
(ii) The cor melex reflect (or transmit) the whole light. In this case it appears white.
(iiil) / The absorption of light by the coloured complexes takes place in the visible region of the spectruma hich extends from 4000 to 7000 in $w$ avelength. The cobur of the absorbed light is different from that of the transmitted light

## EXAMPLES :

(i) Hydrated cupric sulphate containing $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{2+}$ ions is blue (colour of the transmitted light) because it absorbs yelow light.

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(ii) Oupricammonium sulphate containing $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}{ }^{2+}\right.$ ions is violet, because it absorbs yellow green light.
(iii) Anhydrous cupric sulphate is colour less, since it absorbs light in the infra-red region
(iv) $\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]^{2-}$ ion absorbs light in the ultra - violet region and hence is colourless.
(v) $\left[\mathrm{T}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ absorbs green light in the visible region and hence it is purple whigis the colour of the transmitted light. $\left[\mathrm{Ti}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ ion shows absorption maxima at a waselendyay about 5000 w hich corresponds to thew ave number, $=20000 \mathrm{~cm}^{-1}$ as show below


Fig : 9 Visible absor the maximum absorption
This energy ( $=57$ Koderies/ mole) is equal to the energy difference, $\Delta_{0}$ betw een $t_{2 g}$ and $e_{g}$ levels and henee is sufficiento excite the single d-electron in $t_{2 g}$ orbital to eg orbital. This type of electronimension the to $\mathrm{t}_{\mathrm{g}}$ level is called d-d or ligand field transition. The colour of

(2) Number of unf)fred ele ctrons and magnetic properties of octahedral com plexes

CHis be lpful in deter mining the number of unpaired electrons in a given High Spin- and Low Spin- octahedral complex, and consequently, with the help of "spin only" formula $\mu_{s}=\sqrt{n(n+2)} B M$

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According to crystal field theory of complex compounds, since the number of unpaired electrons in the central metal ion with $d^{4}$ to $d^{7}$ configuration in high spin and low spin octahedral complexes is different their magnetic moments are also different
(3) Distortion of octahedral comple xes and Jahn Teller Effect

The six-coordinated complexes in which all the six distances betw een the ligand electron clouds and central metal ion are the same are said to be regular (i.e. symmetrical) octahedral complexes. On the other hand the six - coordinated comple ecammexich the distances are not equal are said to be distorted octahedral complexes, since their shise is changed (i.e distorted). The change in shape is called distortion.
Distorted octahedral complexes may be of the following three types.
(i) Diagonally distorted octahedral complexes which are obtained wismention of a regular octahedron takes place along a tw o-fold axis
(ii) Trigonally distorted octahedral complexes in which thê ©isistitior takès place along a threefold axis.
(iii) Tetragonally distorted octahedral complexes which ar alaknow n as tetragonal com plexes. These are obtained $w$ hen the distortion of a regula octahedron takes place along a four-fold axis.
eg.(i)Mbst of the square planar complexes of Cution are distorted octahedral (i.e. tetra-gonal), e.g. the tetrammine $\mathrm{Ou}(+2)$ complex, $\left[\mathrm{C}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ in aquous solution is actually $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right.$ $\left.\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ in which twow ater mole a larger distance from the central $\mathrm{O}^{2+}$ ion than the four coplanar $\mathrm{NH}_{3}$ ioneles and consequently the complex has a tetragonal shape rather than square plakien:
(ii) Low -spin octagedralk complexes of $\mathrm{N}^{2+}, \mathrm{Pd}^{2+}$ and $\mathrm{Pt}^{2+}$ (all $\mathrm{d}^{8}$ ion) undergo strong distortion and assure planar geometry in which the w o ligands along the z -axis are at larger distane and ligands in the xy-plane are at shorter distance from $\mathrm{M}^{2+}$ ion. $\mathrm{M}^{\mathrm{II}}$ (diars) $\mathrm{I}_{2} \mathrm{I}_{2}$ is atex exmple of such complex.
(iii) h CuCl 2 crystal each $\mathrm{Cu}^{2+}$ ion is surrounded by six $\mathrm{Cl}^{-}$ions ; four are at a distance of $2.30 \AA$ and the other two are $2.95 \AA$ aw ay.

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(iv) $\mathrm{h} \mathrm{CuF}_{2}$ crystal four $\mathrm{F}^{-}$ions are 1.93 aw ay from $\mathrm{Cu}^{2+}$ ion while the two F ions are $2.27 \AA$ apart.
Any non-linear molecular system possessing degenerate electronic state will be unstable and will undergo distortion to form a system of low er symmetry and lower energy and thus will remove dig eneracy.
Symmetrical and Unsymmetrical $\mathrm{t}_{\mathrm{tg}_{\mathrm{g}}}$ - and $\mathrm{e}_{\mathrm{g}}$ - orbital
$\mathrm{t}_{2 g}$ orbitals $\left\{\begin{array}{l}\mathrm{t}_{2 g}{ }^{0}, \mathrm{t}_{2 g}{ }^{3}, \mathrm{t}_{2 g}{ }^{6} \rightarrow \text { symmetrical } \\ \mathrm{t}_{2 g}{ }^{1}, \mathrm{t}_{2 g}{ }^{2}, \mathrm{t}_{2 g}{ }^{4}, \mathrm{t}_{2 g}{ }^{5} \rightarrow \text { unsymmetrical }\end{array}\right.$


## No Distortion Condition

The d-orbitals which have both $\gamma_{8}$ ano $\mathrm{e}_{\mathrm{g}}^{-}$sets as symmetrical orbitals lead to perfectly symmetrical Conditions for vasous types of eistortions can be summarized as:
$\mathrm{t}_{\mathrm{tg}}($ sym $)+\mathrm{e}_{\mathrm{g}}($ sym $)$
$\mathrm{t}_{2 \mathrm{~g}}$ (unsym)
Slight distortion
$\mathrm{e}_{\mathrm{g}}$ (unsym)
 $\rightarrow$ Strong distortion

## III Phase Equilibria

The phase kule $w$ as derived from thermodynamics considerations and is an importay tool concerning heterogeneous equilibria. Phase rule gives the relationship between the conditions which must be specified to describe the state of a system at equilibrium. This rule is important for both chemical and physical heterogeneous equilibria.

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PHASERULE
The rule is stated in terms of the number of phases ( $P$ ), the number of components (C) and the degrees of freedom (F) of a heterogeneous system.

Phase rule states that in a heterogeneous system at equilibrium the number of degrees of freedom plus the number of phases are equal to the number of components plus 2.

Mathematically it is expressed as

$$
\begin{equation*}
F=C-P+2 \tag{i}
\end{equation*}
$$

Explanation of the terms used in Phase Rule
 the heterogeneous system in equilibrium are cafed phases.

$$
\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g})
$$

There are three phases in equilibrium state ${ }^{2}$ solids and one is gas $\left(\mathrm{CO}_{2}\right)$, water system can be expressed ${ }^{\circ}$

$$
\begin{array}{rl}
\mathrm{H}_{2} \mathrm{O}(\mathrm{~s}) & \rightleftharpoons \\
\mathrm{H} & \mathrm{O}(I) \\
\text { Ice } & \text { water } \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
\end{array}
$$

In this system therefare thre ehases viz solid, liquid and vapours.

## Component-

In a heterogeneaus systen, in equilibrium the minimum number of variables which afenecessary to explain the chemical composition of a phase, by a chemic doguation, called component. The meaning of component can be understood by taking following examples:
(e) Icévatert - Vapours system


This system has three phases i.e. solid (ice), liquid (water) and gas (vapour). Chemical composition of each phase can be expressed by $\mathrm{H}_{2} \mathrm{O}$ in the form of chemical equation:

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Phase

| $\mathrm{H}_{2} \mathrm{O}(\mathrm{S})$ | $=\mathrm{H}_{2} \mathrm{O}$ |
| :--- | :--- |
| $\mathrm{H}_{2} \mathrm{O}(I)$ | $=\mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ | $=\mathrm{H}_{2} \mathrm{O}$ |

Thus water system is a one component system.



This system has two phases i.e. solid $\mathrm{NH}_{4} \mathrm{Cl}$ and mix Here, although system has three components, fut chemical composition of both phases can be expressed by a single component i.e. $\mathrm{NH}_{4} \ell$. Since $\mathrm{NH}_{3}$ and $\mathrm{HC} \ell$ are in equimolar ratio

| Phase | Component |
| :--- | :--- |
| $\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s})$ | $=\quad \mathrm{NH}_{2} \mathrm{C} \ell \mathrm{V}$ |
| $\mathrm{NH}_{3}(\mathrm{~g})+\mathrm{HCl}(\mathrm{g})$ | $=\quad \mathrm{NH}_{2} \mathrm{Cl}$ |

Thus, this system falso a diemponent system. If some additional amount of either $\mathrm{NH}_{3}(\mathrm{~g})$ or H (纽 is added in this system at equilibrium then each phase can not be exassed by FHen $_{4} \mathrm{Cl}$, then one more component with be required and numberso components w ith be two in the system.
(c) Wher*solid $\mathrm{Ca}^{\mathrm{C}} \mathrm{CO}_{3}$ is heated in a closed vessel, following heterogeneous equilibrium establishes:
$\mathrm{CaCO}(\mathrm{s}) \rightleftharpoons \mathrm{CaO}(\mathrm{s})=\mathrm{CO}_{2}(\mathrm{~g})$
This system consists of three phases i.e. solid $\mathrm{CaCO}_{3}$, solid CaO and gaseous $\mathrm{CO}_{2}$. Although system has three components but they are not independent of each other. Any of these two can be independently variable. Thus out of three,

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two components may be selected to express the composition of any phase. Thus number of components in this system are two
(i) When $\mathrm{CaCO}_{3}$ and CaO are taken as components

| Phase |  | Component |
| :--- | :--- | :--- |
| $\mathrm{CaCO}_{3}(\mathrm{~s})$ | $=$ | $\mathrm{CaCO}_{3}+0 \mathrm{CaO}$ |
| $\mathrm{CaO}(\mathrm{s})$ | $=$ | $\mathrm{CaCO}_{3}+\mathrm{CaO}$ |
| $\mathrm{CO}_{2}(\mathrm{~s})$ | $=\mathrm{CaCO}_{3}-\mathrm{CaO}$ |  |

(ii) When CaO and $\mathrm{CO}_{2}$ are taken as components

| Phase |  | Component |
| :--- | :--- | :--- |
| $\mathrm{CaCO}_{3}(\mathrm{~s})$ | $=$ | $\mathrm{CaO}+\mathrm{CO}_{2}$ |
| $\mathrm{CaO}(\mathrm{s})$ | $=$ | $\mathrm{CaO}+0 \mathrm{CO}_{2}$ |
| $\mathrm{CO}_{2}(\mathrm{~g})$ | $=$ | $0 \mathrm{CaO}+\mathrm{CO}_{2}$ |

(iii) When $\mathrm{CaCO}_{3}$ and $\mathrm{CO}_{2}$ are taken今s componets

Phase
$\begin{array}{lll}\mathrm{CaCO}_{3}(\mathrm{~s}) & = & \mathrm{CaCO}_{3}+\rho \mathrm{CO}_{2} \\ \mathrm{CaO}(\mathrm{s}) & =\quad \mathrm{Q} \oplus \mathrm{CO}_{6} \Rightarrow \mathrm{CO}_{2}\end{array}$
$\mathrm{CO}_{2}(\mathrm{~s})$
$0 \mathrm{CaCO}_{3}+\mathrm{CO}_{2}$
Therefore mirntum mise of components which are required to express any phase is/ hy: andthe system is bi-component system
(d) Sodras Sulphate - water system may have different 'phases as $\mathrm{Na}_{2} \mathrm{SO}_{4}$ ' $7 \mathrm{H}_{2} \mathrm{O}, \mathrm{Na}_{2} \mathrm{~S}$ \% $10 \mathrm{H}_{2} \mathrm{O}, \mathrm{Na}_{2} \mathrm{SO}_{4}$ solution, Ice, vapours etc. Any phase can be exped by chemical formulae $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and $\mathrm{H}_{2} \mathrm{O}$.

Therefore it is also a two component system.
(e) In $\mathrm{CuSO}_{4} \cdot 5 \mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \rightleftharpoons \mathrm{CuSO}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}(\mathrm{s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ system also the number of components are two.

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Number of components may also be calculated by the following formula
(1) For components which do not ionize

The number of components can be calculated by the following formula.

$$
C=C^{\prime}-m
$$

where $C=$ number of components
$C^{\prime}=$ total number of undissociated components
$m=$ number of chemical equations which correlate undissocated specie $\rho$ w ith each other.
(2) For ionised species

The number of components can be calculated by the formy

$$
C=C^{\prime \prime}-(n+1)
$$

$\mathrm{C}=$ number of components
$\mathrm{C}^{\prime \prime}=$ total number of species (including ions)
$\mathrm{n}=$ total number of equilibria (equilibrium stas)
Ex. 1 Find out the number of compontens in the folfw ing systems:
(i) $\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}\left(\mathrm{s} /+\mathrm{CO}_{2}(\mathrm{~g})\right.$
(ii) $\mathrm{NH}_{4} \mathrm{C} \ell(\mathrm{s}) \rightleftharpoons \mathrm{NH}_{3}(\mathrm{~g})=$ wherfthe partial pressures of $\mathrm{NH}_{3}$ and are equal)
(iii) $\mathrm{KC} \ell_{-} \mathrm{NaC} \ell_{-} \mathrm{V}^{2}$ (b) system
(iv) $\mathrm{KCl}-\mathrm{NaBl} \mathrm{N}_{2} \mathrm{~N}$ 童 system
(v) Aqu*थus bolutiobbf
Sol/ (i)

$(\mathrm{s}) \rightleftharpoons \mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})$
$\mathrm{CaCO}_{3}, \mathrm{CaO},\left(\mathrm{CO}_{2}\right)$
$\mathrm{m}=1\left[\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})\right]$
$C=3-1=2$

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(ii) $\mathrm{NH}_{4} \mathrm{C}^{\mathrm{NH}_{4} \mathrm{C} \ell(\mathrm{s})} \rightleftharpoons \mathrm{NH}_{3}(\mathrm{~g})+{ }^{\mathrm{HC} \ell(\mathrm{g})}$
$\mathrm{C}^{\prime}=3\left[\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s}), \mathrm{NH}_{3}(\mathrm{~g}), \mathrm{HCl}(\mathrm{g})\right]$
$\mathrm{m}=2\left[\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s}) \rightleftharpoons \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{HCl}(\mathrm{g})\right]$ and $\left[\mathrm{P}_{\mathrm{NH} 3}=\mathrm{P}_{\mathrm{HCl}}\right]$
$C=3-2=1$
(iii) $\mathrm{KCl}-\mathrm{NaCl}-\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ system
$\mathrm{C}^{\prime}=3\left[\mathrm{KCl}, \mathrm{NaCl}, \mathrm{H}_{2} \mathrm{O}(/)\right]$
$\mathrm{m}=0$
$C=3-0=3$
(iv) $\mathrm{KCl}, \mathrm{NaBr}, \mathrm{H}_{2} \mathrm{O}(I)$ system
$\mathrm{C}=5\left[\mathrm{KCl}, \mathrm{NaBr}, \mathrm{KBr}, \mathrm{NaCl}, \mathrm{H}_{2} \mathrm{O}(I)\right]$
$\mathrm{m}=1[\mathrm{KCl}+\mathrm{NaBr} \rightleftharpoons \mathrm{KBr}+\mathrm{NaCl}]$
$C=5-1=4$
(v) Aqueous solution of Na'sl
$\mathrm{C}^{\prime}=2\left[\mathrm{NaCl}, \mathrm{H}_{2} \mathrm{O}\right]$
$\mathrm{m}=\mathrm{O}$
$C=2-0=2$
This can be *idistate by fillowing examples.
Ex. 2 Find outhen numer of components in the following systems.
(i) KCl -Nall $-\mathrm{H}_{2}$ (I) system
(ii) K@l- Na B $\Rightarrow \mathrm{H}_{2} \mathrm{O}(I)$ system
(iii) A agous solution of $\mathrm{NaC} /$
(iv) Aqueous solution of acetic acid
(v) Aqueous solution of sulphuric acid.

Sol. 2 (i) $\mathrm{KCl}-\mathrm{NaCl}-\mathrm{H}_{2} \mathrm{O}$ (I) system
$C=C^{\prime \prime}-(n+1)$

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$$
\begin{aligned}
& \mathrm{C}^{\prime \prime}=6\left[\mathrm{KCl}, \mathrm{NaCl}, \mathrm{~K}^{+}, \mathrm{Na}^{+}, \mathrm{Cl}^{-}, \mathrm{H}_{2} \mathrm{O}\right] \\
& {\left[\begin{array}{l}
\mathrm{NaCl}(\mathrm{~s}) \rightleftharpoons \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \\
\mathrm{KCl}(\mathrm{~s}) \rightleftharpoons \mathrm{K}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})
\end{array}\right]}
\end{aligned}
$$

$$
C=6-(2+1)=3
$$

