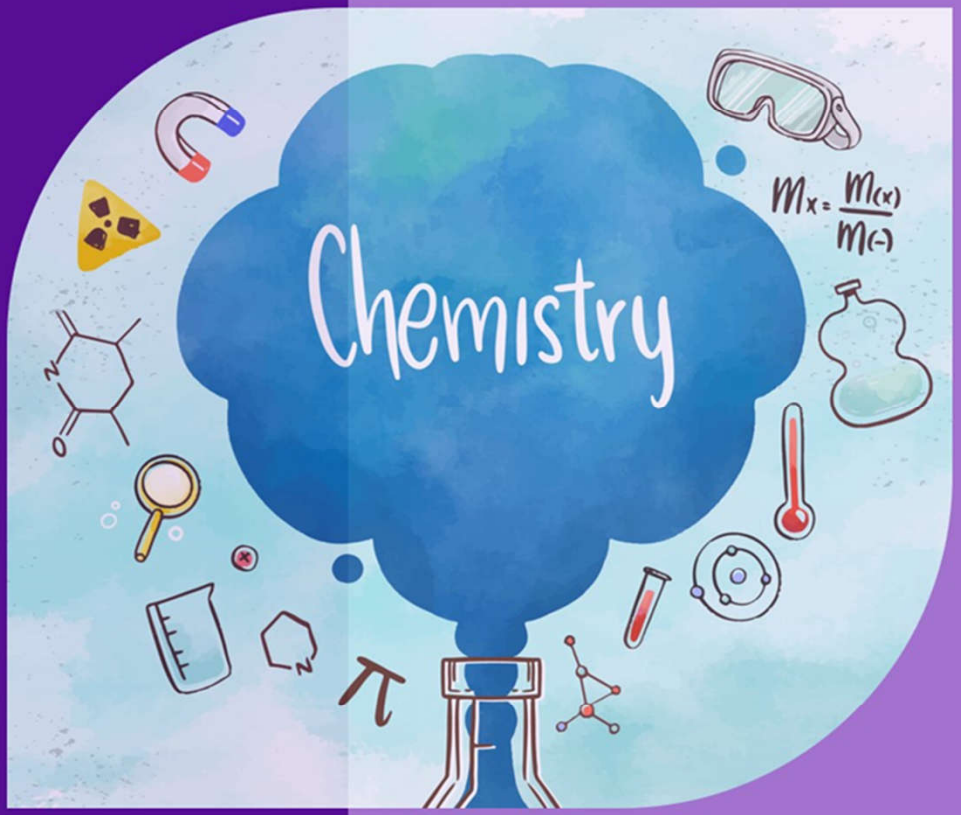
ENGINEERING ADMISSION PROGRAM 2020

CHEMISTRY

LECTURE : C-03

CHAPTER 04 : CHEMICAL EQUILIBRIUM

Acid - base eq.



$$A \rightleftharpoons B$$

Reversible

$$Eq: R_f = R_b$$

experimental

time	A	B
0s	10	0
2s	7	3
4s	5	5
6s	3	7
8s	3	7
10s	3	7
5 years	3	7

amount equal

- **Chemical equilibrium arises with the equal rate not equal amount.**
- **It's a permanent state.**
- **It's a dynamic state on which catalyst has no effect.**
- **A reversible reaction doesn't terminate rather reaches equilibrium. And sometimes equilibrium is considered as termination.**

Activity or active mass

Aqueous: Molar Concentration (M)

Gas: Partial Pressure (atm)

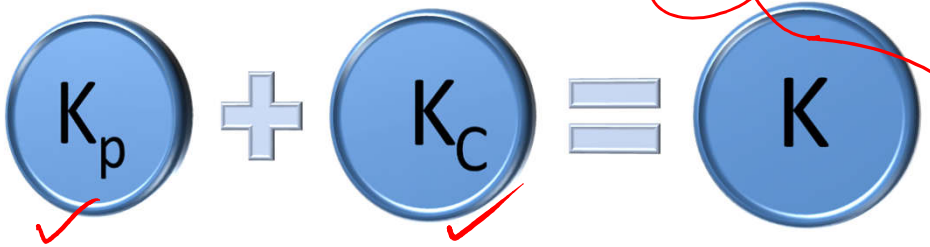
Liquid : 1

Solid : 1

Partial pressure= Total pressure× mol fraction

Concentration = mol ÷ volume (L)

Equilibrium constant



$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

$$K_p = \frac{P_C{}^c\ PDd}{P_A{}^a\ PBb}$$

All information are at Eq

K_p / K_c $K = \frac{P}{R}$

If, K>1; (R<P); More than 50% reactant is converted to product. $\frac{P}{R} > 1$

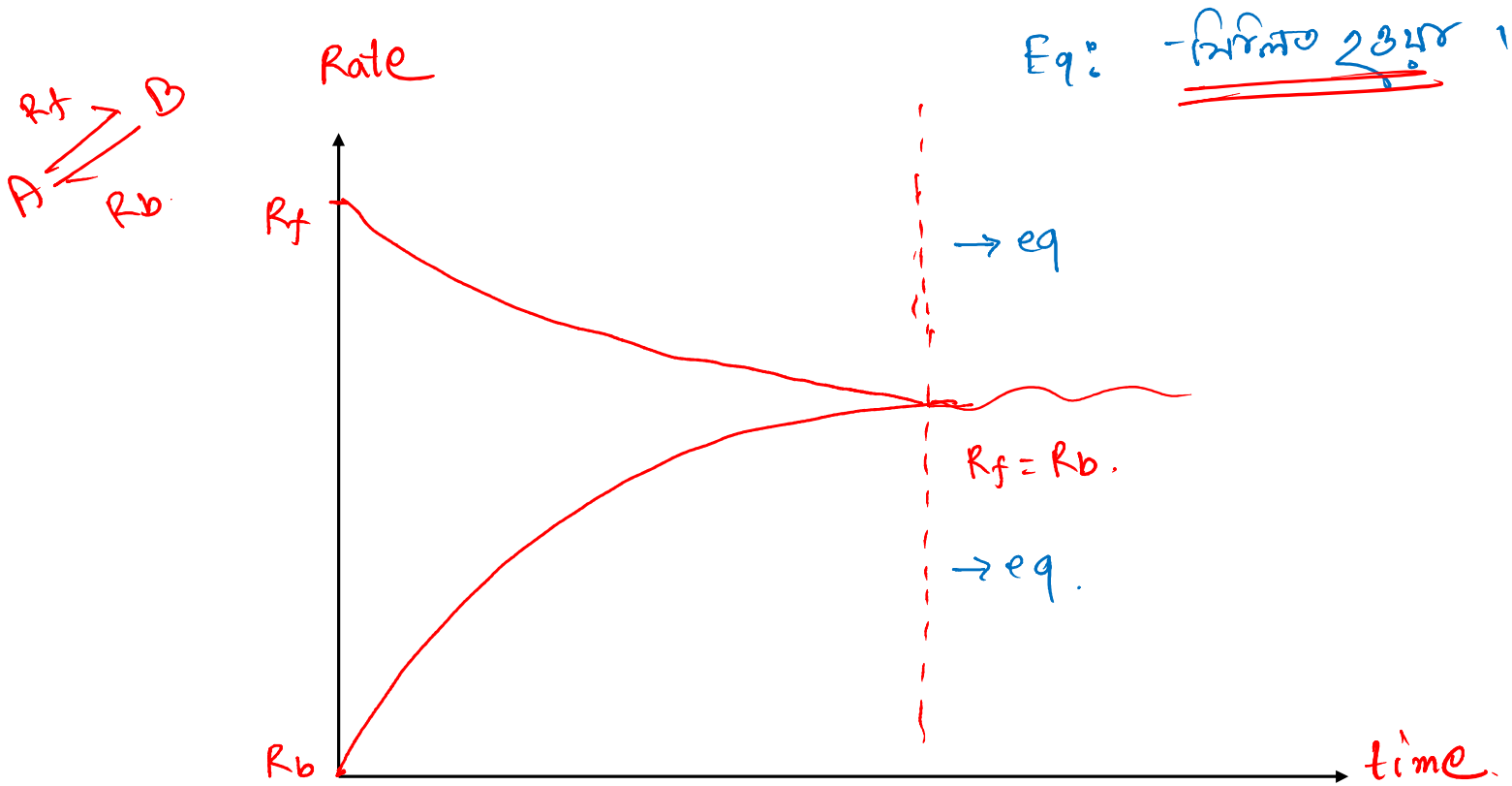
→ spontaneous → spontaneous.

If, K< 1; (R >P) ; Less than 50% reactant is converted to product. $\frac{P}{R} < 1$

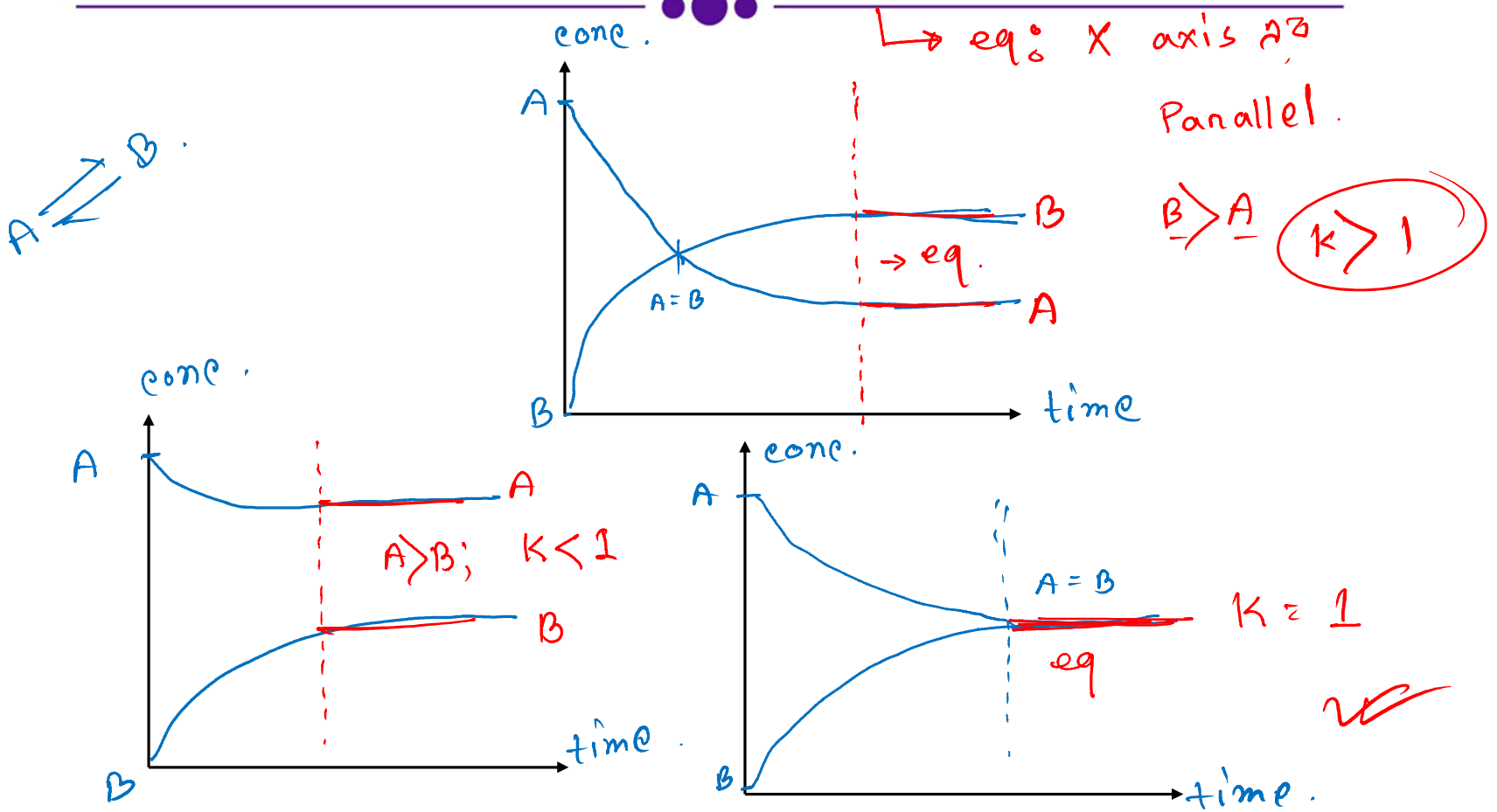
→ Non spontaneous.

If , K= 1; (R=P); Exactly 50% conversion (extremely rare) $\frac{P}{R} = 1$

Rate vs time



Conc vs time


A ⇌ B
conc.
A
B
A=B
eq.
time
→ eq; X axis এ
Parallel.
B > A
K > 1
conc.
A
B
A > B; K < 1
time
conc.
A
B
A = B
eq
K = 1
time

Unit of K_P ,K_C

Actually there is no unit for them, but for our exam 'YEAH'

$K_c = (molL^{-1})^{\Delta n}$; Here Δn= product mole − reactant mole

(aq) + Gas.

$K_P = (atm)^{\Delta n}$; Here Δn= product mole − reactant mole

(gas) only.

Poll Question 01

❑ $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$; unit of K_p is?

(a) atm^{-1}

(b) atm^{-3}

(c) *Unitless*

(d) atm^2 ar

K_P or K_C ?

$K_P = K_C(RT)$

Without the total pressure of the system , Kp can't be calculated.

$K_P = K_C(RT)^{\Delta n}$

- If, pressure is given: K_p
- If volume is given : K_C
- Without both pressure and volume: K_C

volume + Pressure ⇒ Kp + Kc

Type -01 (Equation based)

If, A ⇌ B; K then.....

a. $B \rightleftharpoons A; K^{-1}$

b. $nA \rightleftharpoons nB ; K^{n}$

$K_p = K_c (RT)^{\Delta n}$

Δn= product mole − reactant mole

(only gas)

$\Delta n = 0$ হলে ; $K_p = K_c$

ex; $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

$\Delta n = 0$

$K_p = K_c$

Math Problem

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $K_P = \frac{1}{27}\ atm^{-2}$

BUET (17-18)

$\frac{2}{3}NH_3(g) \rightleftharpoons H_2(g) + \frac{1}{3}N_2(g)$ $K_P = ?$

(i) Reverse (ii) 1/3 ×

$K_P' = (27)^{1/3}$

$\Delta n = (1 + 1/3) - 2/3$

$= 2/3$

$K_P' = 3\ (atm)^{2/3}$.

$(atm)^{\Delta n}$

Poll Question 02

For a reversible reaction $\Delta n = \frac{1}{2}$, at what temperature K_P becomes 8× greater than K_C?
$[R = 0.0821\ L\ atm\ mol^{-1}\ K^{-1}]$ **[BUET 2014-15]**

(a) 779.5 K
(b) 550.5K
(c) 650K
(d) 880K

$K_P = K_C \cdot (RT)^{\Delta n}$

$\frac{K_P}{K_C} = (RT)^{\Delta n}$

$8 = (0.0821 \times T)^{1/2}$

$T = \square$ K

Type-02 (general)

In a 3L container 12g H_2 ,140g N_2 react and produce 34g NH_3 at the equilibrium state. Calculate the Eq. constant?

→ Kc
→ mol

$$1N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Os: 5 6 0

Eq: 5−x 6−3x 2x

→4 →3 →2

$n_{H_2} = \frac{12}{2} = 6$ Os.

$n_{N_2} = \frac{140}{28} = 5$

$n_{NH_3} = \frac{34}{17} = 2$ eq

$2x = 2$

$x = 1$

$$K_c = \frac{(2/3)^2}{(4/3)^1 \times (3/3)^3}$$

$= \square \ (mol\,L^{-1})^{-2}$

Type-03 (No initial amount)

In a 2L container H_2 and N_2 react and produce 1 mol NH_3 at the equilibrium state. Calculate the Eq. constant?

eq

Kc ✓

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

	N_2	H_2	NH_3
0s	1	3	0
eq	$1-x$	$3-3x$	$2x$
	0.5	1.5	1

$2x = 1$

$\therefore x = 0.5$

$$K_c = \frac{(1/2)}{(0.5/2)(1.5/2)^3} \checkmark$$

$= \square \ (\text{mol l}^{-1})^{-2}$

Type-04 (percentage at equilibrium)

In a 4L container there is 20%(mol) NH_3 the equilibrium. if the total pressure of the container is 1.5 atm. Calculate the Eq. constant. [RUET'03-04,05-06,10-11]

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Os:	1	3	0
eq:	$1-x$	$3-3x$	$2x$
	0.67	2	0.67

Total mol : $1-x+3-3x+2x$

$= 4-2x$

$$\therefore \frac{2x}{4-2x} \times 100 = 20$$

$$\frac{x}{2-x} = 0.2$$

$$x = 0.4 - 0.2x$$

$$x = 0.33$$

$$K_c = \frac{(0.67/4)^2}{0.67/4 \times (2/4)^3} = \square \ (mol\,l^{-1})^{-2}$$

$$K_p = \frac{\left(\frac{0.67}{3.34} \times 1.5\right)^2}{\left(\frac{0.67}{3.34} \times 1.5\right)\left(\frac{2}{3.34} \times 1.5\right)^3}$$

$$= \square \ atm^{-2}$$

Type 05: Reaction quotient (Q)

→ Initially Product থেকে...

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

$$Q_p = \frac{P_C{}^c * P_D{}^d}{P_A{}^a * P_B{}^b}$$

→ Q, K হলে ...

if, $K < Q$; ←

if, $K > Q$; →

Q is for any state,

K is for equilibrium state.

Math Problem

	CO_2	+	H_2	=	CO	+	H_2O
Ts :	5		6		1		1
eq:	$5-x$		$6-x$		$1+x$		$1+x$

if $K_c = 0.137$ & $V = 2L$, calculated the concentration of all at equilibrium ?

$$Q_c = \frac{1/2 \cdot 1/2}{5/2 \cdot 6/2} = 0.033$$

$Q_c < K_c$ →

$$K_c = \frac{(1+x/2)(1+x/2)}{(5-x/2)(6-x/2)}$$

$x = 0.74$ ✓

$= -4.8$ ✗

$$[CO_2] = \frac{5-0.74}{2}$$

$$[H_2] = \frac{6-0.74}{2}$$

$$[CO] = [H_2O] = \frac{1+0.74}{2}$$

Type 05 (Van't hoff equation)

Arhenious
$K = A \cdot e^{-Ea/RT}$
↓
Rate constant

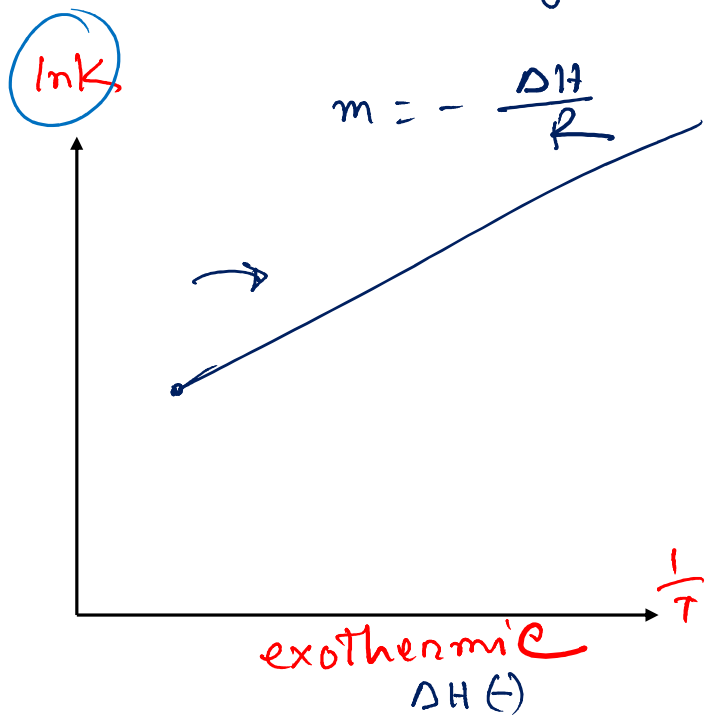
Relation between temperature and eq. constant

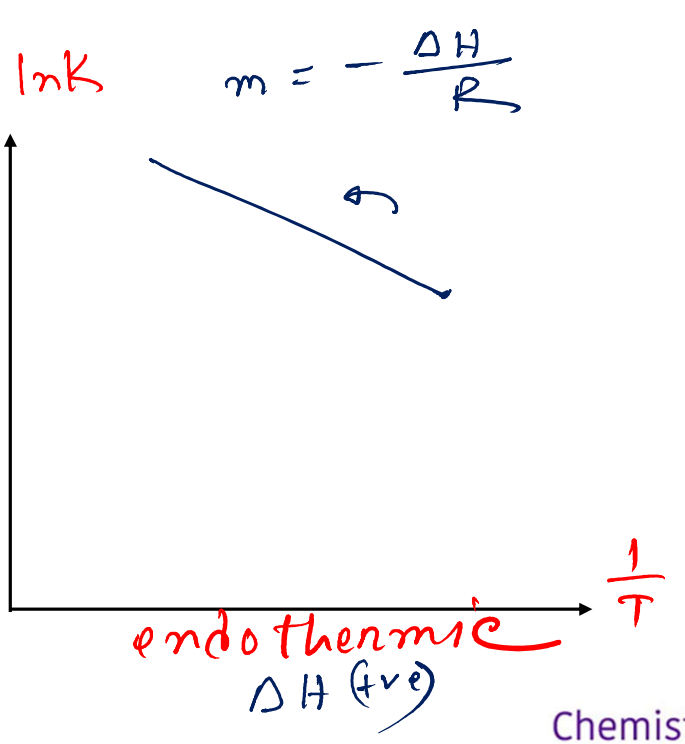
→ K_P / K_C

conc ✗
Pressure ✗
catalyst ✗

$$\ln K_P = -\frac{\Delta H}{RT} + C$$

$y = mx + c$





Math Problem

If the slope of $\ln K_p$ vs T^{-1} is $-100K$. Then ΔH= ?

$$m = -\frac{\Delta H}{R}$$

$$+100\,K = +\frac{\Delta H}{8.314\ J\,mol^{-1}K^{-1}}$$

$$\Delta H = 100\,K \times 8.314\ J\,mol^{-1}K^{-1}$$

$$\Delta H = 831.4\ J\,mol^{-1}$$

Eq. constants at two diff. temperature

$T_1 \rightarrow K_1$

$T_2 \rightarrow K_2$

$$m = \frac{y_1 - y_2}{x_1 - x_2}$$

$$\Rightarrow -\frac{\Delta H}{R} = \frac{\ln K_1 - \ln K_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$\Rightarrow \ln\frac{K_1}{K_2} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Rightarrow \Delta H = \text{J}$$

Math Problem

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g);\ \ \Delta H = +90\ kJmol^{-1}.$

At 0 °C temperature Eq. constant is 0.00564 atm.

calculate the Eq. constant at 27°C.

$\Delta H = 90 \times 10^3\ J mol^{-1}$ H.W

Type -07: Dissociation rate (∝)

The amount dissociated for per mole

⇒ ∝ সংখ্যা Math ধর্মের নয়।

Math Problem

In a 2L container, 4mol H_2 & 2mol N_2 react. 20% of N_2 is converted to NH_3. calculate the Eq. constant. [BUET'06-07, BUTex'07-08]

$3H_2 + N_2 \rightleftharpoons 2NH_3$

	$3H_2$	N_2	$2NH_3$
Os:	4	2	0
eq:	$4-3x$	$2-x$	$2x$
	2·8	1·6	0·8

N_2

$\alpha = 0{\cdot}2$

$1 \rightarrow 0{\cdot}2$

$2 \rightarrow 0{\cdot}4$

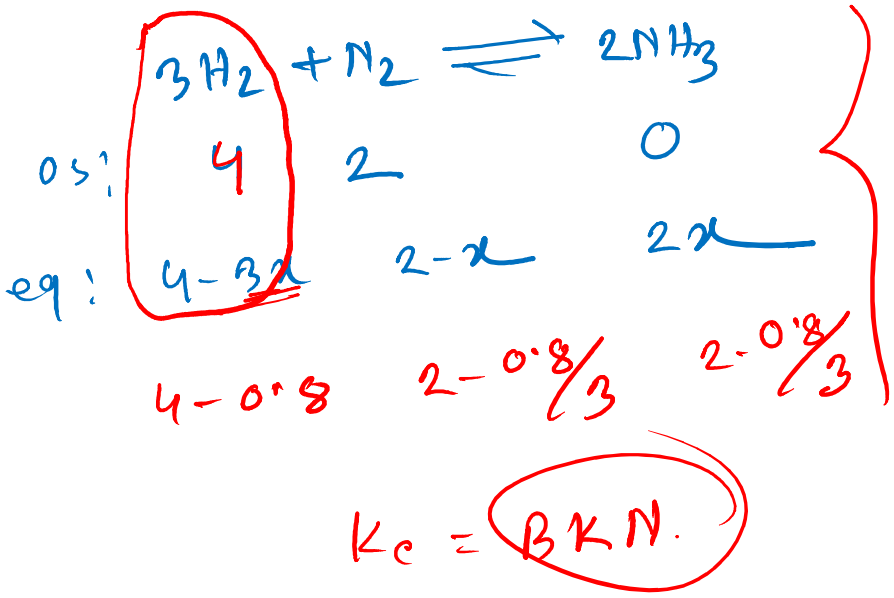
$x = 0{\cdot}4$

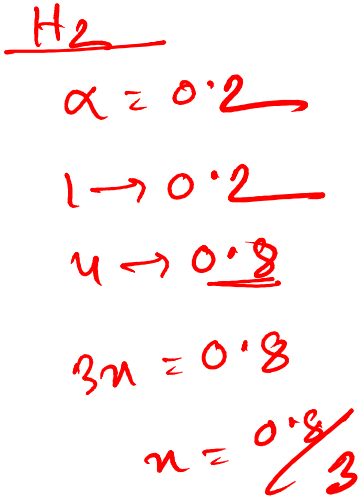
K_c

$K_c = B.K.N.$

Math Problem

In a 2L container 4mol H_2, 2mol N_2 react .20% of H_2 is converted to NH_3. Calculate the Eq. constant.





Type-08 (two conventional reactions)

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

TM

$K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P$

$N_2O_4 \rightleftharpoons 2NO_2$

$K_p = \frac{4\alpha^2}{1-\alpha^2} \cdot P$

Acid-Base

Theory	Acid	Base
Arhenious	Produce H^+ in solution.	Produce OH^- in solution
Bronsted-Lowry	H^+ donor	H^+ acceptor
Lewis	Electron pair acceptor	Electron pair donor

Dissociation constant of acid

Ka

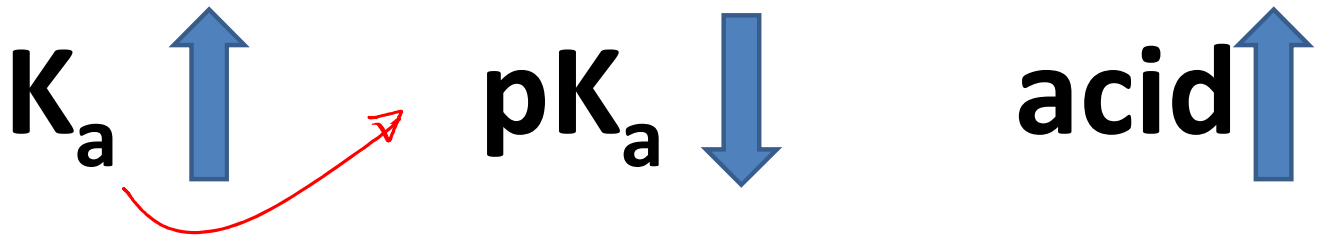
$HCl \rightarrow Ka = \frac{[H^+][Cl^-]}{HCl}$

$pKa = -\log Ka$

$H_2SO_4 \rightarrow Ka = \frac{[H^+]^2[SO_4^{2-}]}{H_2SO_4}$

$H_2CO_3 \rightarrow Ka = \frac{[H^+]^2[CO_3^{2-}]}{H_2CO_3}$

$-\log$ { বড় → ছোট
ছোট → বড় }



✓ Strong. K_a↑ pK_a↓

Poll Question 03

Which one is the strongest acid?

(a) H_2SO_4
(b) HNO_3
(c) H_2CO_3
(d) $HClO_4$

S (+6) (oxi-acid.)
N (+5)
C (+4)
Cl (+7)

$HClO_4 > H_2SO_4 > HNO_3 > H_2CO_3$

HNO_3 (+5) $> H_3PO_4$ (+5)

Name	Formula	K_a	pK_a
Hydrochloric acid	HCl	1.0×10^{7}	−7.00
Phosphoric acid	H_3PO_4	7.5×10^{-3}	2.12
Hydrofluoric acid	HF	6.6×10^{-4}	3.18
Lactic acid	$CH_3CH(OH)CO_2H$	1.4×10^{-4}	3.85
Acetic acid	CH_3CO_2H	1.8×10^{-5}	4.74
Carbonic acid	H_2CO_3	4.4×10^{-7}	6.36
Dihydrogenphosphate ion	$H_2PO_4^-$	6.2×10^{-8}	7.21
Ammonium ion	NH_4^+	5.6×10^{-10}	9.25
Hydrocyanic acid	HCN	4.9×10^{-10}	9.31
Hydrogencarbonate ion	HCO_3^-	5.6×10^{-11}	10.25
Methylammonium ion	$CH_3NH_3^+$	2.4×10^{-11}	10.62
Hydrogenphosphate ion	HPO_4^{2-}	4.2×10^{-13}	12.38

Dissociation constant of base

K_b

$pK_b = -\log(K_b)$

$K_b \uparrow \quad pK_b \downarrow \quad$ Base $\uparrow$

Conjugated acid-base

H_2SO_4 HSO_4^-

Acid $- H^+ \rightarrow$ Con.Base ;

HCl ① Cl⁻

K_a K_b

SO_4^{2-} HSO_4^-

base $+ H^+ \rightarrow$ con. Acid

① HSO_4^- H_2SO_4

K_b K_a

$H_2SO_4 \rightarrow HSO_4^-$ ✓

~~SO_4^{2-}~~

$$K_a \times K_b = K_w = 10^{-14}$$

25°C

$$K_a \times K_b = K_w = 10^{-14}$$

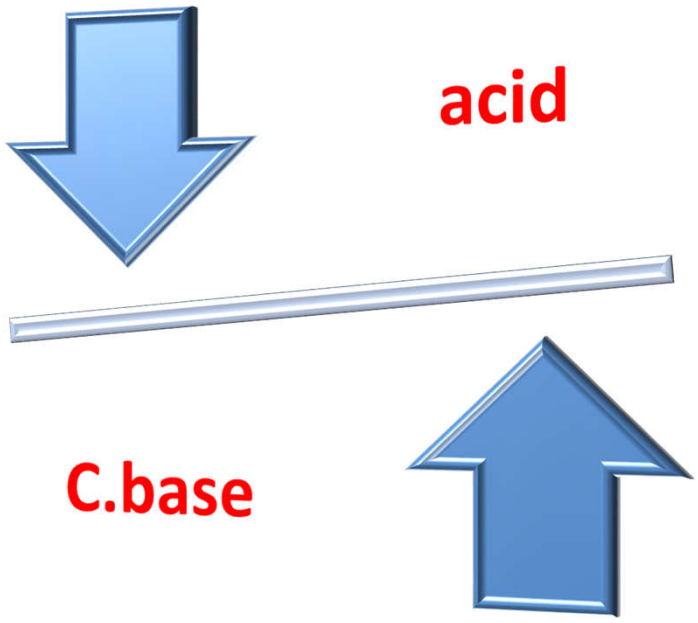
$$K_a \times K_b = \cancel{K_w} = \cancel{10^{-14}}$$

$K_a \cdot K_b = 10^{-14}$

$$K_a \propto \frac{1}{K_b}$$

$K_a \uparrow$; $K_b \downarrow$

Acid ↑ ✓ C.base ↓ ✓



Ionic product of water

$$K_w = [H^+]\,[OH^-]$$

At 25°C , $K_w = 10^{-14}\ mol^2L^{-2}$

Temp ↑ K_w ↑

pH & pOH

$pH = -\log(H^+)$

$pOH = -\log(OH^-)$

$At\ 25°C,\ \mathrm{pH} + \mathrm{pOH} = 14$

Acidic, $pH < 7$

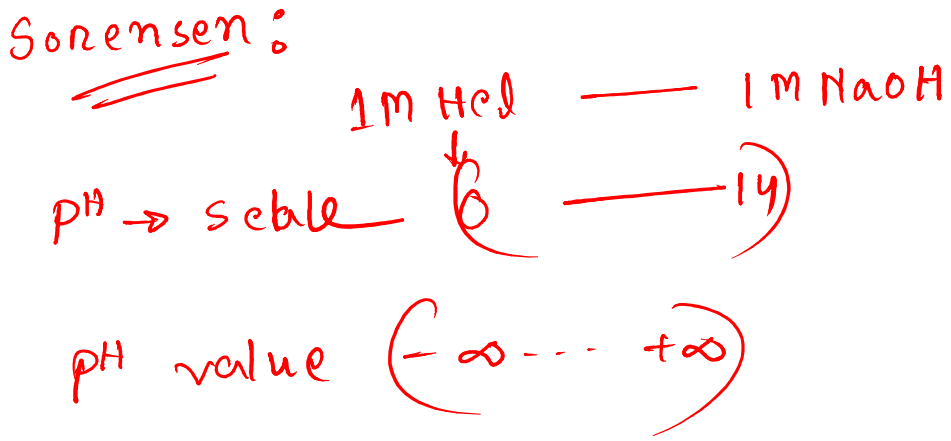
Basic; $pH > 7$

Neutral: $pH = 7$

$25°C$

Math Problem

Is it possible for pH value to be smaller than 0 and greater than14?



Math Problem

The $[H^+]$ of a fruit juice is 3.3×10^{-2}M. **[BUET'08-09]**

a. Calculate pH ?

b. Is it acidic or basic?

c. Calculate pOH?

a. $pH = -\log(3.3 \times 10^{-2})$

$= 1.48$

25°C

b. Acidic

c. $pOH = 14 - pH$

$= 12.52$

Poll Question 04

1.35g HCl is dissolved in 3L solution. pH=? [KUET'10-11]

(a) 2.91
(b) 1.91
(c) 7.40
(d) 7.00

$n_{HCl} = \frac{1.35}{36.5}$

$[HCl] = \frac{1.35/36.5}{3}$

$HCl \rightleftharpoons H^+$

$pH = -\log\left(\frac{1.35/36.5}{3}\right)$

$=$

Math Problem

pH of 10^{-8} M H_2SO_4 is = ?

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

$-10^{-8} \quad 2\times10^{-8}$

H_2O

$pH = -\log\left(\frac{2\times10^{-8}}{\text{acid}} + \frac{10^{-7}}{\text{water}}\right)[H^+]$

$= 6.92$

Diluted.

Diluted. Weak

[acid.]/[base] এর মান 10^{-5} এর কম হলে

Weak acid

$HCl \rightarrow H^+ + Cl^-$

$C \quad 0 \quad 0$

$C-C \quad C \quad C$

strong

$pH = -\log(c)$

weak

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

$C \quad 0 \quad 0$

$C-\alpha C \quad \alpha C \quad \alpha C$

$pH = -\log(\alpha C)$

$pH = -\log(\sqrt{K_a \times C})$

$K_a = \alpha^2 C$

$\alpha \rightarrow$ Dissociation rate

Math Problem

At 298K temp. for acetic acid $K_a = 1.8 \times 10^{-5}$ mol dm^{-3} .
calculate pH of 0.1 mol dm^{-3} solution. **[BUET'06-07,BUTex'07-08]**

$$pH = -\log\sqrt{K_a \cdot C}$$

$$= -\log\sqrt{1.8 \times 10^{-5} \times 0.1}$$

$$= \square = 2.88$$

A: weak acid + salt

Buffer Solution

B: weak base + salt

i. Resistant for little amount of weak acid or base.

ii. Weak acid or base is a must for making buffer solution.

acid + base
w s

w > s

iii. In the acid-base mixture, to form a buffer solution, weak one has to be larger in amount.

Poll Question 05

Which mixture act as buffer solution? [DU'13-14]

acid. (ω)

$n = V \cdot S$

(a) 0.2 M 10 mL CH_3COOH + 0.2 M 10 mL NaOH

(b) 0.2 M 10 mL CH_3COOH + 0.1 M 10 mL NaOH

(c) 0.1 M 10 mL CH_3COOH + 0.2 M 10 mL NaOH

(d) 0.1 M 10 mL HCl + 0.2 M 10 mL NaOH

pH of buffer

$n = V \cdot S$

Henderson- Hasselbalch equation:

Acidic $pH = pK_a + \log \frac{n_{salt}}{n_{acid}}$

Basic $pOH = pK_b + \log \frac{n_{salt}}{n_{base}}$

$\frac{[salt]}{[Acid]}$

Math Problem

$n = V \cdot S$

A buffer solution is consisted by

400 mL 0.1 M NaOH and 600 mL 0.2 M CH_3COOH.

pH of the buffer solution is ? [For CH_3COOH , $pK_a = 4.76$] [BUET'17-18]

~~Acid~~ → weak

$n_a = 0.6 \times 0.2 = 0.12$

$n_b = 0.4 \times 0.1 = 0.04$

$n_a > n_b$.

Buffer yes !!

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

limiting. salt

$$pH = pKa + \log \frac{n_{salt}}{n_{acid}}$$

$$pH = 4.76 + \log \frac{0.04}{0.12 - 0.04}$$

$$= 4.58$$

Math Problem

To form a buffer solution with 10.0 pOH, with $50cm^3$ 0.05M HCOOH how much (cm^3) 0.10M HCOONa need to be added? $[K_{HCOOH} = 1.8 * 10^{-4}]$

$pOH = 10$

$pH = (14-10) = 4$

$pH = pKa + \log \frac{n_{salt}}{n_{acid}}$.

$pKa = -\log Ka$

$4 = -\log(1.8\times10^{-4}) + \log \frac{V_s \cdot S_s}{V_a \cdot S_A}$

$4 = -\log(1.8\times10^{-4}) + \log \frac{V_s \cdot 0.1}{50 \times 0.05}$

$V_s = 45\ cm^3$

লেগে থাকো সৎ ভাবে,
স্বপ্ন জয় তোমারই হবে।