Nishant Jindal

Q. find $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ & $[PO_4^{3-}]$ in 0.1M HCl & 0.1M H_3PO_4 (aq) soln.

Given $Ka_1 = 10^{-4}$, $Ka_2 = 10^{-7}$, $Ka_3 = 10^{-11}$.

0.1
10^{-4}
10^{-10}
10^{-20}

$H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$

$0.1 - x \quad 0.1 + x \quad x$

$10^{-4} = \dfrac{(0.1+x)\,x}{0.1-x} \quad x = 10^{-4}$

$H_2PO_4^- \longrightarrow H^+ + HPO_4^{2-}$

$x - y \quad 0.1 \quad y - z$

$10^{-7} = \dfrac{0.1 \times y}{x} \Rightarrow y = 10^{-10}$

$HPO_4^{2-} \longrightarrow H^+ + PO_4^{3-}$

$y - z \quad 0.1 \quad z$

$H_3PO_4 \longrightarrow 3H^+ + PO_4^{3-}$

$0.1 - x \quad 3x \quad x$

$Ka_1 \times Ka_2 \times Ka_3 = 10^{-22} = \dfrac{[H^+]^3[PO_4^{3-}]}{[H_3PO_4]}$

$10^{-22} = \dfrac{10^{-3} \times z}{0.1}$

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pH of a solution containing salt :→

CH_3COOH
HCN
$HCOOH$
acid

Salt
CH_3COONa
KCN
$HCOONa$

NH_4OH or $\ddot{N}H_3$
$C_6H_5\ddot{N}H_2$ (aniline)
(base)

Salt
NH_4Cl
$C_6H_5NH_3^+Cl$

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$CH_3COOH \rightarrow CH_3COO^- + H^+$

acid — base — conjugate acid-base pair

K_a

HCN	CN^-
$HCOOH$	$HCOO^-$
NH_3 or NH_4OH	NH_4^+
$C_6H_5NH_2$	$C_6H_5NH_3^+$

CH_3COOH $\quad$ CH_3COO^-

K_a

Acc. to Arrhenius

$CH_3COOH \rightarrow CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Acc. to Bronsted

$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$ $\quad K_a = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

$\Rightarrow$ Na^+, K^+, Cl^-, Br^-, I^-, NO_3^- do not react with H_2O

CH_3COONa

$Na^+ + H_2O \not\rightarrow$

$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$ $\quad K_b$

$$K_b = \frac{[CH_3COOH][OH^-][H^+]}{[CH_3COO^-][H^+]} = \frac{K_w}{K_a}$$

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CH_3COOH

K_a

CH_3COO^-

$K_b = \frac{K_w}{K_a}$

$K_a K_b = K_w$

$$\underset{C-x}{CH_3COO^-} + H_2O \longrightarrow \underset{x}{CH_3COOH} + \underset{x}{OH^-}$$

$$\frac{K_w}{K_a} = K_b = \frac{x \cdot x}{C-x} = \frac{x^2}{C-x} = \frac{C\alpha^2}{1-\alpha}$$

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

Q: find pH of :

(1) 0.1M CH_3COONa (Given Ka of $CH_3COOH = 10^{-5}$) $K_b = \frac{10^{-14}}{10^{-5}} = 10^{-9}$

(2) 0.01M KCN (Given Ka of $HCN = 10^{-10}$ M)

(3) 0.1M NH_4Cl [Given Ka of $NH_4^+ = 10^{-9}$ M)

(1) $CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$ $K_b = 10^{-9}$

$C - x$ x x

$10^{-9} = \frac{x^2}{C-x} = \frac{x^2}{0.1-x}$ $x = 10^{-5}$ $pOH = 5$

$pH = 9$

1. Acetic acid (CH_3COOH) is partially dimerised to $(CH_3COOH)_2$ in the vapour phase. At a total pressure of $0.200\ atm$, acetic acid is 92.0% dimerized at $298\ K$. The value of equilibrium constant (Kp) of dimerisation under these conditions is

(A) 57.5 (B) 9.7 (C) 97 (D) 194

$$2A \longrightarrow A_2$$

$$1-\alpha \qquad \alpha/2$$

2. Which of the following statement(s) is/are correct?

(a) The ratio of the radii of the first three Bohr orbits of hydrogen atom is $1:8:27$.

T (b) The ratio of magnitude of total energy: kinetic energy: potential energy for electron in any orbit of hydrogen atom is $1:1:2$.

(c) The frequency of a green light is 6×10^{14} Hz, then its wavelength is 500 nm.

(d) The ratio of de-Broglie wavelength of a H-atom, He-atom and CH_4-molecule moving with equal kinetic energy is $4:2:1$.

$\lambda = \frac{h}{\sqrt{2mKE}}$

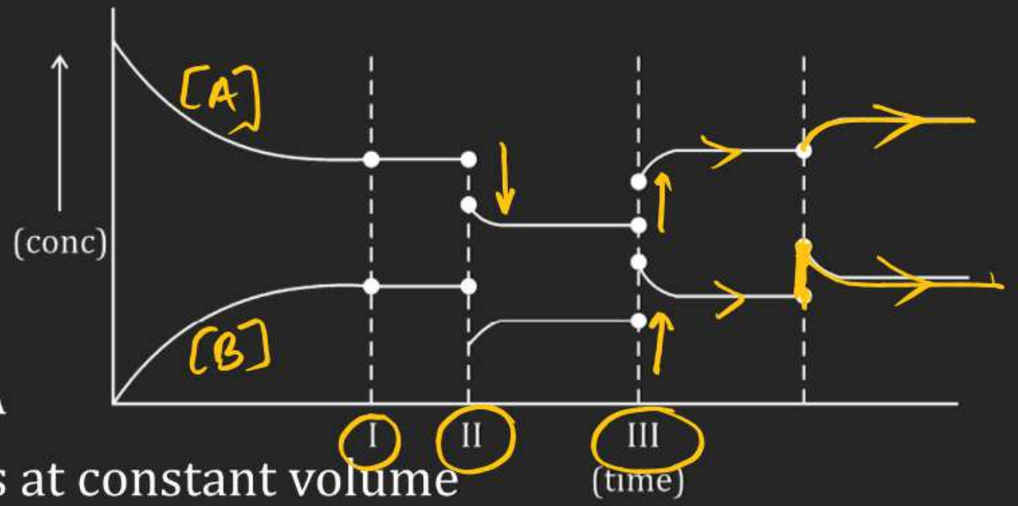
$\frac{1}{1} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{16}}$

$1 : \frac{1}{2} : \frac{1}{4}$

3. Consider the following equilibrium

$A(g) \rightarrow 2B(g)$

and the following graph :



Select the correct statements :

(A) Effect (I) represent the removal of reactant A

(B) Effect (II) represent the insertion of inert gas at constant volume

(C) Effect (III) represent the decrease in volume of container

(D) Effect (IV) represent the addition of moles of gas 'B'

4. A mixture containing substance 'X' & 'Y' is mixed with a substance 'Z'. If 'Z' reacts with both X & Y then select the correct option(s)

(A) Moles of X + moles of Y = Total moles of Z reacted "is always applicable"

(B) Equivalents of X + equivalents of Y = Total equivalents of Z reacted "is always applicable"

(C) $\frac{\text{Equivants. of X}}{\text{n-factor of Z in reaction with X}} + \frac{\text{Equivants of Y}}{\text{n-factor of Z in reaction with Y}}$ = Total moles of Z reacted ; is always applicable

(D) $\begin{matrix}\text{moles of Z}\\ \text{reacted in reaction}\\ \text{with X}\end{matrix} + \begin{matrix}\text{moles of Z}\\ \text{reacted in reaction}\\ \text{with Y}\end{matrix}$ = Total moles of Z reacted ; is always applicable

$x + z$

eq $q x$ = eq $q z$

$y + z$

eq $q y$ = eq $q z$

6. The value of n in the following processes: $AO_4^{n-} + 2e \rightarrow HAO_n^{2-}$ is

$AO_4^- + 2e^- \longrightarrow HAO^{2-}$

$(+7)$

$1 + x - 2 = -2$

$x = -1$

7. The minimum mass (in g) of $CaCO_3$ required to establish the equilibrium:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_C = 0.05M$ at a certain temperature in a $1.0\ L$ container is

JEE ADVANCED PAPER-2

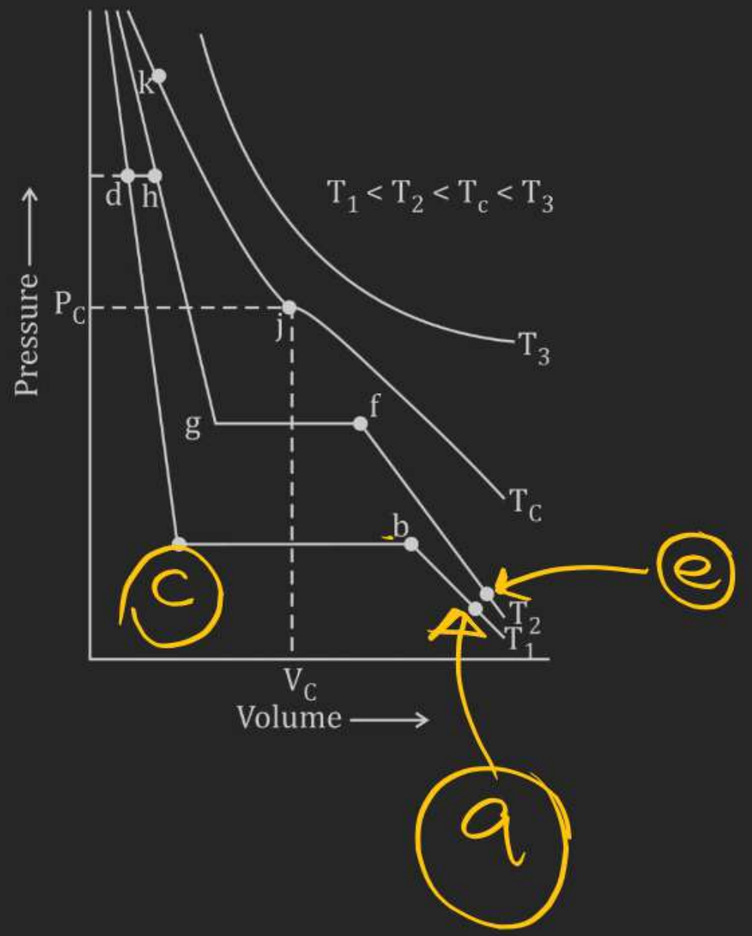
1. Isotherms of carbon dioxide at various temperatures are represented in Figure
The number of correct statement is/ are(s):

(A) CO_2 exist only in gaseous state between the points $'a'$ and $'b'$ at temperature T_1 ?

(B) At point 'c' CO_2 start liquefying when temperature is T_1 ?

(C) No condensation takes place when the temperature is T_3 whatsoever the pressure.

(D) Between point 'c' and 'd' at temperature T_1 both liquid and gaseous CO_2 exist at equilibrium?



Paragraph (Match list):

For the reaction: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g); K_p = 2.463$ atm at 900 K. The reaction is performed in a rigid vessel of 15.0 litre capacity maintained at 900 K, starting with the following amounts of $CaCO_3(s)$ (given in Column I)Given R=0.082 L·atm·K^{-1}·mol^{-1}. Match the correct information given in Column II for the amount given in Column I.

Column I		Column II	
(A)	100 g	(P)	50% dissociation of $CaCO_3$
(B)	50 g	(Q)	100% dissociation of $CaCO_3$
(C)	25 g	(R)	Addition of small amount of CO_2 (g) may result shift of equilibrium in backward direction
		(S)	Addition of 10 g of $CaCO_3$ (s) may result increase in moles of CO_2 (g)